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Thermoelectric Properties of Mn-Si Ceramics

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We have studied thermoelectric properties of Mn-Si ceramics by paying attention to effects of grain size on thermoelectric properties. The solid-state reaction and spark plasma sintering were used to prepare the sample, whose thermoelectric properties such as Seebeck coefficient and electrical conductivity were measured. The starting Mn and Si materials were sintered with the powder obtained by milling for 0, 12 and 24 hours. Fineness of the materials, i.e. smaller grain material which yields the higher density material has been found to improve thermoelectric properties. The effect of dopant on thermoelectric properties was investigated preliminary. Some dopants such as Sb and Fe are found to be effective to improve the thermoelectric effects.

Key words: Thermoelectric material, Mn-Si ceramics, SPS method, Seebeck Coefficient, Dopant

1. INTRODUCTION

The interests of the environmental problems such as global warming due to the CO_2 emissions have rapidly risen lately. Thermoelectric materials can directly convert the thermal energy into the electric energy though the seebeck effect without the exhaust of waste materials. Thus, thermoelectric technology has been expected to yield a new technique to achieve energy savings and the effective use of waste heat.

The evaluation of the thermoelectric materials can be described by the power factor P and the figure of merit Z, which are expressed as

$$P=S^2\sigma \quad \text{and} \quad Z=P/\kappa$$

respectively. Here S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. The high Z means high efficiency of the thermoelectric conversion, and thus in order to obtain the good thermoelectric materials, large S, high σ and low κ are required. However, it is difficult to control these parameters independently because of their dependence on the carrier density [1].

Thermoelectric devices of Bi-Te, Si-Ge and so on have been already developed for practical use. But, these materials have weak points such as an expensive price and a limited amount of potential resources. So, we pay attention to silicides thermoelectric materials that have an advantage of a low cost, nonpoison and a light burden for earth. Many of the 3d-transition metal silicides are compounds, which have been developed as the materials having a superior heat-resistance. Since $MnSi_2$ has semi-conducting properties and a large thermoelectric power, it can be used as thermoelectric materials [2-5]. Actually, Mn-Si prepared by mechanical alloying (MA) and spark plasma sintering (SPS) recently yielded the figure of merit $Z=7.65\times10^{-4}$ K^{-1} at 873K[5]. The ranges of composition of the Mn-Si were synthesized from the liquid phase lines between $MnSi_{1.71}$ and $MnSi_{1.75}$ and possibly extend to the composition $MnSi_{1.77}$ at temperature below the peritectic line. Atomic positions were measured for the four phases: $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, $Mn_{27}Si_{47}$ and Mn_4Si_7, which have similar tetragonal cells [5]. The purpose was development of Mn-Si ceramics with higher efficiency, which can be used for high-temperature thermoelectric power generator.

In this paper, Mn-Si ceramics were prepared by solid-state reaction method and SPS, which yields the rapid heating and the short sintering time [6]. The effect of grain size on thermoelectric properties was paid attention; samples were sintered from powder obtained by milling for different times. This effect has not been studied little so far.

Grinding ↓	Mn(3N), Si(5N) <250 μm
Weighing ↓	Si/Mn=1.75, 1.80, 1.85
Mixing ↓	1 hr.
Solid-state Reaction ↓	1000 ℃, 5 hr., vacuum
Milling ↓	0, 12 or 24 hr.
SPS Sintering	980 ℃, 30 min., 55 MPa., vacuum

Fig.1 The process of sample preparation.

2. EXPERIMENT

2.1 Sample preparation

The process of sample preparation is shown in Fig.1. A lump of Mn (3N) and Si (5N) was grinded for <250 μm and was weighted for the desirable molar ratio Si/Mn=1.75, 1.80 and 1.85. Weighted powder was mixed for 1 hour. The polycrystalline powder of Mn-Si was prepared by

Table I. The mean particle diameter of milled powder in molar ratio Si/Mn=1.85 and density of sintering materials in each samples.

Grinding time (hours)	0	12	24
Mean particle diameter in Si/Mn=1.85 (μm)	93.0	7.1	3.4
Density of sintering materials in Si/Mn=1.75 (g/cm^3)	4.62	4.79	4.90
Density of sintering materials in Si/Mn=1.80 (g/cm^3)	4.57	4.71	4.79
Density of sintering materials in Si/Mn=1.85 (g/cm^3)	4.44	4.58	4.71

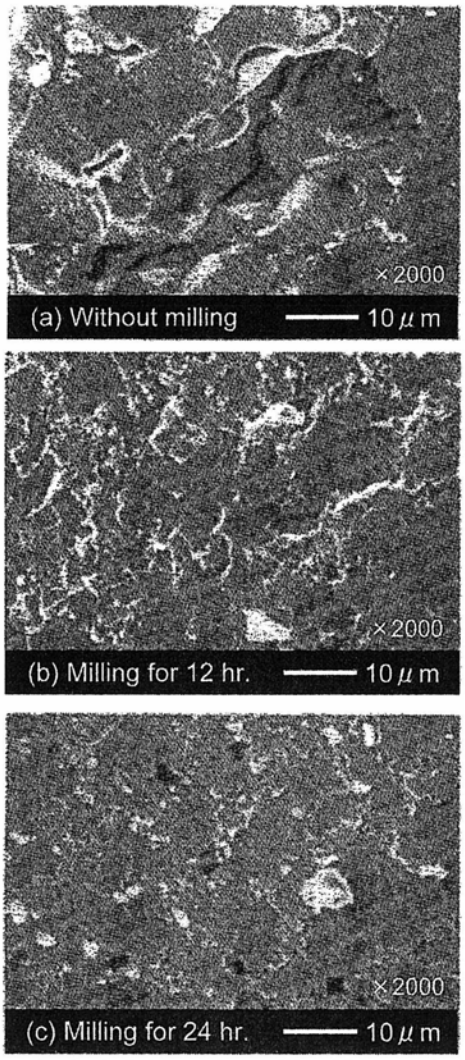

Fig.2 Cross-sectional SEM images for the sintered samples in molar ration Si/Mn=1.85

the solid-state reaction, which was carried out at 1273K for 5 hours in vacuum atmosphere. The polycrystalline powder of Mn-Si was used as the starting powder, which was milled in a cylindrical ball mill filled with φ3.2mm stainless balls. Then the SPS sintering was carried out at 1253K for 30 minutes under 55MPa. The SPS method enables to prepare the Mn-Si materials at lower temperature than the melting point by about 165K.

2.2 Effect of grain size

The materials were prepared from powder, which was milled for 0, 12 and 24 hours to investigate the effect of grain size on thermoelectric properties.

3 RESULTS AND DISCUSSIONS

3.1 Effect of grain size

The mean particle diameter of milled powder with molar ratio Si/Mn=1.85 was estimated by the SEM images. Results are shown in Table I. Cross-sectional SEM images for the sintering materials in molar ratio Si/Mn=1.85 are shown in Fig.2. The smaller milled powder was obtained as the milling time became longer. The density of sintering materials in each sample was measured and is also shown in Table I. The theoretical density of $Mn_{15}Si_{26}$ is 5.16 g/cm^3. The maximum value of the density was 4.90 g/cm^3 which is 95% of the theoretical density. The minimum value of density was 4.44 g/cm^3, which is 86% of the theoretical density. When smaller milled powder was used, high density sintering material was obtained.

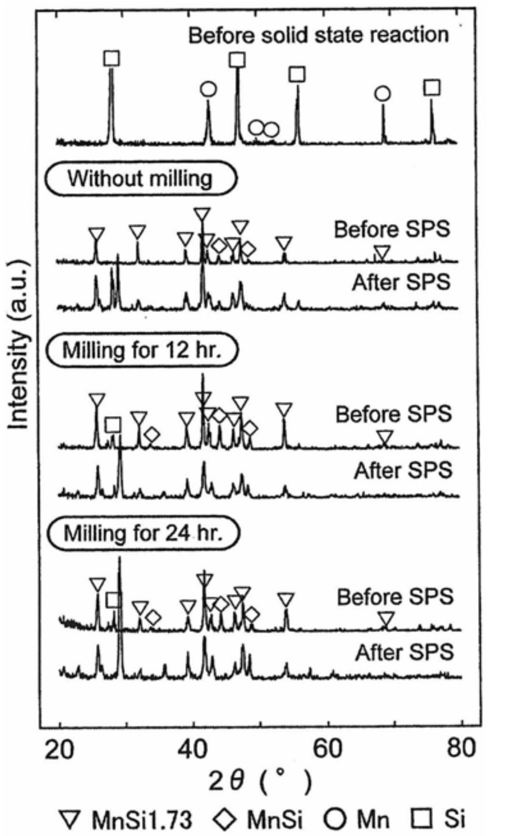

Fig.3 X-ray diffraction patterns for each samples in molar ration Si/Mn=1.85.

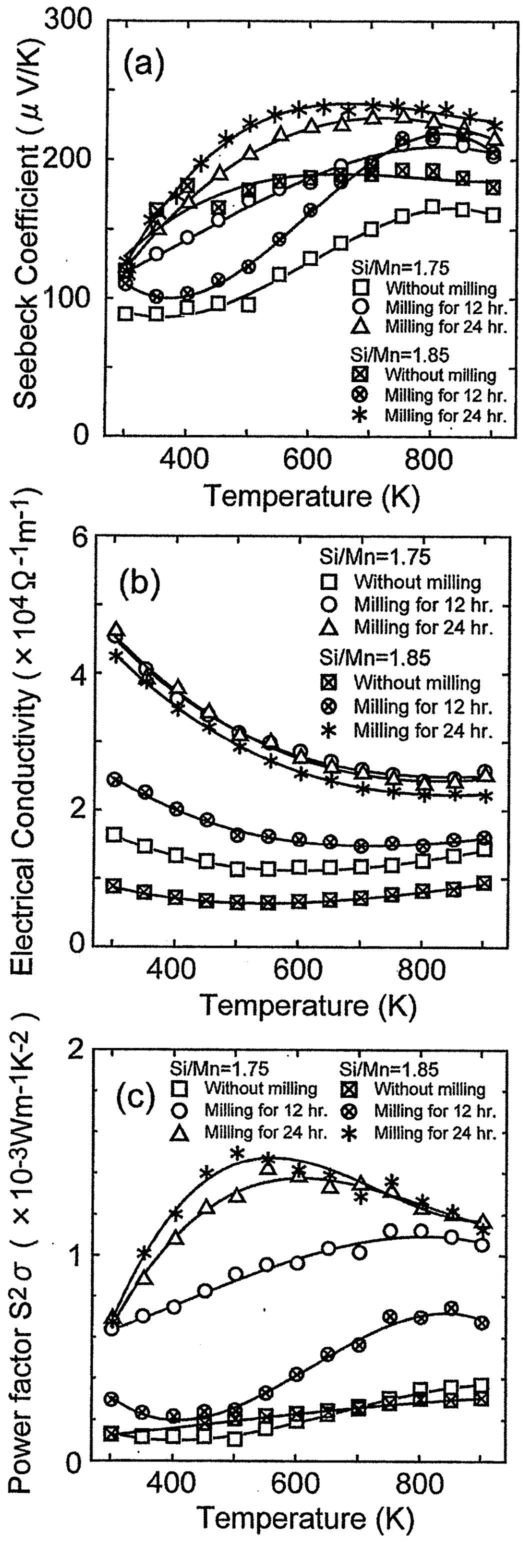

Fig.4 (a)Seebeck coefficient, (b)Electrical conductivity and (c)Power factor as a function of temperature. The data for molar ration Si/Mn=1.75 and 1.85.

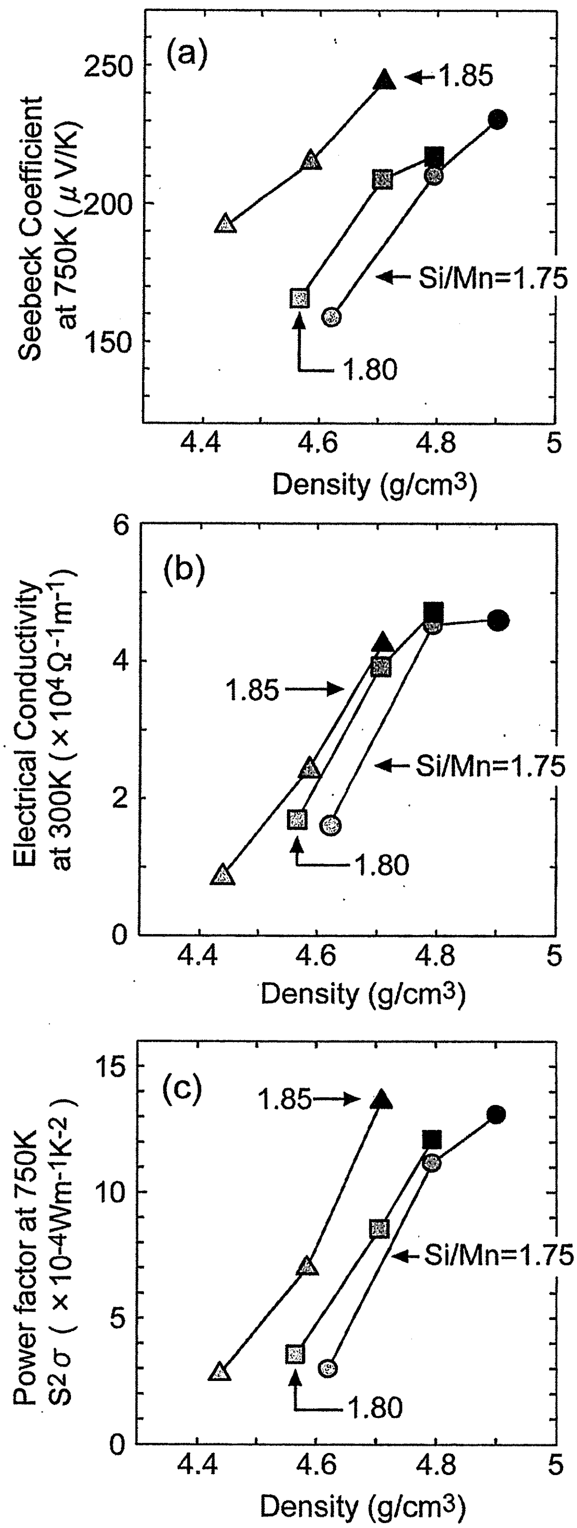

Fig.5 (a)Seebeck coefficient at 750K, (b)Electrical conductivity at 300K and (c)Power factor at 750K as a function of density for Mn-Si ceramics. The data for molar ration Si/Mn=1.75 (circle), 1.80 (square) and 1.85 (triangle).

The phase in the sintering materials was characterized by X-ray diffraction (XRD) pattern, which is shown in Fig.3. The XRD pattern of the powder before solid-state reaction had only Mn and Si peak. The powder before SPS without milling had $MnSi_{1.73}$ and MnSi peak. But, the powder before SPS in milling for 12 and 24 hr had peaks of $MnSi_{1.73}$, MnSi and Si. This reflects non-reacted Si appear after milling. The samples after SPS sintering without milling had $MnSi_{1.73}$, MnSi and Si and then complete reaction did not occur. $MnSi_{1.73}$ and MnSi phase were confirmed in the samples after SPS sintering in milling for 12 and 24 hr (no Si peak could be detected). The peak of $MnSi_{1.73}$ was confirmed clearer by the use of the longer milling time powder.

Now let us discuss thermoelectric properties. Temperature dependence of thermoelectric properties such as Seebeck coefficient S (μV/K), electrical conductivity σ ($\Omega^{-1}m^{-1}$) and power factor $S^2\sigma$ ($Wm^{-1}K^{-2}$) are shown in Fig.4. The effects of grain size for the three compositions on thermoelectric properties are shown in Fig.5. The smaller grain powder improved Seebeck coefficient. This result reflects that non-reaction material such as MnSi and Si become fewer for smaller grain powder by longer milling time. The best value of Seebeck coefficient was obtained to be 246.0μV/K at 750K, and the value is nearly the same level as that by Umemoto et al who obtained the large value of Seebeck coefficient 256μV/K at 850K recently [5]. Smaller grain materials, i. e., high density materials also improved electrical conductivity. This is considered to originate from the larger diffusion of a carrier between grains. However the maximum value of electrical conductivity was 30% lower than Umemoto's data so far [5]. The smaller grain powder improved power factor. The temperature dependence of the power factor is similar to that of the Seebeck coefficient.

3.2 Effect of dopant

The sintering materials were prepared with dopant such as In, Sb, Pt, Cr and Fe in order to investigate the effect of dopant on thermoelectric properties preliminary.

The temperature dependence of the ratio of the power factor $P=S^2\sigma$ ($Wm^{-1}K^{-2}$) between the non-doped and the doped samples are shown in Fig.6. Actually, the doping effect did not improve the Seebeck coefficient. Some of the doped sintering materials yields even 2-12% lower than non-doped. On the other hand, it is clearly observed that there is the effect of the dopants such as In, Sb, Cr and Fe on the improvement for the electrical conductivity. Then, the doped samples such as Sb, Cr and Fe yield power factor higher than non-doped sample. The improved result of power factor is due to the higher electrical conductivity.

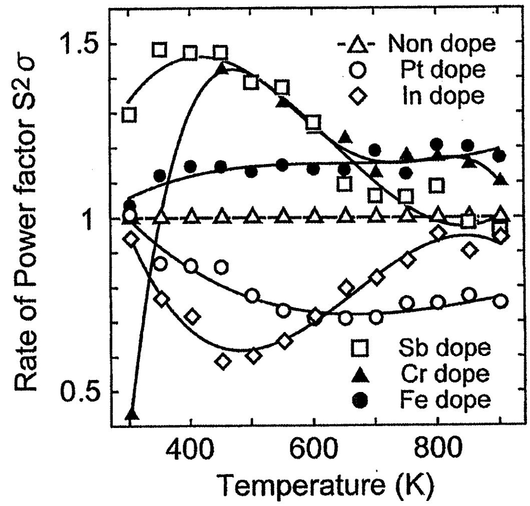

Fig.6 Rates of the Power factors between Non-doped and doped Mn-Si as a function of the sample temperature are ploted a for non-doped (△with dashed line),Pt-doped (○), In-doped (◇), Sb-doped (□), Cr-doped (▲) and Fe-doped (●).

4. CONCLUSION

The effect of grain size on thermoelectric properties of Mn-Si ceramics was investigated. Fineness of the materials, i.e. smaller grain size of materials improves thermoelectric properties such as Seebeck coefficient and electrical conductivity.

The above results indicate much more smaller grain size samples will improve the thermoelectric properties. However if we prepare much smaller grain size samples, the samples become easy to burn. Thus the sample preparation process needs to be proceed under the inert gas atmosphere or the vacuum.

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