Mg$_2$Si Thermoelectric Device Fabrication with Reused-silicon

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Mg$_2$Si thermoelectric devices are fabricated using reused-Si by a liquid-solid phase reaction and a spark plasma sintering process. Seebeck coefficients are comparable to those for a device prepared with pure Si. However, electric conductivities are lower, resulting in lower power factors. Al-doping up to 4% is found to be effective to improve the electrical conductivity.

1. Introduction

Thermoelectric (TE) devices have attracted much attention in recent years because they can convert waste heat into electrical energy directly. The device is made of semiconductors and is normally the shape of a rectangular parallelepiped. When a temperature gradient is applied between both sides of the device, carriers are generated at the high temperature side of the device and flow toward the low temperature side because of diffusion, resulting in potential difference between both sides of the device. TE performance is generally indexed by dimensionless figure of merit and is given by

\[ ZT = \frac{S^2\sigma}{\kappa} \]

where $Z$ is figure of merit, $T$ is absolute temperature, $\sigma$ is electric conductivity and $\kappa$ is thermal conductivity. The numerator of $ZT$ is called power factor. $ZT$ of about unity is required for industrial mass production, corresponding to thermoelectric conversion efficiency of about 10%. Mg$_2$Si is considered to be one of the candidates for thermoelectric device materials because of its large figure of merit [1]. In addition, it consists of nontoxic and abundant elements. We have investigated sintering effects on grain size and microstructure of the Mg$_2$Si TE devices, especially interfaces between Mg$_2$Si sintered compacts and Ni electrodes [2, 3].

Additionally, Si, one of the constituent elements of Mg$_2$Si, is widely used in the electronics and semiconductor industry and 70% of high-purity Si ingots are discarded as industrial waste during the slicing and polishing processes. Reusing such wasted Si is, therefore, crucial with respect to the reduction of the industrial waste and of Mg$_2$Si TE device manufacturing cost. Mg$_2$Si TE devices have been fabricated by the melting method using pure Mg (99.95%) [4] and recycled Mg [5] reacted with refined reused-Si so far, as well as using pure Si [6]. In general, the melting process is difficult to handle because the melting point of Mg$_2$Si (1358 K) and the boiling point of Mg (1363 K) are very close. Then to decrease reaction temperature, we employ a liquid-solid phase reaction process because it enables us to synthesize Mg$_2$Si at lower temperature than the melting point of Mg$_2$Si (1358 K) [7].

The purpose of this study is to develop synthesis and sintering processes with reused-Si generated from a slicing process using fixed abrasive grain wire saws. Waste Si from the process includes a relatively low amount of impurities. This report describes our recent results on Mg$_2$Si synthesis by the liquid-solid phase reaction process with refined reused-Si, on TE device
fabrication using the above-mentioned Mg$_2$Si by a spark plasma sintering (SPS) process and on its thermoelectric properties.

2. Experiments

Non-doped and 1 at% to 8 at% Al doped Mg$_2$Si are synthesized by the liquid-solid phase reaction process with the refined reused-Si. Pure Mg powder and the refined reused-Si powder are mixed in stoichiometric ratio. The mixed powder is located in a quartz tube and heated at 750 °C (higher than the melting point of Mg and lower than that of Mg$_2$Si) for 180 min in Ar flow. The synthesized compounds are milled into powder of less than 75 μm in diameter. Then the powder is sintered with an SPS equipment (CSP-II-DPA, SS Alloy) at around 800 °C and 50 MPa for 10 min. in vacuum. The cylindrical sintered compacts with a diameter of 10 mm and a height of 4 mm are cut into a rectangular parallelepiped with 4x4x7 mm$^3$ in size to fabricate the thermoelectric devices.

The synthesized powder and sintered compacts are evaluated by X-ray diffraction (XRD; MiniFlexII, Rigaku) for crystallinity, scanning electron microscopy (SEM; JSM-6510LA, JEOL) for microstructure measurement, energy dispersive X-ray analysis (EDX; JED-2300EDS, JEOL) for qualitative elemental composition analysis and semi-quantitative elemental composition analysis by using the ZAF correction using no standard references. The Seebeck coefficients and electrical conductivities are measured with ZEM-3 (ULVAC Riko) from 100 °C to 500 °C with a temperature difference of a few degrees Kelvin. The bulk density is measured by the Archimedes method. Theoretical density of Mg$_2$Si is 2.00 g/cm$^3$.

3. Results and Discussion

Figure 1 shows an XRD pattern for refined reused-Si powder used in this study. Almost all peaks are assigned to poly-crystalline silicon except the small peak near the Si (111) peak. This unknown peak is attributed to neither silicon oxide nor impurities, such as Ni, Fe and Al or their oxides. A broad roll of the intensity below 30 ° may be attributed to silicon oxide because the powder contains a few percent of oxygen.

![Fig. 1. XRD pattern of refined reused-Si.](image)

Non-doped and Al doped Mg$_2$Si are synthesized by the liquid-solid phase reaction process with refined reused-Si. Figures 2 and 3 show XRD patterns for the non-doped and 4 at% Al doped Mg$_2$Si, respectively. Each figure has XRD patterns for the synthesized powder and for the sintered compact. Almost all of the powder and compact peaks are found to be attributed to Mg$_2$Si except
for a small MgO peak. Peaks from elemental Mg or Si are not detected. Such elements degenerate the TE performance if remaining in the sintered compacts. Unknown peaks ranging from $20^\circ$ to $24^\circ$ have appeared for the sintered compacts. These unknown peaks have appeared for the other Al doped sintered compacts.

Table I summarizes composition ratios of the synthesized starting powder and the sintered compacts with and without Al doping. Mg to Si ratios for powder are close to the stoichiometric value while those for sintered compacts are lower than that. This indicates Mg loss during the sintering process. For the Al 1% doped sample, Al was not detected due probably to a low detection threshold of the EDX.

![Fig. 2. XRD patterns of non-doped Mg$_2$Si powder (lower) and sintered compact (upper) using refined reused-Si.](image)

![Fig. 3. XRD patterns of 4% Al doped Mg$_2$Si powder (lower) and sintered compact (upper) using refined reused-Si.](image)
Table I. Composition ratio, Al concentration and relative density of the synthesized powder and the sintered compacts.

<table>
<thead>
<tr>
<th>Al concentration at %</th>
<th>powder</th>
<th></th>
<th>compact</th>
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<td></td>
<td>Mg/Si</td>
<td>Al %</td>
<td>Mg/Si</td>
<td>Al %</td>
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<td>2.15</td>
<td>8.33</td>
<td>1.83</td>
<td>6.37</td>
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</tbody>
</table>

Fig. 4. SEM micrograph for the Al 4 % doped sintered compact. White arrows show voids. The bar denotes 5 μm.

Fig. 5. Elemental mapping for the same area of Fig. 4.
Table I also shows bulk densities of the each sample. The relative densities are higher than 95% and thus the samples are successfully sintered. From XRD analysis (not shown here) the Al 8% doped sample has relatively a large amount of impurities such as MgO, which has a bulk density of 3.58 g/cm³, compared with other samples. This may be one of the reasons for the excessively high density.

Figure 4 shows an SEM micrograph for the Al 4% doped sintered compact. The compact consists of grains with diameters of a few μm to several tens μm. There are many voids in the compact despite the large relative density.

Figure 5 shows elemental mapping for the Al 4% doped sintered compact. Observed area is the same as that of Fig. 4. Al and O are segregated at the grain boundaries. Neither Al nor Al₂O₃ XRD peaks are detected even though Al and O exist at the grain boundaries, as shown in Figs. 2 and 3.

Figures 6, 7 and 8 show Seebeck coefficients, electric conductivities and power factors for non-doped and various Al doped Mg₂Si TE devices as well as those for a 1% Al doped Mg₂Si TE device prepared from pure Si and Mg for comparison as a function of temperature. The non-doped device has the highest Seebeck coefficient among them at lower temperatures, while it has the lowest electric conductivity, resulting in poor power factor. The electrical conductivity drastically increases by Al-doping, resulting in rise in the power factor. The highest power factor of 1.58 mWm⁻¹K⁻², which is about 60% of the highest value for the device prepared with pure silicon, is obtained for the 4% Al doped device at 300 °C.

![Graph of Seebeck coefficient vs. temperature](image)

**Fig. 6.** Seebeck coefficient for non-doped and various Al doped Mg₂Si TE devices as well as those for a Mg₂Si TE device prepared from pure Si and Mg as a function of temperature.
Fig. 7. Electric conductivity for non-doped and various Al doped Mg$_2$Si TE devices as well as those for a Mg$_2$Si TE device prepared from pure Si and Mg as a function of temperature.

Fig. 8. Power factor for non-doped and various Al doped Mg$_2$Si TE devices as well as those for a Mg$_2$Si TE device prepared from pure Si and Mg as a function of temperature.
4. Conclusion

Non-doped and Al doped Mg$_2$Si for TE devices have been successfully synthesized by the liquid-solid phase reaction process with refined reused-Si to decrease reaction temperature. High relative density shows success of sintering by the SPS. The SEM image and elemental mapping reveal the presence of voids and segregation of Al. Maximum $ZT$ is estimated to be 0.3 for Al 4% doped sample if the thermal conductivity is same as that of sample synthesized with pure Si. This value is about 60% of $ZT$ of the device prepared with pure silicon. To increase the electric conductivity, we intend to revise dopants and doping level. Further investigation on Mg/Si ratios and concentration of trace elements are required to disclose effects of them on TE performances.

Acknowledgment

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References