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Thermoelectric Properties of $MnSi_{\sim1.73}$ Produced by Cold Pressing and Sintering

T. Iizuka, M. Kato, I.J. Ohsugi, T. Kojima, I.A. Nishida
H. Kohri*, I. Shiota* and T. Suzuki*
Salesian Polytechnic, 2-35-11, Igusa, Suginami, Tokyo 167-0021, Japan
Fax: +81-3-5310-6200, e-mail: kato-m@ikuei-sp.ac.jp
*Kogakuin University, 2665-1, Nakano-machi, Hachioji, Tokyo 192-0015, Japan
Fax: +81-426-28-4596, e-mail: kohri@cc.kogakuin.ac.jp

Sintered bodies of $MnSi_{\sim1.73}$ with a relative density of 92% was successfully produced by a low cost technique, namely, the cold pressing and sintering, which will enable to establish a practical production process for $MnSi_{\sim1.73}$ with a superior thermoelectric properties. The figure of merit was estimated at $3.7\times 10^{-4}K^{-1}$, which is comparable to that of sintered materials produced by the conventional sintering using hot pressing. Attempts were made to process the simultaneous sintering of p-type $MnSi_{\sim1.73}$ and n-type $FeSi_2$ in order to produce a p-n junction module which is expected to possess a superior thermoelectric performance to the conventional $FeSi_2$ module. It was found that the direct p-n junction may be processed by introducing a functionally graded structure into the junction.
Key words: manganese silicide, iron disilicide, ceramic technology, p-n junction, thermoelectric properties

1. INTRODUCTION

Thermoelectric power generation is a direct thermal-to-electric energy conversion, which is utilized for high reliability power sources such as those in spacecrafts. Economical thermoelectric materials useful to collect exhaust heat are paid attention as well as efficient thermoelectric materials used such a special purpose. Typical of them is in 3d transition metal oxides. Especially $FeSi_2$ is promising, because it withstands a high temperature above 900°C in the atmosphere, the raw materials Fe and Si are harmless, and the earth is abundant in them. $FeSi_2$ also possesses a number of advantages, i.e., a high thermoelectric performance is obtained even when it is processed from industrial materials with a low purity, the energy cost is low, and the conventional ceramic technology is applicable.

$FeSi_2$ doped with Mn is a p-type semiconductor, while with Co an n-type. The authors have processed sintered materials with a relative density above 90% by using the cold pressing and sintering, and successfully produced the U-shaped p-n junction module [1].

The maximum value of dimensionless figure of merit $(ZT)_{max}$ of n-type $FeSi_2$ is 0.4, while that of p-type is 0.2 [1]. For this reason, attention is paid to $MnSi_{\sim1.73}$ whose $(ZT)_{max}$ is 0.7, to improve the performance of the U-shaped p-n junction module. Many reports have been made on the crystal structure of this compound. The constitution of this compound is known to be $MnSi_{2-x}$ $(0.250\leqq x\leqq 0.273)$; $Mn_{15}Si_{26}$ is weighty [2-4]. It has originally been developed as a heat-resistant material, while it has a p-type semiconducting property also. It is consequently expected that a p-n junction module with a higher performance than that of the conventional $FeSi_2$ modules will be produced by combining a p-type $MnSi_{\sim1.73}$ and an n-type $FeSi_2$. The sintered materials of $MnSi_{\sim1.73}$, however, have been processed only by the hot pressing. It is difficult to use $MnSi_{\sim1.73}$ instead of $FeSi_2$ unless some economical process is realize to process a high density $MnSi_{\sim1.73}$.

In this work, $MnSi_{\sim1.73}$ sintered materials with a high density are processed by the practical cold pressing and sintering, which is conventionally used for $FeSi_2$, and their thermoelectric properties are evaluated. Discussion is also done to realize the p-n junction of p-type $MnSi_{\sim1.73}$ and n-type $FeSi_2$.

2. EXPERIMENTAL PROCEDURE

The raw materials were 3N electrolytic Fe, 6N single crystal Si, 3N electrolytic Mn, 3N electrolytic Co, and 4N oxygen-free Cu. A certain amount of Mn is cleaned with ethanol including 5% HCl. They are weighed in a certain constitution and arc-melted in an argon atmosphere to obtain an ingot. The Si content was adjusted at a slightly larger value than the required amount, namely the constitution is expressed by $MnSi_{1.78}$, considering the reduction in the arc-melting and powdering processes. The constitution of $FeSi_2$ for the n-branch of the p-n module is adjusted at $Fe_{0.96}Co_{0.04}Si_{2.1}$ with 1wt% Cu [5,6], which was employed in order to form the semiconducting β-FeSi2 without heat treatment and to lower the melting point of $FeSi_2$ for simultaneous sintering of $FeSi_2$ and $MnSi_{\sim1.73}$. The ingot had been ground into powder with an average size of several μm in an aluminous mortar for several hours. The manganese silicide powder obtained was applied with the X-ray diffraction observation to ensure that it consisted only of $Mn_{15}Si_{26}$.

The powder was changed into slurry by adding some 0.5wt% poly vinyl alcohol (PVA) solution and dried to remove excess water, before the cold pressing to improve the strength of the green sample. The powder including 10wt% water and 0.3 or 1wt% PVA was formed under a pressure of 50 MPa, and then it was again ground into particles with an average diameter of

90~180 μm. They were filled into a 30mm×4mm die, and cold-pressed under a pressure of 400 MPa to be formed into a green sample with an apparent relative density above 60%.

The green sample was sandwiched between aluminous plates. It was put into a heat-resistant boat and placed in an electric furnace. The inside of the boat was filled with aluminous powder to prevent the thermal deformation and to ensure a uniform temperature in the boat. The sample was roasted to remove the PVA. The temperature was gradually increased up to 400°C at a rate of 80°C/h, the air being blew into the furnace. After the temperature reached 400°C, the air blow was stopped and the furnace was evacuated. The temperature was again increased up to 1135°C at a rate of 180°C/h, and then the temperature was held for 3 or 24 hours for sintering.

The sintered material obtained was polished, and its density was determined on the basis of the buoyancy method. The sintered material obtained was polished, and its density was measured by the buoyancy method. The density measured was divided by the ideal density reported by Knott et al. on the basis of the crystal structure of $Mn_{15}Si_{26}$ to determine the relative density [2]. Thermoelectric properties were measured at room temperature. One end of the specimen was heated by a small heater to apply a temperature difference ΔT of the order of several K in the longitudinal direction. The values of the thermoelectric power E_0 were measured for the certain temperature differences to obtain the E_0-T curve. The thermoelectric power was determined from the gradient of the curve. Resistivities were measured at room temperature on the basis of the four-terminal method. Applying a current of ±50~100A, the potential difference was measured at the middle of the specimen with a distance between terminals of 3 mm.

Examination was made on processing a p-n junction of the p-type $MnSi_{\sim 1.73}$ and the n-type $FeSi_2$. Soldering must not be applied to this junction, because the junction temperature is assumed to be about 950°C, which is similar to the $FeSi_2$ module case. Powder of $Fe_{0.96}Co_{0.04}Si_{2.1}$ (expressed by the $FeSi_2$ powder hereafter) was filled into a rectangular die, and a 0.1 mm paper was placed at the junction to make a 5 mm gap. After that, the powder of $MnSi_{\sim 1.73}$ was filled in the die, and the sample was pressed under a pressure of 400 MPa. An attempt was also made to form an intermediate layer between the $FeSi_2$ and the $MnSi_{\sim 1.73}$ powders. The layer was filled by 1/16 of the $FeSi_2$ powder. Sintering was performed under the same conditions as that in the $MnSi_{\sim 1.73}$ case. Two attempts were made to form the junction; i.e., the direct junction and the indirect junction with an intermediate layer. For the intermediate layer, three types of powders; i.e., (1)$MnSi_{\sim 1.73}$ and $FeSi_2$ particles mixed at a ratio of 1:1, (2)mixture of $MnSi_{\sim 1.73}$ and $FeSi_2$ melted and ground, and (3)$MnSi_{\sim 1.73}$ and $FeSi_2$ fine powders mixed at a ratio of 1:1, melted and ground.

3. RESULTS AND DISCUSSION

Figure 1 shows examples of the green samples and the sintered materials. The sintered materials were polished. They were lustrous and sufficiently shrunk in the longitudinal direction. No clacks and no deformations were observed in them.

The maximum relative-density of the samples sintered for 3 hours at 1135°C 89%, which was independent of the amount of PVA and the temperature for roasting. The thermoelectric power was 90 μV/K and the resistivity was 1.81 mΩcm, which were inferior to the values for the hot-pressed sample reported by Kawasumi (110 μV/K and 1.25 mΩcm) [7]. The performance of thermoelectric materials is expressed by the figure of merit $Z=\alpha^2/(\rho\kappa)$ [K^{-1}], where α is the thermoelectric power, ρ the resistivity, and κ the thermal conductivity. Abrikosov and Ivanova estimated the a- and the c-components of κ in the single crystal at 3.677 and 1.788 W/(Km), respectively [8]. Assuming that the crystallites are distributed at random, we estimated the ideal value at 3.05 W/(Km). The figure of merit of the sample obtained in this experiment was consequently estimated at 1.47×10^{-4} K^{-1}, which was about a half of that of the hot-pressed sample by Kawasumi, viz., $3.4\times10^{-4}K^{-1}$. There also was a problem that the sample might be melted accidentally at the sintering temperature, which was near to the melting point 1145°C.

For this reason, the samples were sintered at 1120°C for 24 hours. The relative density of the sample sintered under this condition was 93%. The resistivity was 1.92 mΩcm, which was greater than that of the hot-pressed sample, while the thermoelectric power showed a high value, namely 150 μV/K. The figure of merit of this sample was estimated at 3.8×10^{-4} K^{-1}, which was 10% greater than that of the hot-pressed sample, namely 3.4×10^{-4} K^{-1}. The actual thermal conductivity of this sample estimated at a lower value because of the boundary scattering of phonons. The figure of merit was consequently estimated at a higher value. The estimation in this experiment was made only for the room temperature, so that it should also be made for higher temperatures. For all that, it is found from the results of this experiment that $MnSi_{\sim 1.73}$ sintered material may readily be produced by the cold pressing and sintering, which are practical and economical.

The direct p-n junction was apparently formed, but it was easily broken when the sample was polished. No clacks however were observed inside the sample.

Effective junction could not be processed even by introducing an intermediate layer consisting of $MnSi_{\sim 1.73}$ - $FeSi_2$ particles. The $FeSi_2$ branch bent near the junction.

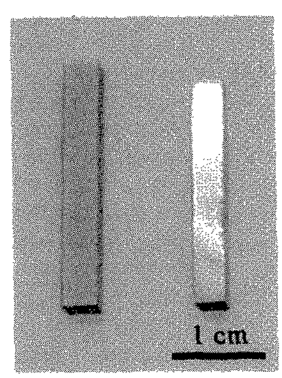

Fig.1 A green sample (left) and a sintered compact (right) of $MnSi_{\sim 1.73}$.

When the ratio of the powders was adjusted at 1:1, the sample melted especially at the junction, although the sintering temperature 1135°C was lower than the melting point 1145°C of $MnSi_{1.73}$. The intermediate layer might be not suitable to form the junction, because the density of the sintered material might be decreased by sintering at a lower temperature. Cu doped in the material might cause to melt the junction. This problem is now under review.

When the mixture particles were used for the intermediate layer, it did not join to the $MnSi_{1.73}$, but it joined to the $FeSi_2$. This fact suggested that a functionally graded layer may be effective to establish the p-n junction.

4. CONCLUSION

Sintered materials of $MnSi_{1.73}$ with a sufficiently practical characteristics can successfully be produced by using the cold pressing and sintering suitable for mass-production. The sintered materials produced in this work possessed a high figure of merit at room temperature, which is comparable to that of the materials produced by the conventional hot pressing. Attempt was made to process a p-n junction of $MnSi_{1.73}$ and $FeSi_2$ to accomplish a higher thermoelectric performance than that of the conventional $FeSi_2$ p-n junction. It is found from the result that such a junction between different silicides may be realized by introducing a functionally graded structure into the junction.

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