Effect of Ball-Milling on Sinterability of Si–Ge Powders Prepared by Gas Atomization of the Corresponding Melts

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溶融体のガスアトマイズより作製された Si–Ge 粉体の焼結性に及ぼすボールミル効果

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Each p- and n-type powder of $\text{Si}_{0.8}\text{Ge}_{0.2}$ for thermoelectric elements was prepared by gas atomization of the corresponding melts. Then, the relationship between the characteristics of Si–Ge powders and their sinterability was studied. Particular emphasis was placed upon understanding the effect of ball-milling on the sinterability of the as-prepared powders. The composition of the as-prepared powder was different from the batch composition due to melting and evaporation of the dopant above 1550 K. Ball-milling made the particle size of the as-prepared powders small, presumably together with introducing distortion to the crystal lattice. Densification of as-prepared powders was abruptly promoted above 1500 K by a pulse-current sintering; however, this densification temperature of the powders after ball-milling was lowered by approximately 100 K. The grain size and elemental inhomogeneity of the dense body after sintering were also reduced by ball-milling process.

[Received April 25, 2003; Accepted July 24, 2003]

Key-words: Silicon-germanium, Ball-milling, Sinterability, Gas atomization, Thermoelectric element

1. Introduction

Thermoelectric element converts thermal energy to electrical energy using temperature difference in the element and is composed of joined p- and n-type thermoelectric materials.¹⁾ The power generator using Si–Ge thermoelectric elements for artificial satellites is one of the most successful applications.²⁾ Si–Ge thermoelectric elements were mostly made by hot pressing of powders obtained by pulverizing the corresponding ingots.^{3)–6)} Here, the sinterability of pulverized thermoelectric material is quite significant because many physical properties on the thermoelectricity such as resistivity and thermal conductivity are firmly connected to the density of shaped bodies. Vining et al. fabricated Si–Ge dense bodies of $2.87\text{--}3.05 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$ in density by hot pressing of powders with various grain sizes ranging from 1–100 μm .⁷⁾ Beatty and coworkers obtained dense bodies of the density of more than 98% by the same sintering process from ultra-fine (5 to 10 nm) Si–Ge powders.^{8),9)}

An atomizing technique suitable for production of homogeneous metal or metal alloy powders^{10)–12)} has also been applied to the preparation of Si–Ge powders. A Si–Ge dense body obtained by hot pressing of atomized fine powders gave the reduction of the inhomogeneity on the Si and Ge distribution.¹³⁾ However, the characterization and sinterability of gas-atomized Si–Ge powders have not been studied in detail.

Pulse-current sintering is a recently developed densification technique by delivering on-off DC pulse electric current to powders under pressing.^{14)–16)} Pulse current may play an important role as a trigger for sintering at many contact points between particles. It can yield a dense body of metals or ceramics in a very short period compared with other hot pressings. Noguchi obtained a shaped body of density

greater than 99% for 1 min as sintering soak time from poorly sinterable Si–Ge powders by this technique.¹⁷⁾

In this study, semiconducting Si–Ge powders were obtained by the gas atomizing of the melt, followed by the densification using a pulse-current sintering. The effect of ball-milling on the sinterability of gas-atomized Si–Ge powders was then discussed based on the powder characterization.

2. Experimental

2.1 Sample preparation

A mixed powder of 80 mol%Si and 20 mol%Ge was doped by adding 0.2 mol%B and 0.3 mol%P for p- and n-type semiconductor formations, respectively. After melting with a microwave-heating furnace in vacuo, the powder was atomized from a nozzle with compressed argon. As-prepared Si–Ge powder was further pulverized by a Fritsch planetary ball-mill at 400 rpm in argon.

A powder sample of 3 g was charged into a cylindrical carbon vessel with an inner diameter of 20 mm, and then uniaxially compressed with a carbon punch at 49 MPa. The sintering was carried out to fabricate a compact for a soaking time of 180 s in vacuo, providing a pulse current of approximately 2000 A and 3 V. The sintering temperatures of as-atomized and pulverized powder were 1473 to 1533 K and 1273 to 1513 K, respectively. The carbon vessel was enclosed with a carbon thermal insulator to realize a temperature uniformity of the charged powder. The sintering temperature was measured with a Pt–(Pt–13% Rh) thermocouple, the top of which was inserted into the vessel wall adjacent to the sample. Sintered bodies from as-prepared and pulverized powders were named sample A and sample P, respectively, as shown in Table 1. Also, p- and n-type Si–Ge were denoted with the suffixes of p and

Table 1. Si-Ge Sintered Bodies

Sintered body from as-prepared Si-Ge powder (p-type)	Sample Ap
Sintered body from as-prepared Si-Ge powder (n-type)	Sample An
Sintered body from pulverized Si-Ge powder (p-type)	Sample Pp
Sintered body from pulverized Si-Ge powder (n-type)	Sample Pn

n, respectively.

2.2 Characterization

Quantitative analyses of elements of as-prepared powders were carried out by the following methods: Gravimetric method of silicon dioxide for Si, inductively coupled plasma-atomic emission spectrometry (ICP) for Ge and B, and molybdenum blue spectrophotometric method for P. The size distribution of the powder was obtained by a laser diffraction method. The density of the sintered body was measured by an Archimedes method and the microstructure of the body surface was observed after etching with reagent ($\text{HNO}_3 + \text{HF} + \text{H}_2\text{O} = 5 : 5 : 1$). The transverse rupture strength was determined by the span of 10 mm from the sample of $2.5 \text{ mm} \times 3.0 \text{ mm} \times 15 \text{ mm}$ which was cut from the sintered body. The morphology of the powder and fracture surface was observed by SEM. Determination of the crystalline phase and elemental analysis of both powders and sintered bodies were carried out by XRD and EPMA, respectively. Oxygen contents of the powder and sintered body were determined by measuring carbon dioxide generated from the melted sample in a carbon crucible.

3. Results and discussion

3.1 Characteristics of powder

The chemical compositions of as-prepared powders obtained here were Si 79.7 mol%, Ge 20.1 mol% and B 0.21 mol% for p-type Si-Ge, and Si 79.8 mol%, Ge 20.0 mol% and P 0.18 mol% for n-type Si-Ge. The decrease of phosphorous of the n-type powder by 40% compared with the batch composition was probably due to its volatility with high vapor pressure when melted.

As-prepared n-type powder of relatively large spherical particles was observed in Fig. 1(a). The compositional inhomogeneity of Ge was observed on the surface of the powder (Fig. 1(b)), although a solid solution should be completely formed in the whole composition.¹⁸⁾ It is considered that the segregation of Si- and Ge-rich phases occurred during the cooling stage after Si and Ge starting powders were melted to form a solid solution. This phenomenon may be attributed to the low rate of diffusion of Ge in the Si-rich phase;¹³⁾ nevertheless, a gas-atomizing process seems to be one of the quenching methods. As-prepared p- and n-type powders were relatively large particles with mean sizes of 72 and 66 μm , respectively, as shown in Fig. 2. Figure 3 shows the SEM images of pulverized powders after ball-milling for 1, 10 and 50 h. All pulverized powders were composed of various figures, which were partly flocculated. The size distributions of as-prepared powders were shifted to less than 5 μm of the mean size by pulverizing for 10 h, as shown in Fig. 4. However, two peaks of approximately 1.5 and 15 μm of the distribution appeared by the ball-milling for 50 h. The appearance of the peak of 15 μm was attributed to the flocculation due to an increase in the surface energy of the

Fig. 1. (a) SEM image and (b) mapping image of Ge of as-prepared n-type Si-Ge powder. Light gray: Ge-rich phase.

Fig. 2. Particle size distributions of as-prepared p- and n-type powders.

Fig. 3. SEM images of pulverized n-type Si-Ge powders ball-milled for (a) 1 h, (b) 10 h and (c) 50 h.

powder by prolonged ball-milling time. Consequently, the mean particle size of the powder decreased until 10 h, while it increased thereafter, as shown in Table 2. Therefore, the densification was hereafter carried out using the p- and n-type powders ball-milled for 10 h, of which the mean particle sizes were 3.0 and 2.6 μm , respectively.

Fig. 4. Change in particle size distribution of as-prepared Si-Ge powders by ball-milling.

Table 2. Mean Particle Size of Si-Ge as-Prepared and Their Pulverized Powders (μm)

	p-type Si-Ge	n-type Si-Ge
As-prepared	72.1	66.1
Pulverized 1h	-	4.6
5h	-	3.2
10h	3.0	2.6
30h	-	9.2
50h	-	8.9

Fig. 5. XRD patterns of as-prepared n-type Si-Ge powder and its pulverized powders ball-milled for 1–100 h.

Figure 5 shows the XRD patterns of pulverized n-type powders after ball-milling for 1–100 h. It has been proven that all the XRD profiles originate from $\text{Si}_{0.8}\text{Ge}_{0.2}$ because they are located between those of Si and Ge. The XRD pattern indicated as-prepared powder to be in the fairly well-crystallized state. The intensities and widths of the peaks, respectively, decreased and increased gradually with the ball-milling time, which is probably due to the decrease in the crystallite size and the increase in the heterogeneous distortion in the particles, respectively. The XRD patterns of dense bodies that were made from these as-prepared and

Fig. 6. Density of sintered bodies from as-prepared p- and n-type Si-Ge powders (samples A_p and A_n , respectively) and their pulverized powders ball-milled for 10 h (samples P_p and P_n , respectively).

pulverized powders by the pulse-current sintering indicated well-crystallized $\text{Si}_{0.8}\text{Ge}_{0.2}$.

3.2 Densification

The densities of samples A_p and A_n increased abruptly at approximately 1500 K to reach the final stage of densification, as shown in Fig. 6. The densities were $2.56\text{--}2.64 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$ at 1493 K, and became more than $2.88 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$ above 1500 K. That is, a temperature above 1500 K was required for the complete densification of as-prepared powders. The density of sample P_p increased gradually until a temperature of 1393 K and then decreased, while that of sample P_n increased rather abruptly until 1433 K and started to decrease at over 1473 K.

In pulse-current sintering, the actual temperature of the sample was higher than the measured temperature in the carbon vessel.¹⁵⁾ The local melting of contact points between the particles occurred to facilitate neck growth by overheating due to local concentration of the electric current.^{19),20)} Consequently, the abrupt densification of as-prepared powders may be due to the liquefaction of small particles and the contact points between larger particles. The suitable sintering temperature range of these powders was limited within only 50 K because the melting point of $\text{Si}_{0.8}\text{Ge}_{0.2}$ was estimated to be 1550 K from the phase diagram of the Si-Ge system.¹⁸⁾ It was proved that the precise control of the sintering temperature was required to obtain a dense body from the powders.

On the other hand, the slow densification of pulverized powders occurred at a lower temperature compared with as-prepared powders. The suitable sintering temperature for sufficient densification was in the range between 1400 and 1450 K, which is much lower than the above estimated melting point of 1550 K. The densification then seemed to proceed by solid-state sintering. The difference of the density between sample P_p and P_n increased with decreasing temperature, depending on the size distribution rather than the mean particle size. Table 2 shows almost the same particle size between two kinds of pulverized Si-Ge powders ball-milled for 10 h, but Fig. 4 shows that the frequency less than $2 \mu\text{m}$ of p-type pulverized powder surpasses that of n-type. The unexpected decreases in the densities of samples P_p and P_n above 1433 and 1473 K, respectively, were presumably attributed to an expansion of the microcrack inside the body accompanied by the

evaporation of Ge that was supported by compositional analysis using X-ray fluorescence spectrometry. The surface activation of pulverized powders due to the introduction of the distortion may promote the evaporation of Ge from samples P_p and P_n . Sinterability of as-prepared p- and n-type Si-Ge powders was confirmedly improved with the mechanochemically increased surface energy of the powders by ball-milling.

Oxygen of 1.0–1.2 mass% was contained in samples P_p and P_n as SiO_2 and/or GeO_2 , which was 20 times more than those of samples A_p and A_n . Pulse-current sintering was not interrupted by the surface oxide layers of the particles; the current passed through the shaped body without any interruption.^{19),20)} However, the above-mentioned effect of the reduction of the grain size surpassed that of the contamination on the sinterability of samples P_p and P_n .

In comparison with the conventional hot pressing method, the densification and grain growth in this study were both similar^{7),21)} but the working time of 180 s was remarkably short.

3.3 Microstructure and element distribution of sintered bodies

No microstructural difference was recognized between the p- and n-type of samples A and P observed in the optical micrographs. The microstructures of samples A_p , P_p and p-type Si from the corresponding gas-atomized powders are shown in micrographs in Figs. 7(a)–(c). For sample A, many irregularly shaped areas 10–40 μm in length in light gray were observed in the matrix in dark gray (Fig. 7(a)). Figure 7(b) shows sample P consisting of many fine particles less than 5 μm in size. The grain boundaries were observed most clearly in the sample of pure Si, as shown in Fig. 7(c), the grain size of which was almost the same as that of sample A.

Figures 7(d) and (e) are the mapping images of Ge of the samples A and P, corresponding to Figs. 7(a) and (b),

respectively. Figure 7(d) revealed that the light gray areas in Fig. 7(a) were rich in Ge. Further analysis of the Si and Ge distributions along the line from A to B in Fig. 7(a) was carried out, as shown in Fig. 8. The inhomogeneity of the Ge distribution of as-prepared Si-Ge powder surface shown in Fig. 1 has been maintained in sample A, presumably due to a short time of 180 s for the pulse-current sintering. The area ratio of the Si-rich (dark gray) and Ge-rich (light gray) phases in Fig. 7(d) was determined to be 0.79 to 0.21 by conventional picture processing. Using the phase diagram of the Si-Ge system, this ratio gave an apparent temperature of 1585 K for solidification, followed by the determination of the compositions of 85Si·15Ge (mass%), and 61Si·39Ge of the dark and light gray areas, respectively. Finally, Fig. 7(e) shows that the inhomogeneity of sample P was improved compared with that of sample A.

Fig. 8. Element distributions of Si and Ge along the line A-B in Fig. 7(a).

Fig. 7. Microstructures (a–c) and mapping image of Ge (d,e) of sintered bodies. Microstructure of sintered bodies from (a) atomized p-type Si-Ge powder, (b) pulverized p-type Si-Ge powder and (c) atomized p-type Si powder (Si-0.5 mol%P). The sintering temperatures of (a)–(c) are 1513, 1393 and 1513 K, respectively. (d), (e): Mapping images of Ge from (a) and (b). Light gray: Ge-rich phase.

Fig. 9. Fracture surfaces of compact bodies from as-prepared p-type Si-Ge powder sintered at (a) 1493 K, (b) 1513 K and (c) 1533 K, and from its pulverized powder sintered at (d) 1353 K, (e) 1393 K and (f) 1513 K, respectively.

3.4 Morphology of sintered bodies

The SEM images of the fracture surfaces of samples A and P show the relationship between the sintering temperature and the microstructure of the dense bodies. Many micropores 10–50 μm in length were observed in sample A_p sintered at 1493 K (Fig. 9(a)), indicating the insufficient densification. The considerable densification of sample A_p occurred in the narrow temperature range between 1493 and 1513 K. The pores disappeared completely above 1513 K (Figs. 9(b) and (c)), having rough fracture surfaces. While fine pores less than 2 μm in size were observed in sample P_p sintered at 1353 K (Fig. 9(d)), they disappeared at 1393 K (Fig. 9(e)). These fracture surfaces of sample P_p sintered at 1353 and 1393 K consisted of small grains without growth. Figure 9(f) shows the abrupt increase in the grain size and the regeneration of some pores in sample P_p at 1513 K. Particularly, the latter implies the formation of microcracks inside the body due to the evaporation of Ge. The enhancement of the sinterability of as-prepared powder pulverized by ball-milling was confirmed from the comparison between the fracture surfaces of samples A_p and P_p sintered at 1513 K and 1393 K (Figs. 9(b) and (e)), respectively. This finding was also supported by the difference in the transverse rupture strengths of samples A_p and P_p (Figs. 9(b) and (e)) of the same density of almost 100%, which were 118 MPa and 161 MPa, respectively.

4. Conclusions

Both p- and n-type Si_{0.8}Ge_{0.2} powders (Si : Ge : B = 79.7 : 20.1 : 0.21 mol% for p-type and 79.8 : 20.0 : 0.18 mol% for n-type) oriented to the thermoelectric element were prepared by gas atomization of the corresponding melts, followed by densification using a pulse-current sintering technique. These Si-Ge powders were characterized and their sinterability was then studied. The effect of ball-milling on the sinterability of the powders was also discussed. The composition of as-prepared n-type Si-Ge powder was different from the batch compositions due to melting and evaporation of the dopant at a high temperature. The mean particle sizes of as-prepared p- and n-type Si-Ge powders were 72 and 66 μm , respectively. The mean particle sizes of both types of as-prepared powders

were shifted to 3.0 and 2.6 μm by ball-milling for 10 h, respectively. The decrease in the crystallite size and the increase in the heterogeneous distortion in the particles correlated with the ball-milling time. The densification of as-prepared powders was abruptly promoted above 1500 K; however, the densification temperature of the ball-milled powders decreased by approximately 100 K. That is, the sinterability of as-prepared powders was improved with the decrease in the crystallite size and the increased surface distortion mechanochemically introduced by ball-milling. The grain size and elemental inhomogeneity of the dense bodies were both reduced.

Acknowledgment The authors wish to express their appreciation to Mr. Takayoshi Shimizu and Dr. Koichi Morii of Daido Steel Company for their assistance in the preparation of gas-atomized powders.

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