Development of a Porous FeSi₂ Thermoelectric Conversion Element

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Heavily porous FeSi₂ bulky materials for thermoelectric conversion elements have been developed via a spark plasma sintering process. FeSi₂ bulky materials with a porosity ratio of about 45% were molded into U-type thermoelectric conversion elements in which the p-type and n-type FeSi₂ were separated by insulating glass fiber sheets. The Doping elements used were Co and Mn. Ag mesh electrodes were firmly attached, simultaneously by the sintering process, to the surface of the sintered products. A thermoelectric power of 0.5-0.7 mV/K at 300-500 K and an apparent internal resistivity of 3.99 × 10⁻³ Ωm at 448-479 K have been obtained, which shows a potential for use in power generation by gas-combustion and heat-exchange type thermoelectric processes.

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1. Introduction

When the temperature gradient is applied in metals or semiconductors, a thermoelectric motive force is generated. In order to utilize this phenomenon, which is well known as the Seebeck effect, efforts have been made to develop a thermoelectric conversion element for many years. Echigo et al., have proposed a novel thermoelectric power generation system, using a porous thermoelectric conversion element. In the proposed reciprocating flow combustion system, a flammable gas is introduced into the porous element and burned at an end of the element. The flowing gas transfers thermal energy from a hot side to a cold side of the element. When the flowing direction changes periodically, thermal energy is stored in the porous element, leading to a large temperature gradient across the element without any additional cooling system. Such porous element should be oxidation-resistant at high temperatures and perform in the wide temperature range. A compound semiconductor FeS₁₂ can be an appropriate material with respect to these requirements.

However, there have been few reports on the properties of porous FeSi₂ elements.

In this paper, a U-shaped porous FeSi₂ thermoelectric conversion element for the reciprocating flow combustion system is presented.

We use a spark plasma sintering (SPS) technique for shaping the element with large porosity ratios. Thermoelectric properties of the element are evaluated to examine its potential for the power generation as a gas-combustion and heat-exchange type thermoelectric device.

2. Porous FeSi₂ Element

Mn- or Co-doped FeSi₂ powders, of which chemical compositions are listed in Table 1, were prepared by an Ar gas atomizer. The powders were annealed at 1123 K for 1.8 × 10⁵ s in an Ar atmosphere to achieve single β-phase. They were then put through a sieve to screen powders between 500 and 700 μm in diameter. After the screening, the powders are chemically polished in an acid solution (conc-HF 1 mL+conc-H₂O₂ 99 mL), rinsed in methanol and deionized water, and dried by a N₂ gas blow.

Figure 1 presents the schematic chart of the SPS process. The screened Mn- or Co-doped FeSi₂ powders are loaded into a carbon punch-and-die unit, in which Mn-doped powder is separated from Co-doped one by insulating glass fiber sheets (Toshiba Monofilax Co., Ltd. Fiber flax paper #300). The porous element should satisfy high gas permeability and a large specific surface (surface area per unit volume) for heat transfer between gas and solids. Therefore, it is desirable to form the element with the porosity ratio as large as possible. Using spherical particles of the FeSi₂ powders, it was difficult to shape the element with the porosity ratio more than 45%. Thus a porous FeS₁₂ element with the porosity ratio of 45% was fabricated by SPS. Here, the porosity ratio P has been calculated by

\[ P = 1 - \rho_{\text{element}} / \rho_{\text{FeSi₂}} \]  

where \( \rho_{\text{element}} \) and \( \rho_{\text{FeSi₂}} \) are the apparent density of the porous element and the density of the FeSi₂ powder respectively; \( \rho_{\text{FeSi₂}} \) is 5 × 10³ kg/m³. Ag meshes (wire diameter 100 μm, open area ratio 35%) are used as electrodes to connect the p-type (Mn-doped) and n-type (Co-doped) parts as well as to

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Si</td>
</tr>
<tr>
<td>p-type: 44.85</td>
<td>50.27</td>
</tr>
<tr>
<td>n-type: 47.11</td>
<td>50.24</td>
</tr>
</tbody>
</table>
Development of a Porous FeSi$_2$ Thermoelectric Conversion Element

connect them with external circuits. SPS processing parameters are shown in Fig. 1. The sintering temperature was measured by a thermocouple inserted in the die cavity as close to the heating specimen as possible.\textsuperscript{11} Cooling rate was controlled to 5 K/s to avoid the element destruction because of thermal contraction. The cylindrical element, which consisted of both p-type and n-type porous semicylinders separated by a glass fiber sheet, was thereby produced. The Ag mesh was connected at lengthwise sides of the element. The size of the element was approximately 30 mm in diameter and 17 mm in length. Then the elements were annealed at 1123 K for $9 \times 10^4$ s in a vacuum of about $10^{-6}$ Pa. X-ray analyses revealed that they were composed of single $\beta$-phase.\textsuperscript{12}

3. Measurements of Thermoelectric Properties

The thermoemf in the internal resistance of the elements were measured under a temperature gradient which was formed by heating at one end of the element and cooling the other end by ambient air or a liquid-N$_2$ filled thermal bath, as shown in Fig. 2. The maximum temperature difference across the element was 143.5 K. The side of the element was covered by a heat insulating fiber sheet in order to avoid lateral thermal gradient. The temperature gradient was measured by using the four Pt–Rh thermocouples glued at the sides of the element. The internal resistance was evaluated using a matched resistive load technique. Output voltage was measured as a function of external load resistance. The relationship between the internal resistance and the matched resistive load is expressed as

$$V/V_0 = R/(R_e + R_0),$$

where $V_0$ is the open circuit voltage, $V$ is the output voltage, $R_e$ and $R_0$ is the internal and the external load resistance respectively. We estimate the internal resistance $R_0$ by fitting $V/V_0$ with eq. (2).

4. Results and Discussions

Figure 3(a) shows a scanning electron microscope (SEM) micrograph of the FeSi$_2$ porous element. As shown in the figure, most of the FeSi$_2$ particles are connected only by a narrow neck so that the element is significantly porous but mechanically rigid. In Fig. 3(b) is shown a SEM micrograph of the interface between a FeSi$_2$ particle and a Ag mesh electrode of the element. Although solubility between Ag and Si or Fe is extremely low, a relatively good contact between the element and the electrodes was obtained due to a large contact area at the interface.

Figure 4 shows the open circuit voltage of the porous FeSi$_2$ element as a function of temperature difference across the element. The voltage increases linearly with increasing the temperature difference and hence relative thermoelectric power are almost constant and 0.5–0.7 mV/K (sum of power generation of the p- and n-type portions) in this temperature range. At the temperature range of 300–500 K, Nishida and Kojima have previously reported that the thermoelectric power is 0.3–0.4 and 0.2 mV/K for Mn- and Co-doped FeSi$_2$ dense sintered plates respectively.\textsuperscript{7,8} Therefore, the sum of the thermoelectric power of Mn- and Co-doped FeSi$_2$ is in good agreement with the measured thermoelectric power of the porous element.

Figure 5 presents the variation of $V/V_0$ with $R$ for the porous FeSi$_2$ element at various temperatures. Calculated $V/V_0$ according to eq. (2) with assumed internal resistances is also illustrated as solid lines. As expected, change of the measured voltage is well fitted with eq. (2), and thus a well-defined ohmic internal resistance can be deduced from the fitting. Figure 6 illustrates the temperature dependence of the deduced internal resistance $R_0$. $R_0$ decreases with increasing temperature, and it is about ten times larger than that calculated from the electrical resistivity of the dense FeSi$_2$ sin-
Fig. 3  (a) A SEM micrograph of the FeSi₂ porous element. Most of the FeSi₂ particles are connected only by a narrow neck so that the element is significantly porous but mechanically rigid. (b) A SEM micrograph of the interface between a FeSi₂ particle and a Ag mesh electrode of the element.

Fig. 4  The open circuit voltage of the porous FeSi₂ element as a function of temperature difference across the element.

Fig. 5  The variation of \( V / V_0 \) with \( R_e \) for the porous FeSi₂ element at various temperatures. Calculated \( V / V_0 \) according to eq. (2) with assumed internal resistances is also illustrated as solid lines. Inset are temperatures both ends of the element.

tered compact;\(^7,8\) no porosity is assumed for the calculation. Yasuda et al., have reported a large porosity dependence of the electrical resistivity for the PbTe thermoelectric conversion device.\(^1,3\) The resistivity of the PbTe elements with relative porosity 25–30% was 10–20 times larger than that of the dense elements due to the reduction of contact areas between PbTe particles. The large internal resistance observed in this experiment is attributed to this reduction of contact areas between FeSi₂ particles as well as between the particles and Ag electrode because of an immature sintering to form porous structures.

It is estimated that the maximum generated power using the present porous element under such circumstance that a larger temperature gradient exists in the element. A large temperature gradient of about 250 K/cm in porous FeSi₂ elements with the almost same dimensions as that of this element has been reported via the reciprocating flow combustion system\(^14\) in the temperature range from 500 to 900 K. From the calculation under the thermal gradient of 250 K/cm, thermoelectromotive force of 255 mV is generated in our porous element with length of 17 mm, since the measured relative thermoelectric power in this experiment is approximately 0.6 mV/K and the thermoelectric power of FeSi₂ is known not to significantly change in a wide temperature range from 300 to 900 K.\(^7,8\) Moreover, we assume a somewhat reduced internal resistance of 0.2 Ω since the temperature range for the flow combustion system is higher than that in this experiment and the internal resistance decreases with increasing temperature as has been shown in Fig. 6. The maximum generated power, expressed by \((1/4)V_0^2/R_0\), is estimated to be 81 mW. In other words, energy density of the present FeSi₂ porous element
5. Conclusion

U-shaped porous FeSi₂ elements for the gas-combustion and heat-exchange type thermoelectric conversion system was developed by SPS technique. Measured thermoelectric power and apparent internal resistivity of the element are 0.5–0.7 mV/K at 300–500 K and 3.99 × 10⁻³ Ωm at 448–479 K respectively. It is estimated under some assumptions that the generated maximum energy density of the element could reach 6.8 kW/m³ in the reciprocating flow combustion system.

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