

Thermoelectric Properties of Mg₂Si Processed by Spark Plasma Sintering Method

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Thermoelectric material Mg₂Si were prepared by using the solid-state reaction and spark plasma sintering. Temperature dependence of thermoelectric properties such as Seebeck coefficient and electrical conductivity was measured. Density dependence of thermoelectric properties was examined in details. It has been found that, when the sample density increases Seebeck coefficient doesn't changes much, while the electrical conductivity and then the power factor increase very much. The result indicates that the preparation of the samples with the higher density by starting from the smaller size powder can improve thermoelectric properties.

Key words: Mg₂Si, thermoelectric material

1. INTRODUCTION

Recently, because of the interest to energy and environmental problems, the thermoelectric conversion system is paid attention much as an effective method for recovering the waste heat. This system uses the Seebeck effect of the semiconductor as an electric generator. The following points are mentioned as an advantage: long lives, no moving mechanical parts, small and light, etc. At present, better performance of thermoelectric material is necessary in the wider application.

So far only the Bi-Te is the thermoelectric material widely used practically. Metal silicides thermoelectric materials such as Fe-Si, Cr-Si, Mn-Si, Mg-Si and so on are better in environmental points of view and also in low cost. Then it is desirable to develop the efficient metal silicide thermoelectric material. Therefore metal silicides have been studied in many aspects [1].

Among metal silicides Fe-Si system has been received very much attention because of the high potential in the resource [2]. However so far the value of the dimensionless figure of merits ZT is a level of 0.2 at most, though the value of ZT=1.0 is a measure for the practical use. Here Z is the indicator for the efficiency of the thermoelectric conversion and is given by

$$Z = P / \kappa,$$

where the power factor P is given by $P = S^2 \sigma$, S is the Seebeck coefficient, σ is the conductivity and κ is the thermal conductivity.

Mn-Si [3-4] and Mg-Si [5-12] also have been received much attention. Recently higher values of ZT such as 0.6-1.0 are achieved and the studies for more improvement have been continued. In the present work, we focus to Mg₂Si as an effective thermoelectric material with a higher potential.

The preparation of Mg₂Si thermoelectric material is difficult, since there is a boiling point of magnesium above the melting point of Mg₂Si by 22 K. The research has been also carried out in the material which replaced the part of silicon by germanium or tin. As a result, n-type which has doped antimony in the material which replaced the about half of silicon by germanium or tin and p-type which has doped silver were shown to exhibit

a good thermoelectric property in a level of ZT=1.0 [5-7]. More recently, the improvement of the thermoelectric property of Mg₂Si has been studied by doping an impurity such as antimony or aluminum or tin [8-12]. In Sb-dope, ZT was 0.67 for 0.6 atm.% at 773 K. In Al-dope, ZT was 0.58 for 0.15 at% at 860 K. In Sn-dope, ZT was 0.78 at 720 K.

In the present work, we pay attention to undoped Mg₂Si thermoelectric material. The purpose of this work is the examination of the effect of the powder size, being directly related with the sample density, on the thermoelectric properties in the metal silicides Mg₂Si. Mg₂Si sample was prepared by using the solid-state reaction and spark plasma sintering (SPS). Actually the preparation of Mg₂Si need to be processed, considering the largely different melting (boiling) points 923 K (1380 K) in Mg and 1687 K (2628 K) in Si and the melting points 1358 K in Mg₂Si. The solid state reaction by the smaller size powder may increase Mg₂Si molecule, which are obtained by the reaction between Mg and Si materials. Using this powder, good crystalline Mg₂Si sample can be obtained by the SPS process. If we can find a good material process, which yields Mg₂Si material with higher thermoelectric ability, this will yield the good starting point of the further improvement by the methods such as doping and alloying.

2. EXPERIMENT

2.1 Sample preparation

Firstly, silicon (Si, 5N, crush state) was milled. This milled Si and magnesium powder (Mg, 3N, about 180 μ m size powder) were mixed with the mole fraction of two to one. Then the polycrystalline powder of Mg₂Si was prepared from the mixed powder by the solid-state reaction, which was carried out at 550 K for 4 hours in vacuum atmosphere. This reacted powder was again milled in a cylindrical ball mill filed with Φ 10.0 mm aluminum oxide balls or Φ 3.2 mm stainless balls for 40 hours in the argon atmosphere. Then, those milled powders were sintered by a SPS method. The sintering conditions were shown in Table I.

Table I Sintering condition

Milling ball	Sintering temp. (K)	Sample name
Φ10.0mm	973	MgSi1
	1073	MgSi2
Φ3.2mm	1073	MgSi3
	1113	MgSi4
	1133	MgSi5

*Sintering time is 1800 seconds.

*The pressure is 25 MPa.

2.2 Characterization

The samples were characterized by the SEM and the X-ray diffractometry (XRD). SEM images are shown in Fig.1. We can see that the low density samples (sintered by 973 K) have a lot of small void and grain boundary, but in the high density samples (sintered by 1133 K), small void and grain boundary has been found hardly. The density of the samples was measured. The result is summarized in Table II. As the sintering temperature rises, the density of the samples becomes higher. The sample of the highest density is the MgSi5 sample, whose density is 98.4 % of the theoretical value ($d=2.002 \text{ g/cm}^3$).

The result of XRD is shown in Fig.2. The XRD patterns of milled powders and sintered samples show the highest density sample Mg₂Si5 consists of only the Mg₂Si phase. The smaller milling ball, yielding the smaller size powder for SPS, and the higher sintering temperature yielded the sample MgSi5 with Mg₂Si phase.

Table II Density of the sintered samples

Sample name	ratio of the density to the theoretical value (%)
MgSi1	74.4
MgSi2	86.1
MgSi3	85.9
MgSi4	93.5
MgSi5	98.4

*The theoretical density is 2.002 g/cm^3 .

2.3 Thermoelectric properties

The temperature dependence of the Seebeck coefficient S ($\mu\text{V/K}$), the electrical conductivity σ ($\Omega^{-1}\text{m}^{-1}$), and the power factor $P=S^2\sigma$ ($\text{Wm}^{-1}\text{K}^{-2}$) are shown in Fig.3 (a)-(c), respectively, for various samples. All the samples show n-type semiconductor. The characteristics for semiconductor appear; the Seebeck coefficient had a peak and gradually decreases in increasing the temperature. It is noticed that the sample MgSi1, which has the lowest density among the samples and the lowest crystal quality from the XRD point of view, yielded the large Seebeck coefficient, about $-425 \mu\text{V/K}$ around the temperature 450 K. The peak of Seebeck coefficient decreases with the increase in the density, but changes are not so large. The electrical conductivity in the low density samples rapidly increases with higher temperature. In the high density samples, the electrical conductivity gradually increases with the increase in temperature. Such difference is considered to arise from different size of pure phase and grain boundary.

The temperature dependence of the power factor P is similar to that of the electrical conductivity σ . It is also seen that the present result of the power factor is comparable to the previous best results obtained very

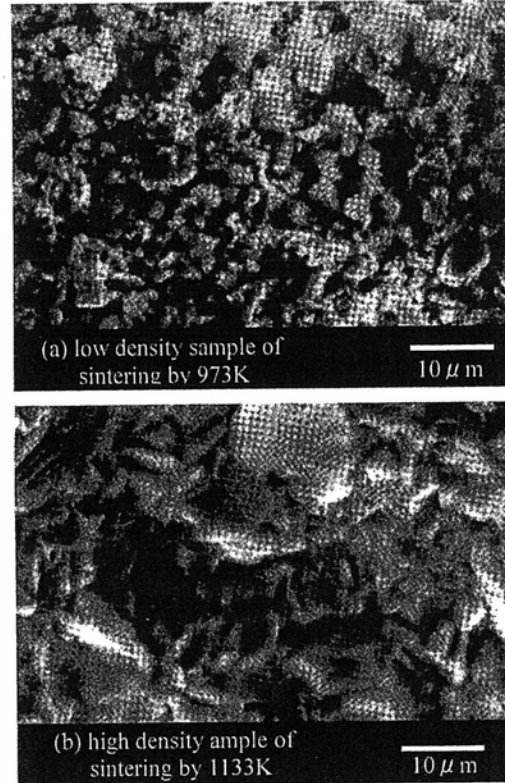


Fig.1 Cross-sectional SEM images of (a) the low sample sintered at 973K and (b) the high density sample sintered at 1133K

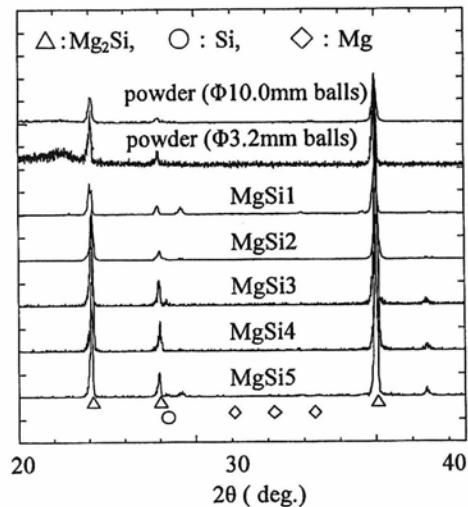


Fig.2 X-ray diffraction pattern for milled powders before SPS and the samples after SPS

recently by Komatsu Group [12]. They prepared the sample by melting the starting materials Mg and Si, then crushing the sample again and using the SPS process.

Thermoelectric properties of S , σ , and P at 500 K as a function of the sample density are shown in Figs.4 (a)-(c). From Fig.4, we see that we can obtain higher power factor, i.e. better thermoelectric properties in the sample with higher density. In the present experiment the sample with the highest density, MgSi5 sample was prepared by the high sintering temperature, 1133 K. Therefore, the

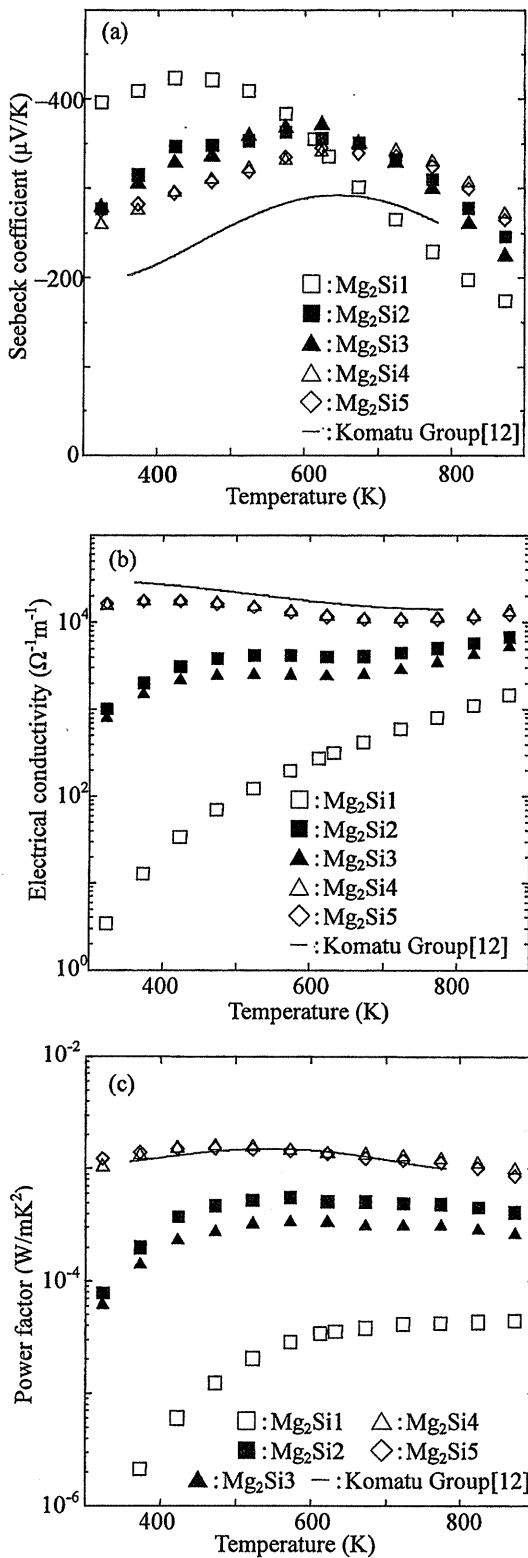


Fig.3 The temperature dependence of (a) the Seebeck coefficient, (b) the electrical conductivity and (c) the power factor of samples with various sintering conditions. Also the results obtained recently by Komatu group is shown for comparison.

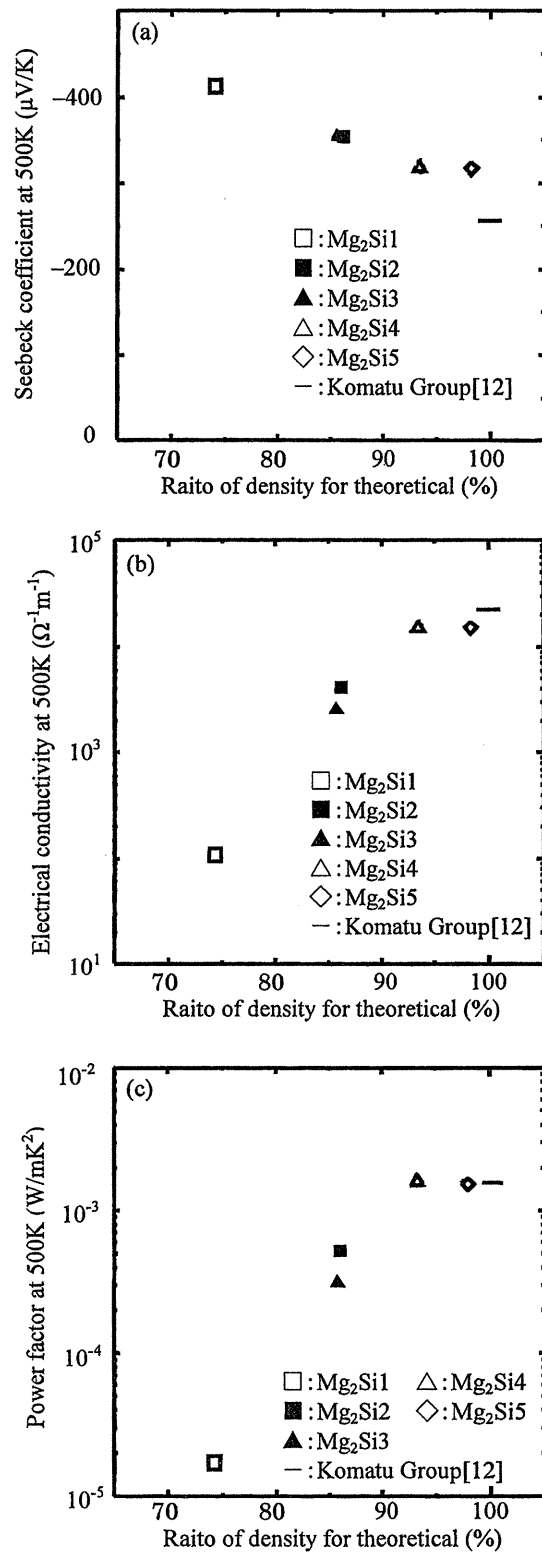


Fig.4 The density dependence of (a) the Seebeck coefficient, (b) the electrical conductivity and (c) the power factor of samples sintered at 500 K with various conditions.

above results indicate that the process starting from the fine material under μm -size level may work well for the improvement of thermoelectric properties by the enhanced reaction between Mg and Si materials.

3. CONCLUSIONS

Thermoelectric samples Mg₂Si were prepared by the solid state reaction and the spark plasma sintering method. All the samples show n-type semiconductor. By sintering the powder with the smaller size in higher temperature, higher density samples were obtained. This higher density samples yielded better thermoelectric property: with the increase in density Seebeck coefficient doesn't change much, but the electrical conductivity and then the power factor increase. Obtained power factor is comparable to the previous best results recently obtained by Komatsu Group [12].

It is noted that the above results mean that the starting powder with the smaller size will improve the thermoelectric ability of Mg₂Si. But, actually if the smaller size powder is used, it is easier to burn. Then the process under the inert gas or the vacuum is necessary.

REFERENCES

- [1] C. B. Vining, CRC Handbook of Thermo electrics (CRC press, edited by D. M. Rowe, Florida 1994) pp.277-285.
- [2] U. Birkholy, E. Groß, U. stöhrer, CRC Handbook of Thermo electrics (CRC press, edited by D. M. Rowe, Florida 1994) pp.287-298.
- [3] Zaitsev, CRC Handbook of Thermo electrics (CRC press, edited by D. M. Rowe, Florida 1994) pp.299-309.
- [4] M. Umemoto, Z. G. Liu, R. Omatsugawa, K. Tsuchiya, Materials science Forum, **343-346** pp.918-923 (2000).
- [5] Y. Noda, N. Otsuka, K. Masumoto, I. Nishida, J. Japan Inst. Metals **53**, pp.487-93 (1989) (in Japanese).
- [6] H. Kon, Y. Noda, Y. Furukawa, I. Nishida, K. Masumoto, J. Japan Inst. Metal, **55**, pp.893-899 (1991); **55**, pp.1018-1022 (1991) (in Japanese).
- [7] Y. Noda, H. Kon, Y. Furukawa, I. Nishida, K. Masumoto, Material Trans. JIM, pp.851-855 (1992); Proceedings of 12th International Conference Thermoelectrics, pp.206-211(1994).
- [8] T. Kajikawa, I. Katsube, S.Sugihara, Trans. Inst. Electr. Eng. Japan A, **116-A**, pp.236-241 (1996).
- [9] T. Kajikawa, K. Shida, S. Sugihara, M. Ohmori, T. Hirai, 16th International conference on Thermoelectrics, pp.275-278 (1997).
- [10] T. Kajikawa, K. Shida, K. Shiraishi, T. Ito, 17th International Conference on Thermoelectrics, pp.362-369 (1998).
- [11] M. Umemoto, et al (private commun.).
- [12] Komatsu group, Report on International cooperative research proposal program (NEDO, 2001) (in Japanese).

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