Paper

Cobalt and Iron Doping Effects on Thermoelectric Properties of Higher Manganese Silicides Prepared by Mechanical Milling and Pulse Discharge Sintering

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ABSTRACT

Higher manganese silicide (HMS) is promising as one of eco-friendly p-type thermoelectric materials which are useful to power generation system using the waste heat with medium temperature from 600 to 900 K. We investigated about the doping effect of cobalt and iron on thermoelectric properties of the HMS compounds in this study. A combined process of vibration ball milling (VBM) and pulse discharge sintering (PDS) is used for fabricating the HMS compounds. Mn and Si powders milled individually using VBM were mixed with Co or Fe fine powders in argon atmosphere. The powder mixtures were sintered and simultaneously the HMS compounds were synthesized using the PDS process. Syntheses of Co-doped and Fe-doped HMS compounds were confirmed. The lattice parameters of a-axis in (Mn\(_{1−x}\)Co\(_x\))\(_{15}\)Si\(_{26}\) compound decreased with Co content (\(x ≤ 0.01\)) and held constant within the range of \(x = 0.01~0.1\), and that in (Mn\(_{1−y}\)Fe\(_y\))\(_{15}\)Si\(_{26}\) compound decreased linearly with Fe content (\(y ≤ 0.1\)). The doping limit of Co in HMS existed around \(x = 0.01\). The thermoelectric performance ZT was decreased with Co content. On the other hand, the maximum ZT of 0.55 was achieved at 773 K by doping Fe with \(y = 0.005\).

KEY WORDS

higher manganese silicide, doping, mechanical milling, synthesis, thermoelectric properties

1 Introduction

The global energy consumption in the industrial activity and human life has been explosively increased year by year and majority of the energy is still dependent upon the fossil fuels, such as petroleum, natural gas, and coal. The energy problem of exhaust of fossil fuels and the environmental problems of air pollution and global warming by combusting the fuels have become serious. Developing alternative energy sources like the recycled energy sources and eliminating the waste in the energy supply and consumption are required. The thermoelectric module that directly converts the thermal energy to electricity can widely apply to the power generation from micro scale to mega scale. Thus, it is a prospective means using the waste heat discharged from energy systems such as automobiles, combined cycles and waste material incineration systems, and it is expected to give us the resolution of environmental problems and the energy security.

Higher manganese silicide (HMS) is a p-type thermoelectric compound MnSi\(_y\) (\(γ = 1.67~1.75\)). Both of Mn and Si as constituent elements in HMS are harmless, and they exist in abundance as mineral resources. HMS can, therefore, become a low-cost and eco-friendly thermoelectric material, and lately it attracts attention as a counterpart material of n-type Mg\(_2\)Si compound that is similarly low-cost and eco-friendly. It has been reported that each of HMS compounds, Mn\(_{11}\)Si\(_{19}\), Mn\(_{26}\)Si\(_{45}\), Mn\(_{15}\)Si\(_{26}\), Mn\(_{27}\)Si\(_{47}\) and Mn\(_7\)Si\(_4\) has a tetragonal crystal structure\(^{11}\). All of HMS compounds have unique very long crystal structures along c-axis, and each compound has the different long-periodic structure. The manganese atoms construct a frame structure, and the silicon atoms construct a helical structure in the frame, regardless of the different long-periodic structure.

In fabricating MnSi\(_y\), thermoelectric elements, an arc melting method, an induction heating method or several types of crystal growth methods were conventionally used. For example, the thermoelectric properties of the Al, Ge and Mo doped HMSs fabricated by modified Bridgman method have been investigated\(^9\)~\(^10\). The fabricated HMS compounds had a typical layered microstructure of HMS layer and MnSi thin layer. These melting methods, however, require huge energy and/or long term, and they make an inhomogeneous
microstructure. Thus, the powder metallurgical methods have some advantages on the HMS fabrication. Groß et al.\(^9\) have made the HMS compound via a powder metallurgical route, and evaluated its thermoelectric properties (\(ZT \approx 0.3\) at 673 K). Umemoto et al.\(^10\) have researched on the manganese silicides made by mechanical alloying (MA) and pulse discharge sintering (PDS). They reported the thermoelectric properties of the samples having the starting compositions of MnSi\(_{1.7}\) and MnSi\(_{1.8}\) (\(ZT = 0.66\) at 873 K). Hashii et al.\(^5\) have researched on the MnSi\(_{1.7}\) powder prepared by gas atomization, which has an advantage on low production cost. In our previous work\(^8\), we reported the influence of the MA conditions on synthesis of HMS having a starting composition of MnSi\(_{1.7}\) prepared by MA and PDS method and its thermoelectric properties (\(ZT = 0.47\) at 873 K). We also reported the thermoelectric properties of HMS compounds synthesized by mechanical grinding (MG) and PDS method\(^6\). In the previous work, each of pure Mn and Si powders was mechanically ground using a planetary ball milling equipment and the HMS compound was synthesized from the ground powder mixture and simultaneously consolidated by PDS. In this research, we changed the planetary ball milling to the vibration ball milling (VBM) that has a high production efficiency and a possibility of mass production, and newly investigated the influence of Co and Fe doping on the thermoelectric properties of the HMS.

2 Experimental

As raw material powders, Mn powder (purity: ≥ 99.9 %, particle size: ≤ 75 μm) and Si powder (≥ 99.9 %, ≤ 75 μm) were used. Furthermore, Co powder (≥ 99.9 %, 5–6 μm) and Fe powder (≥ 99.9 %, 5–6 μm) were added as dopants. All powders were of KOJUNDO CHEMICAL LAB. Co., Ltd., Japan. Firstly, each of Mn and Si powders was put into an alumina milling pot (capacity: 1000 ml) with alumina balls (diameter: 8 mm) with volume ratio of ball to powder of 10 : 1, and mechanically ground for 10 h in an argon atmosphere using a vibration ball milling equipment (VS-1, IRIE SHOKAI Co., Ltd., Japan). Then, the milled powders with particle size of 45 μm or less were individually collected by sieving in an argon atmosphere. Mixing of the milled powders of Mn and Si and the fine powder of Co or Fe was carried out with the starting composition Co\(_x\)Mn\(_{1-x}\)Si\(_{1.7}\) (\(x = 0, 0.003, 0.01, 0.05\) and 0.1) or Fe\(_x\)Mn\(_{1-x}\)Si\(_{1.82}\) (\(y = 0, 0.005, 0.01, 0.03, 0.05\) and 0.1) using a rotary ball milling equipment (ANZ-51S, Nitto Kagaku Co., Ltd., Japan) at 100 rpm for 1 h in an argon atmosphere. The ratio of Si content to (Co,Mn\(_{1-x}\)) or (Fe,Mn\(_{1-x}\)) in the starting composition, 1.82 is the value optimized for getting the best thermoelectric performance in the binary Mn-Si system synthesized by similar VBM-PDS method\(^10\). We use a polyethylene pot (capacity: 500 ml) and zirconia balls (diameter: 5 mm) with volume ratio of ball to powder of 20 : 1. The powder mixture was sintered at 1173 K for 15 min in vacuum under 30 MPa using a PDS equipment (SPS-1050, Fuji Electronic Ind. Co., Japan), and then cooled at a cooling rate of 2 K/min. The sintered samples were cut into quadratic prism (3 × 3 × 13 mm), and the Seebeck coefficient and electrical resistivity were measured using a thermoelectric measurement equipment (ZEM-2, Ulvac-Riko Inc., Japan). The disk-type specimens (10 mm (diameter) × 1 mm (thickness)) were prepared from the sintered samples, and the thermal conductivity was determined with a laser-flash equipment (TC-7000, Ulvac-Riko Inc., Japan). The sintered samples were characterized using X-ray diffractometer (XRD) (RINT2500, Rigaku Co., Japan) with Cu Kα radiation, and a scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX) (SEMEXIII Type-N, Hitachi High-Techologies Co., Japan). The lattice parameter and its standard deviation were calculated using a software named “CellCalc” based on the least square method with respect to the data of interplanar spacing and Miller indices of the crystal Mn\(_{1+x}\)Si\(_{26}\) obtained from X-ray diffraction pattern.

3 Results and discussion

3.1 Influence of Co doping on the thermoelectric properties of HMS

All sintered samples had a relative density of 95 % or more. Fig. 1 shows the SEM image in section of the Co-doped HMS sample with Co content (\(x = 0.005\)). The HMS compound fabricated by VBM-PDS method has a homogeneous microstructure with some small pores, compared with the compound fabricated by modified Bridgman method\(^9\), which has a typical layered microstructure of HMS layer and MnSi thin layer. The XRD patterns of the sintered samples with different Co content is shown in Fig. 2. The HMS compound was detected as a major phase in all Co-doped samples. In the case of higher Co content (\(x \geq 0.01\)), the diffraction peak of CoSi\(_2\) phase appeared. The relation between lattice parameter of a-axis and Co content are shown in Fig. 3. The length of error bar in this figure corresponds to twice standard deviation obtained in the analysis. The lattice parameter of a-axis in the range of \(x = \)
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0~0.01 decreased with Co content. Then they kept almost constant level at the higher Co content ($x \geq 0.01$). This result indicates that Co atoms with an atomic radius smaller than Mn atoms were substituted for the Mn sites in the crystal structure of HMS at $x \leq 0.01$, but the saturation of atomic substitution and the formation of CoSi$_2$ by reaction of surplus Co and Si were occurred at $x \geq 0.01$. From SEM-EDX analysis, it was confirmed that the composite phases of HMS and CoSi$_2$ existed in the HMS matrix.

Temperature dependences of the electrical resistivity of the Co-doped samples are shown in Fig. 4. All samples have the maximum value of the resistivity at about 800~830 K. The resistivity increased with Co content by $x = 0.005$, and it decreased with Co content at $x \geq 0.01$. It is thought that the doping of Co brought the increase of resistivity, and the precipitation of CoSi$_2$ with low resistivity (~0.14 $\mu$Ωm) led to the reduction of the resistivity based on a mixture law. Fig. 5 represents the temperature dependence of the Seebeck coefficient of the Co-doped samples. The maximum values of the Seebeck coefficient of all samples existed at about 760~780 K. In the range of $x = 0$~0.01, the Seebeck coefficient hardly depended upon the Co content, but it decreased with Co content at $x \geq 0.05$. The reduction of the Seebeck coefficient at $x \geq 0.05$ could be related with the formation of CoSi$_2$ based on a mixture law. Although we did not measure the carrier concentration and the carrier mobility in this research, we surmise that Co doping reduces the carrier mobility and hardly affect the change of carrier concentration at $x \leq 0.01$ from the results of the resistivity and the Seebeck coefficient. Temperature dependence of the thermal conductivity of Co-doped samples is shown in Fig. 6. The thermal conductivity of all samples rose in the range of high temperature.
This phenomenon will be due to the bipolar effect. The thermal conductivity increased with Co content. Dimensionless figure of merit $ZT$ was estimated from the thermoelectric properties. Fig. 7 represents the temperature dependence of the dimensionless figure of merit $ZT$ of the Co-doped samples. The maximum $ZT$ of all samples existed at about 760–830 K and the $ZT$ value monotonically decreased with Co content.

3.2 Influence of Fe doping on the thermoelectric properties of HMS

The XRD patterns of the Fe-doped samples are shown in Fig. 8. Synthesis of the HMS compound was confirmed in all Fe-doped samples as same as the Co-doped samples. In the high Fe content ($y \geq 0.03$), $\beta$-FeSi$_2$ phase appeared. The relation between lattice parameter of $a$-axis and Fe content is shown in Fig. 9. The lattice parameter linearly decreased with Fe content, and the tendency was different from the relation in the Co-doped samples. The linear relationship between lattice parameter and Fe content, known as Vegard’s law, indicates that Fe atoms are substituted for the Mn sites in the crystal structure of HMS in the range of $y = 0$–0.1 as a state of solid solution. Miyazaki et al.\textsuperscript{12)} reported that the solid solution could be prepared up to $y = 0.35$. Thus, the linear relationship obtained in the range of $y = 0$–0.1 is a reasonable result. A little amount of $\beta$-FeSi$_2$ in the HMS matrix was also confirmed in the Fe-doped samples with Fe content ($y \geq 0.03$). In this study, the syntheses of the Co-doped and Fe-doped HMSs were made via a solid state reaction route. The frequency of direct contact of dopant powder and Si powder will rise in proportion to the dopant content and the formation amount of CoSi$_2$ or $\beta$-FeSi$_2$ will be increased with increase of the frequency. In the case of Co-doping, however, the solid solubility limit of Co clearly exists at around $x = 0.01$ of Co content. Thus, the lattice parameter was almost constant in the Co content over the solid solubility limit. The CoSi$_2$ will be formed from the excess Co and the residual Si in addition to the former case. On the other hand, in the Fe-doping without solid solubility limit in the range of $y = 0$–0.1, both the formation amount of $\beta$-FeSi$_2$ and the amount of solid-solved Fe would be increased in proportion to the Fe content. As the result, it is considered that both the detection of $\beta$-FeSi$_2$ phase in higher Fe content and the linear decrease of lattice parameter to the Fe content were occurred.

Fig. 10 shows the temperature dependences of the electrical resistivity of the Fe-doped HMS samples with different Fe content.
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increase of the resistivity. Temperature dependence of the Seebeck coefficient of the Fe-doped samples is shown in Fig. 11. The Seebeck coefficient was not systematically changed by Fe doping and slightly increased with Fe content. Fig. 12 represents the temperature dependence of the thermal conductivity of the Fe-doped samples. It was decreased with Fe content by $y = 0.005$ and increased with Fe content ($y \geq 0.005$). The rise of thermal conductivity at $y \geq 0.005$ would be due to the precipitation of $\beta$-FeSi$_2$ with higher thermal conductivity (6.5–10 Wm$^{-1}$K$^{-1}$ at 300–1000 K) than HMS. Dimensionless figure of merit $ZT$ estimated from the thermoelectric properties is shown in Fig. 13. The maximum $ZT$ of all samples existed at about 800 K. The Fe-doped sample with Fe content ($y = 0.005$) had the best thermoelectric performance of $ZT = 0.55$ at 770 K, and the performance has improved by 23% compared with non-doped sample.

4 Summary

Co-doped and Fe-doped HMS compounds were prepared by VBM-PDS method. In the case of Co doping, the Co atoms were substituted for the Mn sites at low Co content ($x \leq 0.01$) and surplus addition of Co brought the precipitation of CoSi$_2$ in the HMS matrix. Although the thermoelectric properties were varied by Co doping, the thermoelectric performance $ZT$ was monotonically reduced with Co content ($x$). In the case of Fe doping, the Fe atoms were substituted for the Mn sites at low Fe content ($y \leq 0.03$) and surplus addition of Fe brought the precipitation of $\beta$-FeSi$_2$ in the HMS matrix as same as Co doping. The changes in the thermoelectric properties by Fe doping showed the behavior different with Co doping. As the result, the Fe-doped sample with Fe content ($y = 0.005$) had the best $ZT$ value of 0.55 at 770 K, and the performance has improved by 23% compared with non-doped sample.

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