Fabrication of thermoelectric oxide modules

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Abstract

Different versions of a thermoelectric unicouple composed of *p*-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ (Co-349) and *n*-type $La_{0.9}Bi_{0.1}NiO_3$ (Ni-113) bulks were constructed using Ag paste containing *p*- and *n*-type oxide powders, prepared from the same bulks, for connection of the *p*- and *n*-legs, respectively. Open-circuit voltage (V_O) of all the unicouples reaches 100 mV at a hot-side temperature (T_H) of 1073 K and a temperature differential (ΔT) of 500 K in air. Internal resistance (R_I) of the unicouple is 13.9 mΩ at 1073 K in air and decreases with increasing temperature. Maximum output power (P_{max}), evaluated using the formula $P_{max} = V_O^2/4R_I$, is 176 mW at 1073 K (ΔT = 500 K) and increases with temperature. This value corresponds to a volume power density of 960 mW/cm^3. The incorporation of oxide powders in Ag paste is shown to be effective to reduce the contact resistance and the thermal hysteresis effect at oxide/metal junctions. A module consisting with 2 couples shows output power of 35 mW at T_H and ΔT of 990 K and 670 K, respectively.

Introduction

Waste heat from automobiles, factories, and similar sources offers a high-quality energy source equal to about 70 % of total primary energy, but is difficult to reclaim due to its source amounts being small and widely dispersed. Thermoelectric generation systems offer the only viable method of overcoming these problems by converting heat energy directly into electrical energy irrespective of source size and without the use of moving parts or production of environmentally deleterious wastes. The requirements placed on materials needed for this task, however, are not easily satisfied. Not only must they possess high conversion efficiency, but must also be composed of non-toxic and abundantly available elements having high chemical stability in air even at temperatures of 800–1000 K. Though CoO_2-based oxides with layered structures have been reported to show good *p*-type thermoelectric properties at high temperature in air [1–3], the much-needed corresponding *n*-type oxides with thermoelectric properties sufficient for power applications have thus far eluded discovery despite concerted efforts. Recently, perovskite $LaNiO_3$ (Ni-113) has been reported to show negative Seebeck coefficient (S) and low resistivity (ρ) values [4, 5].

Though fabrication of thermoelectric modules using oxide materials has recently been reported [6, 7], their performance is much lower than that expected considering the properties of their starting materials. This is thought to be because the contact resistance at electrodes in which oxide/metal junctions are usually formed is very high, thus severely limiting the magnitude of output power. Moreover, cracking or exfoliation due to the great difference of thermal expansion between oxides and metals are also serious problems. Accordingly, the preparation of electrodes possessing good thermal and electrical properties is considered the one of the most important issues in realizing thermoelectric power generation. This paper reports the construction of thermoelectric unicouples and module composed of the Co-349 and Ni-113 bulk materials and their properties.

Experimental

As reported previously, bulk materials of *p*-type Co-349 and *n*-type Ni-113 were prepared using a hot-pressing technique [8]. The specific compositions are $Ca_{2.7}Bi_{0.3}Co_4O_9$ for the *p*-type leg and $La_{0.9}Bi_{0.1}NiO_3$ for the *n*-type leg. Hot-pressed oxide plates were cut to provide a leg element area of 4.5 x 4.5 mm^2 and a leg element length of 4.7 mm. The length direction was made perpendicular to the hot-pressing axis for the purpose of inducing a temperature gradient.

An alumina plate possessing dimensions of 5.0 mm wide, 8.0 mm long, and 1.0 mm thick was used as a substrate. Ag paste was applied to one side of the alumina plate, an Ag sheet having same width and length with the alumina substrate and 0.2 mm thick was put on the alumina plate, and the plate was heated to dry the Ag paste. Ag paste was mixed with *p*-type oxide powder or *n*-type oxide powder in various compositions. The precursor powders of the *p*- and *n*-type legs before hot-pressing were pulverized by ball milling to obtain a grain size smaller than 10 μm, then mixed in varying ratios with the Ag paste (0, 1.5, 6, and 10 wt.%). The Ag pates were applied on the Ag sheets on the alumina plates. After connection of the legs and substrate, the wet Ag paste was dried at 373 K and solidified by heating at 1123 K for 3h under the atmospheric pressure and a uni-axial pressure of 64kg/cm^2 perpendicular to the Ag sheet in air. The unicouple is shown in Fig. 1. Weight of this unicouple is 0.6-0.7 g.

Open-circuit voltage (V_O) was measured by heating the alumina substrate using an electrical furnace at temperatures up to 1073 K in air and cooling the side attached with Pt wires using the Ag paste for the terminals by circulated water. Measurement of internal resistance (R_I) was carried out using a standard DC four terminal method. The current terminals for the substrate were attached on the opposite side. The voltage terminals were prepared on the vertical sides of both *p*- and *n*-legs just under the current terminals. To evaluate thermal hysteresis, R_I was measured before and after subjecting the unicouple a heating–cooling cycle from room temperature to 1073 K repeated 5-times in air.

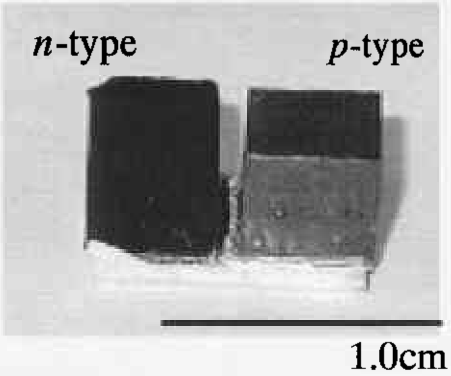

Figure 1 Photograph of a thermoelectric unicouple composed of p-type Co-349 and n-type Ni-113 oxide materials.

A thermoelectric module was fabricated using 2 couples which are connected by the Ag paste mixed with 6 wt.% of the oxide powers. Output power of the module was measured by connecting variable external resistance.

Result and Discussion

S and ρ for p- and n-legs are indicated in Fig. 2. Absolute S values of both materials increase with temperature. Although S is over 200 μV/K for the Co-349, it is lower than 30 μV/K at high temperature for the Ni-113. ρ for the Co-349 decreases with increasing temperature, on the other hand, the Ni-113 shows a metallic-like behavior. The lowest ρ value is about 5 mΩ cm in the region of measured temperature for the Co-349, however, ρ is suppressed lower than 1.0 mΩ cm for the Ni-113.

Figure 3 shows temperature dependence of R_I for different versions of the unicouple constructed using the Ag paste containing various weight percentages of oxide powders. While ρ of the Co-349 leg decreases with increasing temperature, the Ni-113 leg exhibits a metallic behavior. The lowest ρ value in the region of measured temperature is 5.8 mΩ cm at 990 K in the Co-349 leg, however, ρ is held lower than 1.0 mΩ cm in the Ni-113 leg. R_I decreases with increasing temperature for all unicouples. This indicates that R_I is dominated by resistance of the Co-349 leg. Since the difference of ρ values for each leg among the samples is less than 10 %, the incorporation of the oxide powders is seen to be effective to reduce R_I. This is due to the reduction of contact resistance R_C between the oxide leg elements and Ag paste. Considering resistance of Ag on the substrate, R_C at 950 K accounts for 12.5 % and 56.8 % of total R_I for the unicouples with Ag paste containing 6 and 0 wt.% oxide powders, respectively. An increase in R_I, however, is observed when the Ag paste containing 10 wt.% of oxide powders is used. Large pores are seen at the interface between p-leg and Ag by scanning electron microscopic (SEM) observation in this unicouple. The optimum-mixing ratio of the oxide powders is present around 6 wt.%. Applying pressure during solidification of the paste is effective to reduce R_I (the sample of 6 wt.% under pressure in Fig. 3).

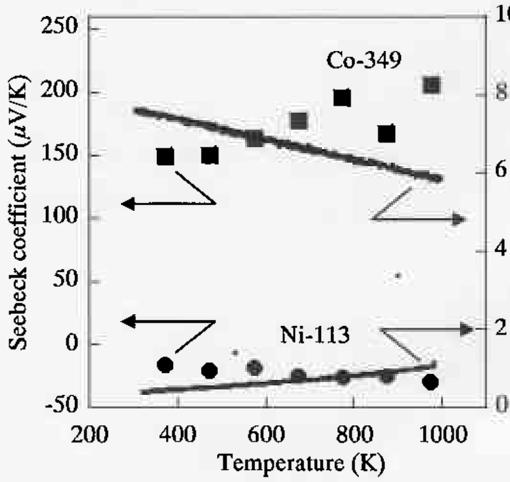

Figure 2 Thermoelectric properties of p-type Co-349 and n-type Ni-113 legs in air.

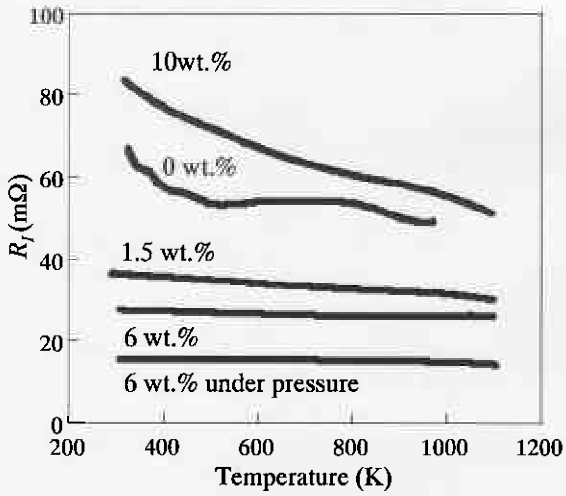

Figure 3 R_I for thermoelectric unicouples constructed using Ag paste containing 0-10 wt.% of oxide powders before the repeated heating-cooling cycle from 1073 K to room temperature. All samples except the sample of 6 wt.% pressure, which was prepared under the uni-axial pressure, were treated under the atmospheric pressure during solidification of the paste.

As shown by Fig. 4, thermal hysteresis effect on R_I values, the increase in R_I by the heating–cooling cycle, is suppressed by mixing oxide powders into the Ag paste. Figure 5 presents SEM images at the junctions of Co-349 legs and Ag paste containing 0 and 6 wt.% Co-349 powder in two samples after being subjected to the cycle of heating to 1073 K and cooling to room temperature was repeated 5-times. The microstructures of counterpart Ni-113 leg/Ag junctions were unchanged by the incorporation of oxide powders. Exfoliation is observed at the interface between the Ag paste and p-leg in the unicouple using Ag paste containing 0 wt.% of oxide powder, but not in the unicouple using Ag paste containing 6 wt.% of oxide powder. The exfoliation seems to be due to the great difference of thermal expansion and/or to poor affinity between the Ag and Co-349 materials, but the addition of Co-349 powder improves the interfacial connection. Moreover, the Ag was shrunk by the heating–cooling cycle because of its being sintering, but the addition of oxide powders seems to be effective to impede the effect of the sintering on Ag. Since the thermal expansion of the Ag paste and Ni-113 leg seems to be similar, exfoliation and shrinking of Ag do not occur.

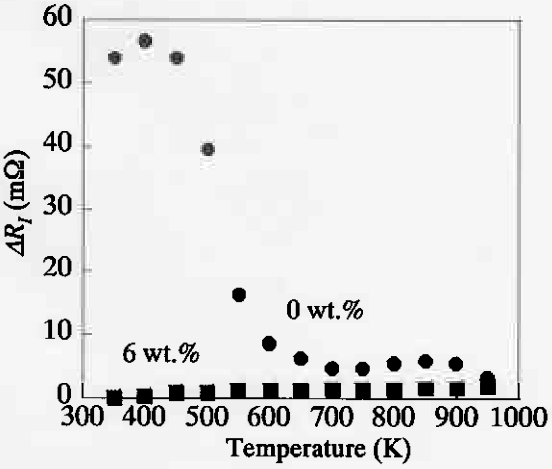

Figure 4 Difference of R_I between before ($R_{I\ \mathrm{before}}$) and after ($R_{I\ \mathrm{after}}$) the heating-cooling cycle, $\Delta R_I = R_{I\ \mathrm{after}} - R_{I\ \mathrm{before}}$ for unicouples using Ag paste containing 0 and 6 wt.% of oxide powders prepared under the atmospheric pressure.

V_O values increase with hot-side temperature (T_H) because absolute S values for both legs increase with increasing temperature and the temperature difference between hot- and cold-side temperatures (ΔT) also increases with increasing T_H and are independent of the content of oxide powders in the Ag paste (Fig. 6). Although S is over 200 μV/K in the Co-349 leg, it is lower than −30 μV/K at high temperature in the Ni-113 leg [5]. V_O values calculated using the measured S values of both legs largely agree with the measured V_O. V_O values reach 100 mV at T_H of 1073 K and ΔT of 500 K.

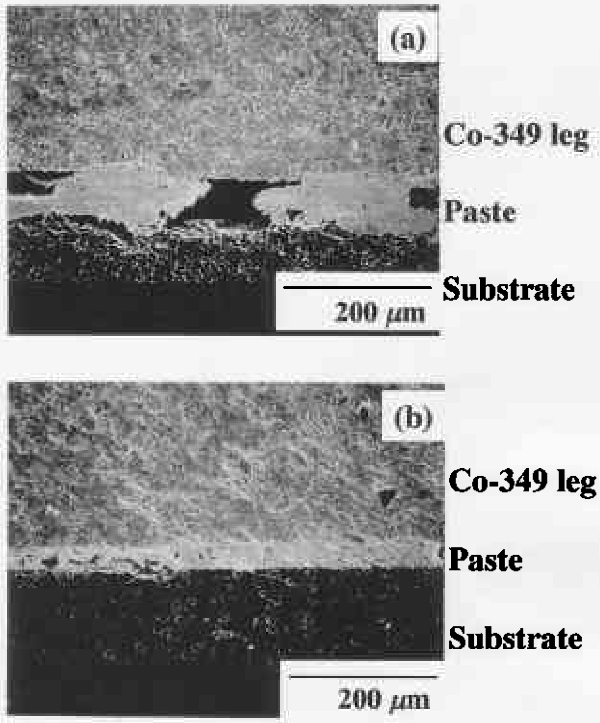

Figure 5 Scanning electron microscopic images at p-leg/Ag junctions containing 0 (a) and 6 (b) wt.% of Co-349 powder after the heating-cooling cycle.

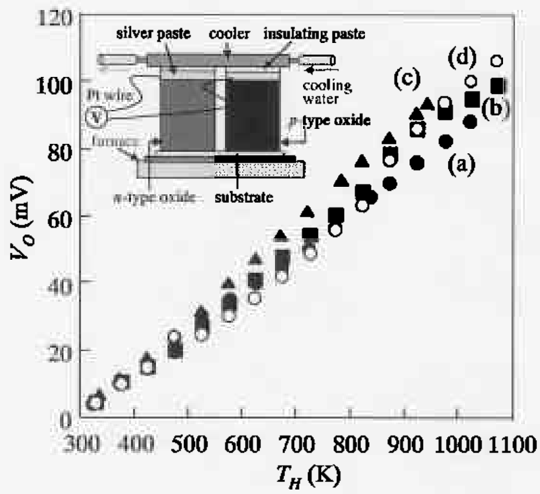

Figure 6 V_O for unicouples constructed using Ag paste containing 0 (a), 6 (b), and 10 (c) wt.% of oxide powders before the heating-cooling cycle and V_O calculated using S values of both p- and n-legs (d).

Output power of these unicouples has yet to be measured directly due to the extremely low R_I values. In the unicouple prepared under the uni-axial pressure with Ag paste containing 6 wt.% oxide powders, however, maximum output power (P_{max}) calculated using the formula $P_{max} = V_O^2/4R_I$, increases with T_H and reaches 176 mW at T_H of 1073 K and ΔT of 500 K (Fig. 7). R_I at T_H was used for calculation of P_{max} because of small temperature dependence of R_I. One of the strong points of unicouples fabricated in this manner is their high power density, which would allow a large amount of electrical power to be generated by a small, lightweight thermoelectric module. In the same oxide thermoelectric unicouple, the volume power density is 960 mW/cm^3 at T_H of 1073 K (inset of Fig. 7). These values are almost 100 times higher than those of devices previously reported [6].

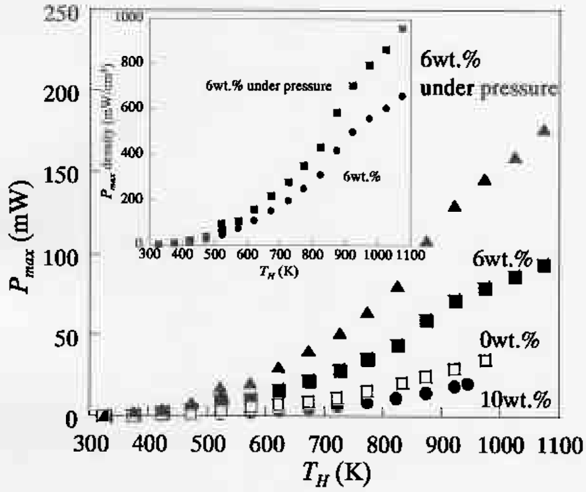

Figure 7 T_H dependence of P_{max} in unicouples constructed using Ag paste containing 0-10 wt.% of oxide powders. Inset: Volume P_{max} density for unicouple constructed using Ag paste containing 6 wt.% of oxide powders prepared under the atmospheric pressure.

Thermoelectric properties of the module composed of 2 unicouples are shown in Fig. 8. From current-voltage plot, the internal resistance is calculated as 22 mΩ. Maximum output is about 35 mW at 985 K of T_H and 670 K of the temperature differential.

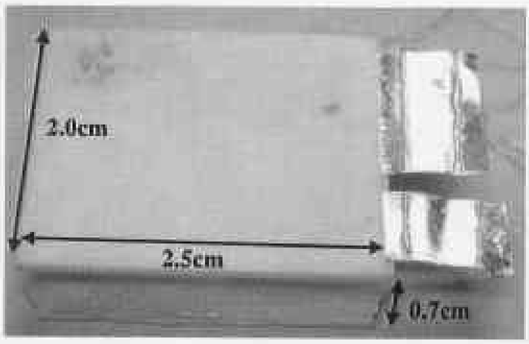

Figure 8 Thermoelectric oxide module composed of 2 unicouples.

Conclusion

A thermoelectric unicouple composed of *p*-type Co-349 and *n*-type Ni-113 oxide materials was constructed and displayed V_O of 100 mV and R_I as low as 14 mΩ at T_H of 1073 K in air. The unicouple could generate up to 176 mW of power, which corresponds to volume power density of 960 mW/cm^3. The result of this paper emphasizes the junctions acting as thermal and electrical buffer layers must be constructed between oxide leg elements and Ag on the substrate. The incorporation of oxide powders into the Ag paste is effective to construct such junctions. Power generation modules fabricated using oxide thermoelectric unicouples with such high power densities could facilitate a revolution in small power sources for mobile devices or automobiles and, moreover, enable recovery of waste heat in the form of electrical energy from sources such as factories and incinerators.

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