Materials Transactions, Vol. 48, No. 7 (2007) pp. 2100 to 2103
Special Issue on Thermoelectric Conversion Materials III

Improvement of Thermoelectric Properties of β-$FeSi_2$ by the Addition of Ta_2O_5

Kentarou Morikawa*1, Hiroyuki Chikauchi*2, Hiroyuki Mizoguchi*2 and Sunao Sugihara

Department of Material Science and Ceramic Technology, Shonan Institute of Technology, Fujisawa 251-8511, Japan

Our goal is the improvement of the thermoelectric properties for $FeSi_2$. We investigated the improvement of thermoelectric properties, that is, the increase of the power factor and the decrease in the thermal conductivity to add Ta_2O_5. The thermal conductivity of specimens with 1 mass% and 3 mass% of additive decreased to half in comparison with the sample without additive, because phonon scattering was enhanced as a result of an increase in the number of pores in the samples by the influence of Ta_2O_5. The figure of merit for sample with 1 mass% and 3 mass% of additive were higher than that for the sample without additive. The highest performance of the sample with 1 mass% of additive was $2.5 \times 10^{-4}\,K^{-1} \sim 2.8 \times 10^{-4}\,K^{-1}$ around 700 K and its dimensionless figure of merit was 0.2 at 700 K.
[doi:10.2320/matertrans.E-MRA2007860]

(Received November 20, 2006; Accepted May 6, 2007; Published June 20, 2007)

Keywords: *iron silicide, tantalum oxide, Seebeck coefficient, electrical resistivity, thermal conductivity, figure of merit, oxide addition, β-phase*

1. Introduction

A modern-day energy problem is the lack of fossil fuels and various environmental issues. Such as the greenhouse effect due to the burning of fossil fuels, which generates CO_2 and NOx. Therefore, the development of a production system for environment-friendly energy is important. Highly successful studies have been carried out on using thermoelectric power, where thermal energy is converted into electric energy directly using temperature differences.

The performance of thermoelectric materials is evaluated as using $Z = \alpha^2/\rho\kappa$. Z indicates the figure of merit, α the Seebeck coefficient, ρ the electrical resistivity and κ the thermal conductivity.[1)] ZT is another parameter used to evaluate the efficiency since the temperatures at which the thermoelectric material is to be used should be considered. At present, Bi_2Te_3, PbTe and SiGe are popular thermoelectric materials. However, they have the demerits that their raw materials are expensive and toxic. Consequently, it is important to develop other inexpensive and eco-friendly thermoelectric materials.

Our goal is the improvement of the thermoelectric properties of n-type $FeSi_2$ such as $(Fe_{0.95}Co_{0.05})Si_2$. $FeSi_2$ is a cheap and eco-friendly resource but has comparatively high thermal conductivity.

In previos studies, trivalent elements such as La_2O_3 and Y_2O_3, and quadrivalent elements such as TiO_2 and $LaSrMnO_3$ (LSMO) were added to n-type $FeSi_2$ to improve the performance.[2–5)] Electrical resistivity was decreased with oxide addition in comparison with the sample without oxide. However, no substantial improvement of performance has been shown. The maximum Z was $2.5 \times 10^{-4}\,K^{-1}$ at 700 K for the LSMO-added sample.

We investigated the improvement of the thermoelectric properties, that is, the increase of the power factor by decreasing the electrical resistivity and the decrease in the thermal conductivity, upon adding the quinquevalent Ta_2O_5.

2. Experimental

The starting material was made by melting Fe, Si and Co powders. These powders were mixed by ball-milling for 24 hours in air to form a composition of n-type $FeSi_2$ such as $(Fe_{0.95}Co_{0.05})Si_2$.[2)] The ingot of the starting material was pulverized to a particle size smaller than 20 μm. The milled powder of n-type $FeSi_2$ was mixed with Ta_2O_5 by ball-milling for 24 hours in air, then 10% polyvinyl alcohol was added to the mixture at a rate of 0.2 cc per gram. The ball-milled powder was molded at 153 MPa in a 10 mmφ die, and pressure was applied at 255 MPa by the CIP technique.

The molded sample was calcined at 670 K for 5 hours in air unit, calcined at 1463 K for 2 hours in a vacuum, and then heat-treated at 1033 K for 12 hours in a vacuum.

The thermoelectric properties were measured by the four-probe method to obtain the Seebeck coefficient and electrical resistivity, and thermal conductivity was calculated from the specific heat, thermal diffusivity and density measured by the laser flash method. The thermal conductivity was evaluated as, $\kappa = D \times C_p \times d$, where κ indicates the thermal conductivity, D the thermal diffusivity, C_p the specific heat, and d the density.

Furthermore, the phase constitution was confirmed from X-ray diffraction patterns. The microstructures of the surfaces of each sample were observed using a scanning electron microscope (SEM), and transmission electron microscope (TEM). Electron probe microanalysis (EPMA) was used for the analysis of the elemental distribution.

3. Results and Discussion

3.1 Thermoelectric properties

The Seebeck coefficient was the highest ($-234\,\mu V/K$ at 873 K) for the sample without additive (denoted as standard), as shown in Fig. 1. When the quantity of Ta_2O_5 increased, the Seebeck coefficient decreased. It was slightly decreased in the sample with 1 mass% and 3 mass% Ta_2O_5 in comparison with the standard, and it was $-210\,\mu V/K$ at 821 K. In the 10-mass%-Ta_2O_5 sample, the Seebeck coefficient was severely decreased to $-166\,\mu V/K$ at 828 K. The results suggest that the decrease is due to the oxide additive.

*1Graduate Student, Shonan Institute of Technology
*2Undergraduate Student, Shonan Institute of Technology

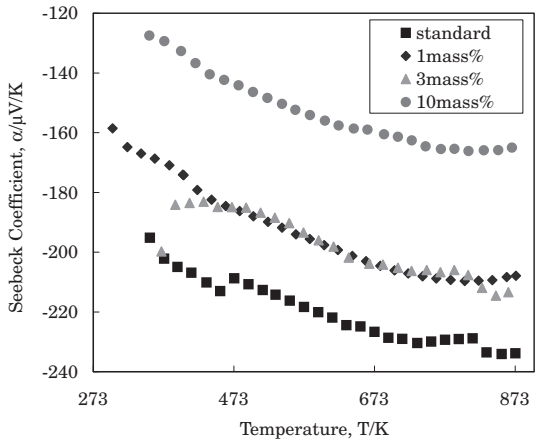

Fig. 1 Temperature dependence of Seebeck coefficient of n-$FeSi_2$ with Ta_2O_5.

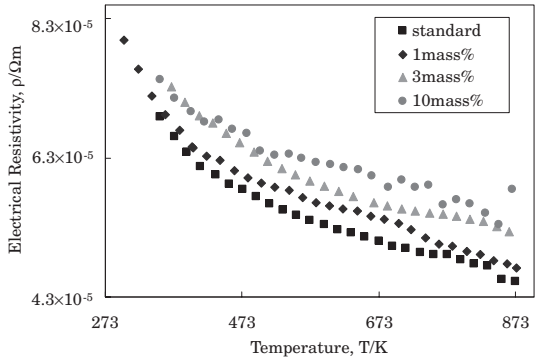

Fig. 2 Temperature dependence of electrical resistivity of n-$FeSi_2$ with Ta_2O_5.

The electrical resistivity was the lowest for the standard sample ($4.53 \times 10^{-5}\,\Omega$·m, 873 K) in Fig. 2. When the quantity of Ta_2O_5 was increased, the electrical resistivity increased. Thus, the quinquevalent Ta_2O_5 addition could not decrease the electrical resistivity of β-$FeSi_2$. This suggests that the cause is a decrease in the density of the sample when the quantity of additive was increased.

Figure 3 indicates that the power factor was the highest for the standard sample. When the quantity of Ta_2O_5 increased, the power factor decreased. It was found that the Seebeck coefficient decreased and electrical resistivity increased when the quantity of Ta_2O_5 increased.

The thermal conductivities of the sample with 1 mass%, 3 mass%, and 10 mass% Ta_2O_5 decreased in comparison with that of the standard sample, as shown in Fig. 4. Phonon scattering was enhanced by the increase in the number of pores in the samples resulting from the influence of Ta_2O_5, and the thermal conductivity was decreased. In particular, the thermal conductivities of the 1-mass%-and 3-mass%-Ta_2O_5 samples decreased to half in comparison with the standard sample. For the 1-mass%-Ta_2O_5 sample, it was 3.2 W/m·K at 790 K, and 2.8 W/m·K at 647 K for the 3-mass%-Ta_2O_5 sample, indicating that the thermal conductivity of $FeSi_2$ with an small amount of additive such as 1 mass% or 3 mass% remains constant at about 3 W/m·K.

The figure of merit, shown in Fig. 5, is higher for the 1-mass%-and 3-mass%-Ta_2O_5 samples than for the standard sample. It was found that the power factor decreased, the thermal conductivity decreased by half, and the figure of merit increased in comparison with that of the standard sample. The highest figure of merit was that of the 1-mass%-Ta_2O_5 sample, $2.45 \times 10^{-4} \sim 2.78 \times 10^{-4}\,K^{-1}$ around 700 K.

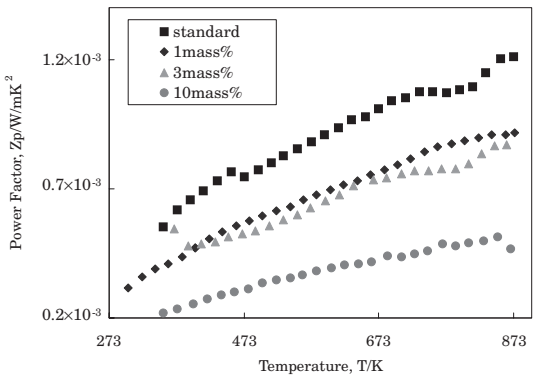

Fig. 3 Temperature dependence of power factor of n-$FeSi_2$ with Ta_2O_5.

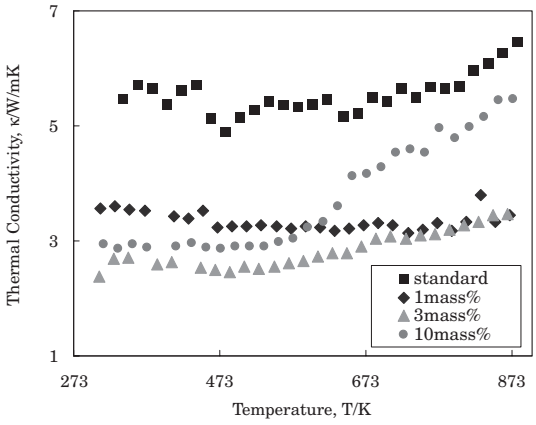

Fig. 4 Temperature dependence of thermal conductivity of n-$FeSi_2$ with Ta_2O_5.

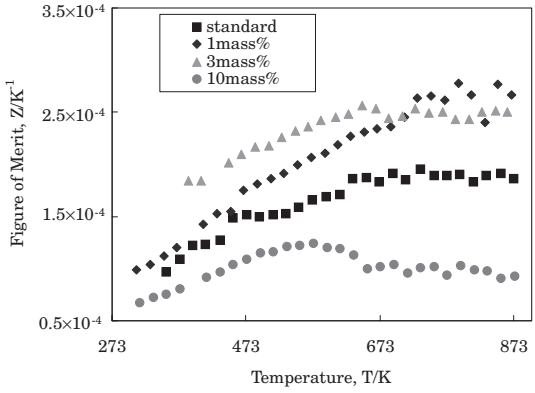

Fig. 5 Temperature dependence of figure of merit of n-$FeSi_2$ with Ta_2O_5.

3.2 Structural analysis

The density of n-type $FeSi_2$ with oxide is shown in Table 1. The density decreased with increasing amount of

Table 1 Density of n-type $FeSi_2$ with Ta_2O_5.

Sample	Density, d/g/cm^3	Density ratio, %
standard	4.64	100
Ta_2O_5 1 mass%	4.47	96.34
Ta_2O_5 3 mass%	4.34	93.75
Ta_2O_5 10 mass%	4.09	88.15

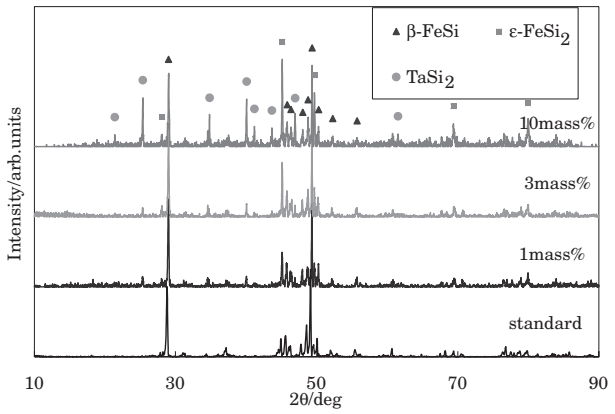

Fig. 6 XRD patterns of n-$FeSi_2$ with Ta_2O_5.

additive. It is thought that the degree of sintering was reduced with the presence of the additive and the number of pores increased in the sample. Therefore, the electrical resistivity increased and the thermal conductivity decreased.

XRD analysis (Fig. 6), confirmed that all samples were mostly composed of the β-$FeSi_2$ phase and the ε-FeSi phase.[6] The Ta_2O_5 peak was not observed. Furthermore, when the quantity of Ta_2O_5 increased, the intensities of $TaSi_2$ and ε-FeSi phase peaks were strong. It is considered that $TaSi_2$ was formed by the reaction of Ta with Si depending on the amount of additive. Therefore, it is thought that the amount of the ε-FeSi phase increases when the quantity of addition increases. As a result, the Seebeck coefficient decreases.

SEM analysis revealed that grain growth was restrained because pore size and quantity increased, when the quantity of Ta_2O_5 was increased, as shown in Fig. 7. In addition, impurities, which were Ta_2O_5 or $TaSi_2$, were confirmed in the grain boundary and pores. It was suggested that electrical resistivity increased and thermal conductivity decreased because the impurity crystals act as scattering centers.

EPMA (Fig. 8) analysis and TEM (Fig. 9) analysis showed that Ta was uniformly dispersed in the samples. It was confirmed that $TaSi_2$ was generated from Ta and Si that existed in the same area. On the other hand, the presence of Ta-oxide was confirmed by TEM analysis; thus it is considered that as the additive quantity increases, some oxide remains. The grain size of $TaSi_2$ or Ta_2O_5 in a sample was a maximum of about 1 µm. It is thought that thermal conductivity changed depending on the size of the dispersed phase in a sample. A small size of the dispersed phase may cause the enhancement of phonon scattering.

4. Conclusion

The thermal conductivity of specimens with 1 mass% and 3 mass% of additive decreased by half in comparison with the standard sample. We found that the presence of Ta_2O_5 and

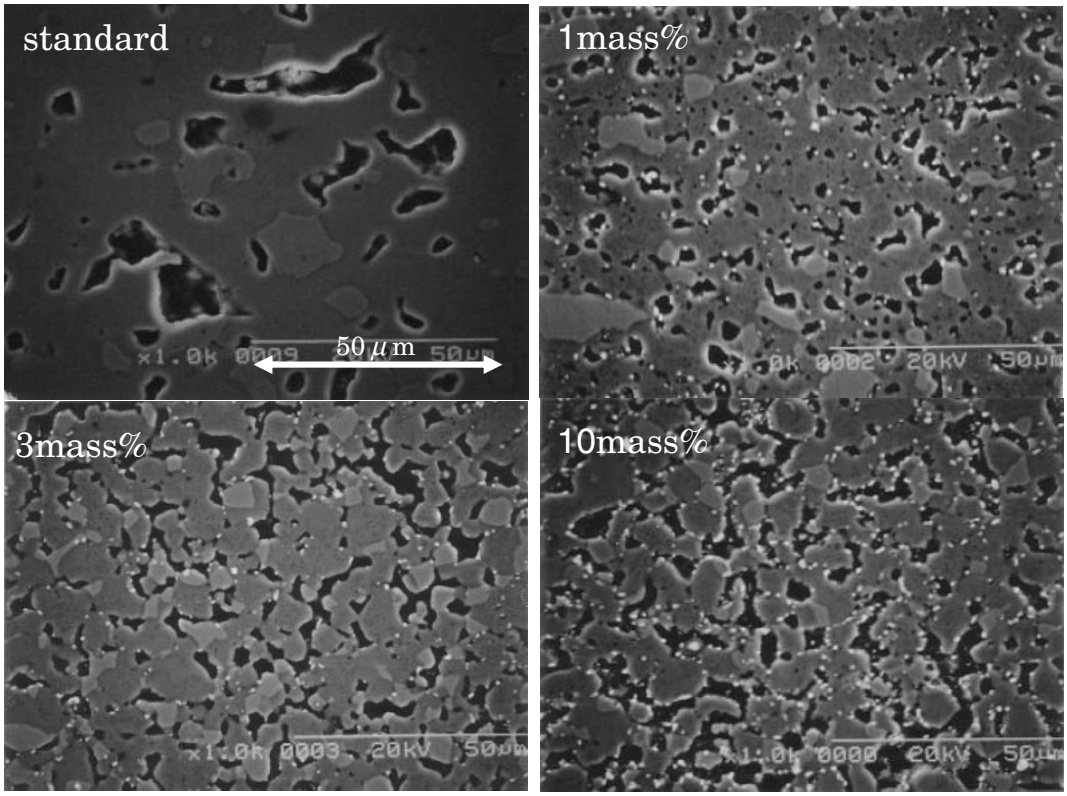

Fig. 7 SEM micrographs of n-$FeSi_2$ with Ta_2O_5.

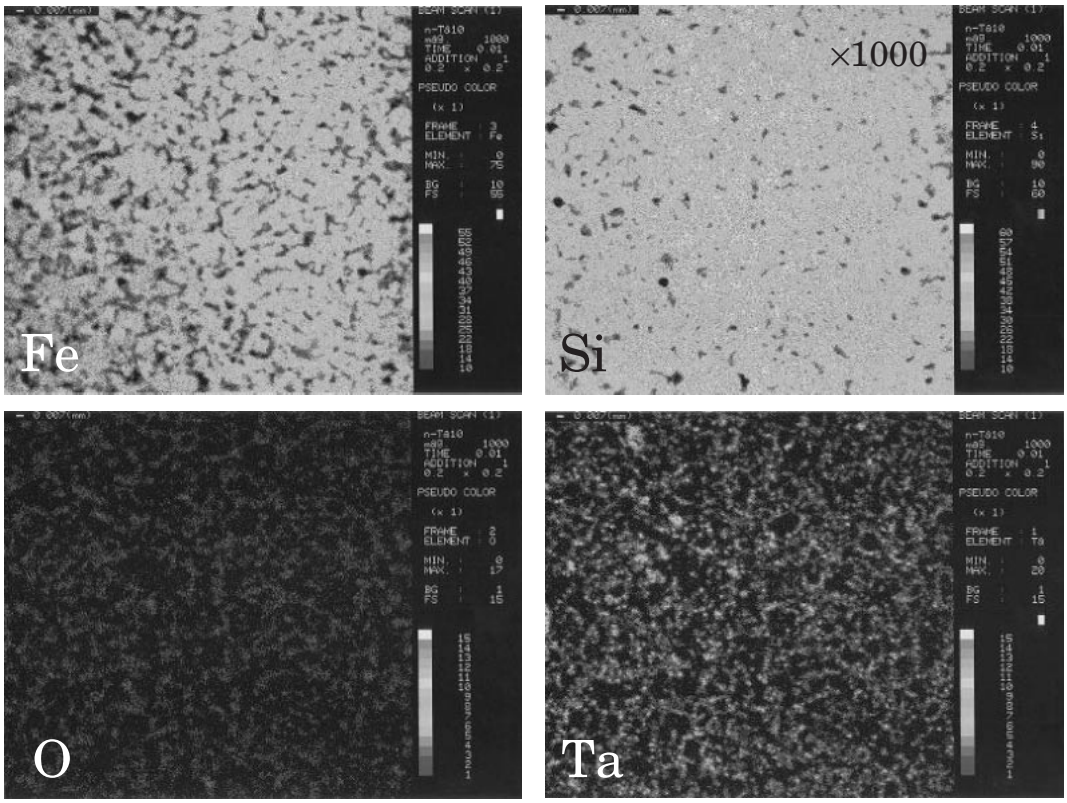

Fig. 8 Results of EPMA analysis of n-$FeSi_2$ with 10 mass% Ta_2O_5.

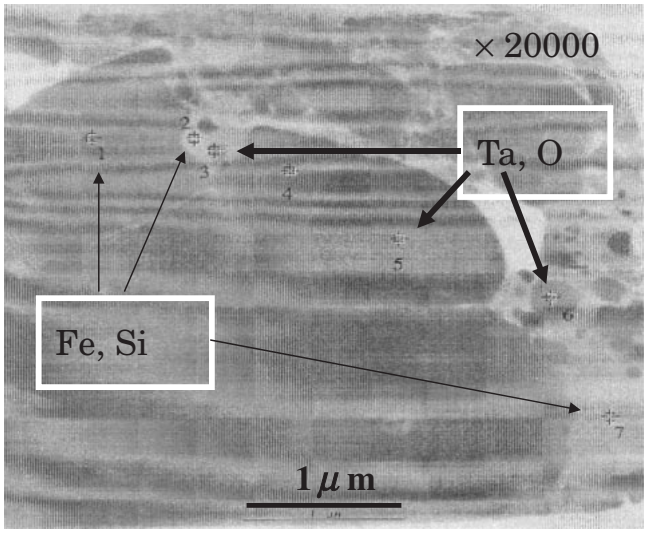

Fig. 9 Result of TEM analysis of n-$FeSi_2$ with 10 mass% Ta_2O_5.

$TaSi_2$ enhanced phonon scattering and resulted in a decrease in the thermal conductivity.

The figure of merit for the sample with 1 mass% and 3 mass% of additive were higher than that of the standard sample. The sample with 1 mass% of additive showed the best figure of merit of $2.5 \times 10^{-4}\,K^{-1} \sim 2.8 \times 10^{-4}\,K^{-1}$ around 700 K.

Acknowledgement

We thank the Kanagawa Academy of Science and Technology for the TEM analysis. We also really greatly appreciate the Kusaka Rare Metal Institute for providing the n-type $FeSi_2$ powder.

REFERENCES

1) S. Sugihara, S. Kawasima, H. Suzuki and I. Yonekura: Electronic Structure of $FeSi_2$ and Thermoelectricity, 9th CIMTEC-World Forum on New Materials, Sym. VII-Innovative materials in Advanced Technologies, ed. by P. Vincenzini **24**, (1999) pp. 753–762.
2) S. Sugihara, S. Kawasima, H. Katanahara, H. Suzuki, S. Mochizuki and R. Sekine: Doping Effects of Metal into Iron Disilicide on Electronic Structures and Thermoelectric Properties, Proceedings of 18th of International Conference on Thermoelectrics Baltimore, (MD, USA, 1999) pp. 577–580.
3) S. Sugihara, S. Mochizuki, H. Suzuki, T. Bak and J. Nowotny: J. Aust. Ceram. Soc. (2001) 33–44.
4) M. Ito, T. Tada and S. Hara: J. Alloy. Comp. **408–412** (2006) 363–367.
5) P. Strange, A. Svane, W. M. Temmerman, S. Szotek and H. Winter: Nature **399** (1999) 756–758.
6) U. Birkholtz and J. Schelm: Phys. Status Solidi **27** (1968) 413–425.