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LETTER

Preparation of polycrystalline bulk Mg_2Si by using NaSi

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Recently, thermoelectric materials have been attracting attention in the field of effective energy saving by utilization of waste heat. Mg_2Si and Mg_2Si-based materials are expected to be used as an alternative to PbTe for application in thermoelectric devices in the temperature range from 500 to 800 K because of their high thermoelectric properties. Moreover, Mg_2Si has the lowest density, i.e., 2.0 g/cm^3, among thermoelectric materials and its constituent elements, i.e., Mg and Si, are abundant and nontoxic [1–4]. According to the Mg–Si phase diagram presented by Okamoto et al. [5], Mg_2Si is the only binary phase of this system and melts at 1354 K. Because the melting point of Mg_2Si is close to the boiling point of Mg (1363 K) and the vaporization of Mg from the Mg–Si melt is significant around this temperature, preparation of Mg_2Si polycrystalline bulk and single crystals from the Mg–Si melt has been performed under 0.2–0.4 MPa of inert gas to suppress Mg vaporization [6–10]. High-pressure processing techniques such as spark plasma sintering (SPS) and hot-pressing (HP) have also been utilized to form a Mg_2Si polycrystalline bulk below the melting point of Mg_2Si. The starting materials for the bulk fabrication were a mixture of Mg and Si powders and Mg_2Si powder prepared by mechanical alloying [11–15].

In our previous papers, we have reported the synthesis of β-SiC powder and porous β-SiC bulk, as well as β-$FeSi_2$ powder and bulk by using Na–Si melts at temperatures lower than those of conventional synthesis methods [16–19]. We have also proposed an experimentally determined phase diagram for the Na–Si binary system, where the melting point of an intermetallic compound NaSi was revealed to be 1071 K [20]. Since this melting point is higher than that of Mg, we attempted the synthesis of Mg_2Si bulk by using a compact body of NaSi powder and Mg melt. The present paper reports the X-ray diffraction, morphology, and thermoelectric properties of Mg_2Si bulk sample prepared by this method.

Starting materials of Mg (Rare Metallic Co. Ltd., 99.9%, <147 μm), Si powder (Koujundo Chemical Lab. Co. Ltd., 99.999%, <75 μm), Na metal (Nippon Souda Co. Ltd., 99.95%) and NaSi were handled in an Ar-filled glove box (M-Bran, $O_2 < 1$ ppm, $H_2O < 1$ ppm). NaSi was prepared by heating equimolar Na and Si at 1073 K for 12 h in a BN crucible (∅6 × 13 mm in inner volume, Shyowa Denko, 99.5%) sealed in a stainless steel tube (SUS316, ∅8 × 80 mm in inner volume). The obtained NaSi was powdered with an agate mortar and pestle and formed into a compact body (14 mm × 3 mm × ca. 1 mm, 8 mmol) by pressing the powder with a rectangular die. The NaSi compact body and Mg powder (55 mmol) were placed in a BN crucible. The crucible was sealed in the stainless steel tube with Ar, followed by heating at 973 K for 24 h in an electronic furnace. The Na remaining after heating was removed by reaction with 2-propanol and ethanol.

The phases formed in the prepared samples were identified by powder X-ray diffraction (XRD; Rigaku Co., RINT-2200) with pyrolitic graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The XRD angles were calibrated with a standard reference material of silicon (NIST SRM 640c, $a = 5.431195$ Å). The lattice parameters of Mg_2Si samples were refined by the least-squares method using the MDI-JADE-6 program. The morphology of the samples was observed with a scanning electron microscope (SEM; Philips, ESEM XL30). The elements in the sample were analyzed with an energy-dispersive X-ray

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analyzer (EDX; EDAX) attached to the SEM by the ZAF (element number, absorption, and fluorescence corrections) quantification method. Seebeck coefficients (α) and electrical conductivities (σ) were measured by a thermoelectric power (ΔE)–temperature difference (ΔT) method and a direct current 4-probe method, respectively, silver paste being used as electrodes.

All XRD peaks of the obtained NaSi were explained with the crystal structure of NaSi reported by Witte and Schnering [21]. The stoichiometry of the obtained sample (Na:Si = 1:1) was also supported by less than 0.3% weight loss of the starting materials. Figure 1a shows a photograph of the bulk sample prepared by heating the NaSi rectangular compact body and Mg powder at 973 K for 24 h. The obtained sample was dense and swollen and had a length of approximately 15 mm. Mg metal was precipitated from the Mg melt on the surface of the sample during the cooling process. When the edge of the sample was cut, the inside of the swollen sample was observed to be filled with Na. As shown in Fig. 1b, a hollow structure was obtained after removal of Na by a reaction with alcohols. The size of the hollow was ca. 3 × 2 mm and the wall thickness was ca. 300 μm. The color of the inner surface was blue-violet.

XRD peaks of Mg and Mg_2Si were mainly observed in the pattern of the outer surface, although there were also small peaks of MgO (Fig. 2a). MgO was probably derived by oxidation of Mg on the surface or from the oxidized surface of the source Mg powder. On the other hand, the inner part consisted of Mg_2Si single phase. The few small extra peaks in the XRD pattern of the inner surface shown in Fig. 2b were due to resin which was used for sample fixing on a holder.

Figure 1c shows an SEM micrograph of the inner surface. Mg_2Si crystal grains 50–200 μm in size were densely

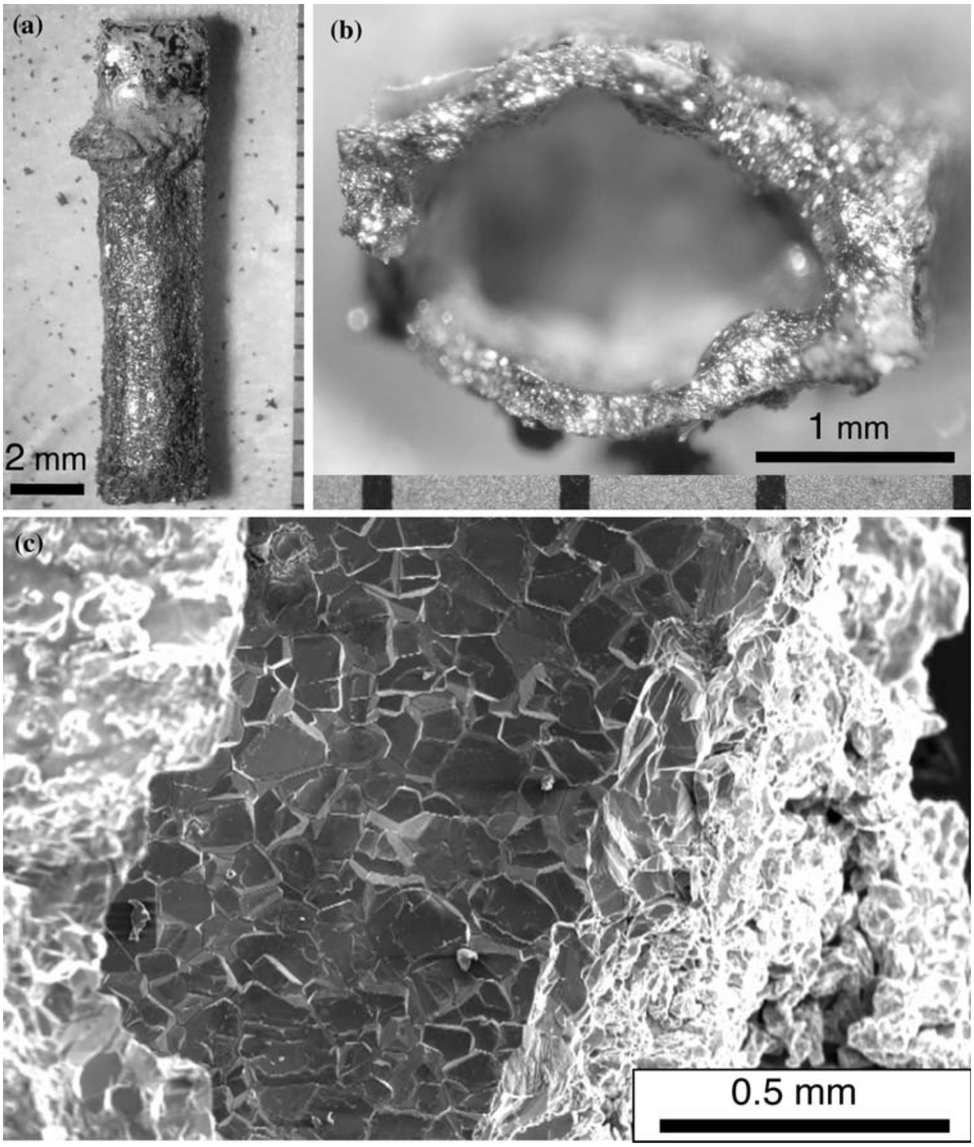

Fig. 1 Photographs of a sample prepared at 973 K for 24 h from a NaSi compact with Mg powder. The external appearance (**a**) and the cross-sectional view (**b**) and a scanning electron micrograph of the inner surface of the sample (**c**)

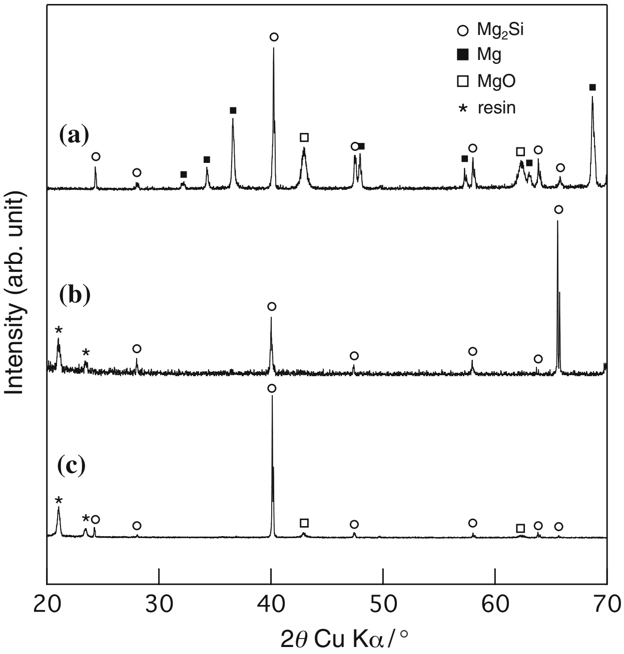

Fig. 2 XRD patterns of the sample prepared at 973 K for 24 h from a NaSi compact with Mg powder; the outer surface (**a**) and the inner surface (**b**) of the as-prepared sample, and the outer surface of the sample heated with Si powder at 873 K for 8 h (**c**)

compacted without any voids and space. Mg_2Si grains with a similar size were also observed in the matrix of Mg metal on the outer surface.

The heating temperature for the synthesis was 973 K, lower than the melting points of NaSi and Mg_2Si, but higher than the melting point of Mg. After the formation of Mg_2Si by the reaction $2Mg + NaSi \rightarrow Mg_2Si + Na$ on the NaSi compact body, Na melt was released and Si in the NaSi remaining inside the body immediately dissolved into the melt. Since the liquidus temperature was estimated to be 953 K for Na-rich compositions in the Na–Si binary system [20] and Na and Mg melts are immiscible with each other [22], the Na-rich Na–Si melt probably reacted with the Mg melt at the melt phase boundary and on the initially formed Mg_2Si grains. The Mg_2Si grains grew at the boundary and toward the Mg melt due to this reaction and Si was supplied from the NaSi grains by diffusion through the Na-rich Na–Si melt. Finally, Na melt remained on the surface and inside of the bulk body.

In order to obtain a Mg_2Si bulk sample for the characterization of thermoelectric properties, the sample shown in Fig. 1b was buried in Si powder in the BN crucible, followed by heating under an Ar atmosphere at 873 K for 8 h. The color of the outer surface changed from metallic silver to blue-violet. The absence of diffraction peaks of Mg in the XRD pattern after heating with Si powder (Fig. 2c) indicated that the Mg on the outer surface reacted with Si powder and formed Mg_2Si.

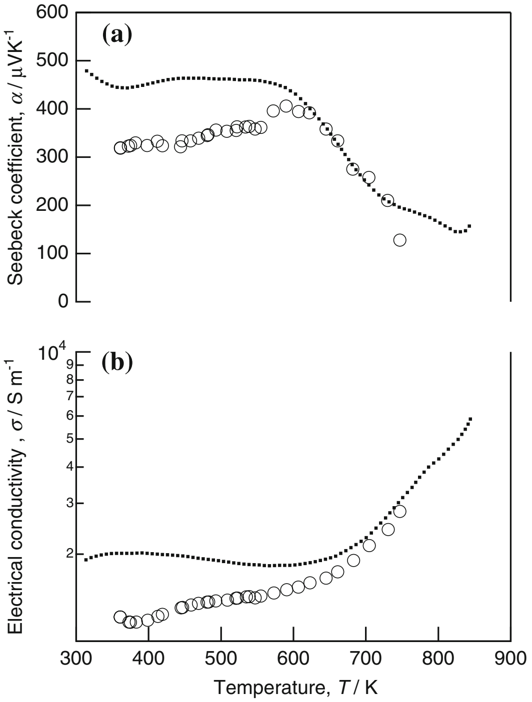

Fig. 3 Seebeck coefficients, α (**a**) and electrical conductivities, δ (**b**) of the Mg_2Si bulk sample prepared from NaSi compact with Mg powder in the present study (*open circles*) and $Mg_{65.7}Si_{33.3}Na_{1.0}$ (*broken line*) reported by Niwa et al. [23]

The temperature dependence of the Seebeck coefficient (α) and that of electrical conductivity (σ) measured for the Mg_2Si hollow bulk sample are shown in Fig. 3. The values of α increased gradually from +319 µV/K at 360 K to the maximum value of +406 µV/K at 590 K, and then decreased to +128 µV/K at 750 K. The σ values increased with increasing temperature from 1.2×10^3 to 2.8×10^3 S/m in the temperature range from 360 to 750 K. The maximum thermoelectric power factor calculated with the formula $\alpha^2 \times \sigma$ was 2.5×10^{-4} Wm^{-1} K^{-2} at 590 K.

Negative Seebeck coefficients were measured for non-doped Mg_2Si single crystals prepared by the Bridgeman method under pressure [10]. Thermoelectric properties of an *n*-type semiconductor have also been reported for a non-doped Mg_2Si polycrystalline bulk prepared by the SPS method [12]. Recently, Niwa et al. [23] found that the polycrystalline bulk of $Mg_{65.7}Si_{33.3}Na_{1.0}$ prepared at 1100 K and 50 MPa by the SPS method to be a *p*-type semiconductor. The positive values of the Seebeck coefficients and the electric conductivity of $Mg_{65.7}Si_{33.3}Na_{1.0}$ are also plotted in Fig. 3. The α and σ values of the Mg_2Si sample prepared in the present study were comparable with those of $Mg_{65.7}Si_{33.3}Na_{1.0}$, particularly above 600 K. The EDX analysis showed that the Mg:Si molar ratio of the Mg_2Si samples prepared in the present study was around 2:1. The Na content in the sample was below the detection limit of the EDX analysis (ca. 0.5 wt%). However, the *p*-type semiconducting behavior of the sample prepared in the present study was probably caused by Na doping similar to the case of $Mg_{65.7}Si_{33.3}Na_{1.0}$, which contained 0.8 wt% of Na. The lattice parameter of the Mg_2Si bulk prepared from NaSi and Mg was $a = 6.35259(5)$ Å. It was slightly longer the lattice parameter of Mg_2Si prepared from Mg and Si powders at 973 K for 8 h ($a = 6.35226(4)$ Å). This result also suggested the contamination of Na in the samples.

To summarize, a hollow bulk sample of Mg_2Si was prepared by reaction of NaSi with Mg in an Ar atmosphere at 973 K for 24 h. The thickness of the wall was about 300 μm. The sample exhibited *p*-type thermoelectric and semiconducting behavior at 360–750 K, which was probably due to Na doping of less than 0.5 wt% in Mg_2Si.

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