Optimum Sintering and Annealing Conditions for β -FeSi₂ Formed by Slip Casting

Kiyoshi NOGI, Takuji KITA* and Xiang-Qun YAN*,†

Joining and Welding Research Institute, Osaka University, 11-1, Mihogaoka, Ibaraki-shi, Osaka 567-0047

*Graduate Student, Department of Materials Science and Processing, Faculty of Engineering, Osaka University, 11-1, Mihogaoka, Ibaraki-shi, Osaka 567-0047

スリップキャスト法で作製した β -FeSi₂ の最適焼結・焼鈍条件

野城 清・木太拓志*・巖 向群*,†

大阪大学接合科学研究所, 567-0047 茨木市美穂ヶ丘 11-1

*大阪大学大学院マテリアル応用工学専攻, 567-0047 茨木市美穂ヶ丘 11-1

Optimum sintering and annealing conditions for iron-disilicide thermoelectric material were determined. The chemical compositions of the starting material were Fe_{0.91}Mn_{0.09}Si₂ and Fe_{0.98}Co_{0.02}Si₂. The mean particle diameter of both powders was about 6 μ m. The powder concentration was 77 mass%, and the hydrogen exponents (=pH) of Fe_{0.91}Mn_{0.09}Si₂ and Fe_{0.98}Co_{0.02}Si₂ were 8.5 and 7, respectively. The green body was demolded in 1 h, and then was dried at 353 K for 8 h in air. Sintering was performed in the temperature range from 1423 to 1453 K for 3 h, and annealing, in the temperature range from 973 to 1143 K for 14 h. Vacuum was used for both sintering and annealing. The relative density increased with increasing sintering temperature. The relative density of the Fe_{0.91}Mn_{0.09}Si₂ specimen was higher than that of the Fe_{0.98}Co_{0.02}Si₂ specimen, because the solidus temperature of Fe_{0.91}Mn_{0.09}Si₂ is lower than that of Fe_{0.98}Co_{0.02}Si₂. The grain size of the ϵ -phase in the specimen sintered at 1453 K was much larger than that in the specimen sintered at 1443 K, and is covered with a thick β -phase layer, which restrains the reaction of ϵ + Si $\rightarrow$ β . The optimum annealing temperature was at 1123 K, at which the eutectoid reaction, $\alpha \rightarrow \beta$ + Si, and the subsequent reaction, ϵ + Si $\rightarrow$ β , mainly occurred. Some compacts were formed by cold isostatic pressing (CIP) or uniaxial pressing. Density and thermoelectric properties of the specimen formed by slip casting were better than those prepared by uniaxial pressing and almost the same as those prepared by CIP. Thus, slip casting is regarded as a superior forming method to conventional methods such as CIP and uniaxial pressing.

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1. Introduction

Thermoelectric materials are able to directly convert heat energy into electrical energy. β -FeSi₂ is one of the most attractive thermoelectric materials^{1)–5)} because it can be used in air at high temperatures due to its superior oxidation resistance property. However, the thermoelectric properties of β -FeSi₂ are quite low. Thus, it is presently expected that β -FeSi₂ cannot be used to generate a large amount of electric power in a huge system such as a power generation plant, but can utilize waste heat from small facilities such as an incinerator or an automobile. Although a method for mass-producing β -FeSi₂ devices has not yet been established, the devices could be inexpensively produced because of the abundance of raw materials.

The conventional production methods of β -FeSi₂ are mainly (1) press forming and pressureless sintering and (2) hot-pressing. The slip casting method is seldom applied to the iron-disilicide system,⁶⁾ but has been applied to CrSi₂ and CoSi, which are also known as thermoelectric materials.^{7),8)} Slip casting has been used for a long time in the ceramics industry as a method of forming ceramic wares of large dimensions or complicated shapes. The molds and associated equipment for slip casting are less expensive than those for other molding methods. Therefore, an investigation should be conducted to determine whether slip cast-

ing is a suitable molding method for the mass production of iron-disilicide thermoelectric devices. The authors reported the optimum slip conditions in a previous paper.⁹⁾

The purpose of this study is to determine the optimum sintering and annealing conditions of iron disilicide, and to compare the properties of the specimen produced by the slip casting method with those produced by conventional methods.

2. Experimental procedure

The chemical compositions of the starting material were Fe_{0.91}Mn_{0.09}Si₂ and Fe_{0.98}Co_{0.02}Si₂. The mean particle diameters of both powders were approximately 6 μ m. The slips were prepared by adding distilled water to the powder, and then the pH of the slips was controlled by adding 3% aqueous ammonia solution. The powder concentration was 77%, and the pHs of Fe_{0.91}Mn_{0.09}Si₂ and Fe_{0.98}Co_{0.02}Si₂ were 8.5 and 7, respectively,⁹⁾ in order to achieve good fluidity. The slip was poured into a mold, as shown in Fig. 1. The green body was demolded in about 1 h, and then dried at 353 K for about 8 h in air. Sintering was performed in the temperature range from 1423 to 1453 K for 3 h, and annealing was performed in the temperature range from 973 to 1143 K for 14 h. A vacuum of 10⁻² Pa was used for both sintering and annealing. In order to compare the productivity of slip casting with that of conventional methods, some compacts were formed also by cold isostatic pressing (=CIP) and uniaxial pressing. CIP was performed at a hydraulic pressure of 200 MPa. Uniaxial pressing was performed at

† Present Address: Hosokawa Micron Co., 1-9, Shoudai Tajika, Hirakata-shi, Osaka 573-1132

現在: ホソカワミクロン, 573-1132 枚方市招提田近 1-9

Fig. 1. Construction of mold.

20 MPa, because the green body formed at pressures above 20 MPa cracked. Density of the specimen was measured by the buoyancy method, and the relative density to the β -phase density, 4.93 g/cm³, was also calculated. The phases in the sintered compacts were determined from the X-ray diffraction (XRD) patterns. The β -phase ratio: $f_{\beta} = I_{\beta} / (I_{\epsilon} + I_{\beta}) \times 100$, (I_{ϵ} = intensity of $\epsilon(210)$, I_{β} = intensity of $\beta(220, 202)$) was calculated from the XRD results in order to evaluate the amount of the β -phase in the specimens in a simple way. The microstructures of the sintered compacts were observed using a scanning electron microscope (SEM) and analyzed using an electron probe X-ray microanalyzer (EPMA). The Seebeck coefficient (α) and the electrical resistivity (ρ) were simultaneously measured in the temperature range from 373 to 1023 K in a vacuum of 10^{-2} Pa.

3. Results and discussion

3.1 Sintering temperature

Figure 2 shows the sintering temperature dependence of the relative density. The relative density increases with increasing sintering temperature, and the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ specimen sintered at 1463 K nearly melted. The relative density of the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ specimen is higher than that of the $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ specimen throughout the entire temperature range. The main reason is that the solidus temperature of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ is lower than that of $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$. The solidus temperatures of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ and $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ are about 1453 and 1493 K, respectively.^{10),11)} Figure 3 shows reflection electron images of the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ specimens sintered at 1443 or 1453 K for 3 h. It was revealed by EPMA analysis that the brightest areas were the ϵ -phases, the gray areas were the α -phases and the black areas were pores. The sizes of the ϵ -phases in the specimen sintered at 1453 K are much larger than those in the specimen sintered

Fig. 2. Sintering temperature dependence of relative density.

Fig. 3. Reflection electron images of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ sintered at T_{sint} for 3 h. (a) $T_{\text{sint}} = 1443$ K, (b) $T_{\text{sint}} = 1453$ K.

at 1443 K. Figure 4 shows reflection electron images of the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ specimens sintered at 1443 or 1453 K for 3 h and annealed at 1123 K for 14 h, which are the optimum annealing conditions as will be discussed later. When the specimens are sintered at 1453 K, many large ϵ -phases and (β + Si)-phases remain.

Fig. 4. Reflection electron images of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ sintered at T_{sint} for 3 h and annealed at 1123 K for 14 h. (a) $T_{\text{sint}} = 1443$ K, (b) $T_{\text{sint}} = 1453$ K.

Kojima et al.¹²⁾ reported two different reaction mechanisms for the β -phase formation below and above the critical temperature, T_c . One is the peritectoid reaction of $\alpha + \epsilon \rightarrow \beta$ above T_c . The other is a two-stage reaction consisting of the eutectoid reaction, $\alpha \rightarrow \beta + \text{Si}$, and the subsequent reaction, $\epsilon + \text{Si} \rightarrow \beta$, below T_c . The latter is the main reaction mechanism of the specimens shown in Figs. 4(a) and (b), because many silicon grains are dispersed in the β -phase. The ϵ -phase in the specimen sintered at 1453 K is covered with a thick β -phase layer, and the β -phase layer restrains the reaction of $\epsilon + \text{Si} \rightarrow \beta$. As mentioned above, the relative density of the specimen sintered at 1453 K is higher than that at 1443 K. However, 1443 K is the optimum sintering temperature, because the annealing time for the 1443 K specimen is significantly shorter than that for the 1453 K specimen.

3.2 Annealing temperature

Figure 5 are reflection electron images of the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ specimens annealed at T_{anl} ($T_{\text{anl}} = 1103, 1123, 1143$ K) for 14 h after sintering at 1443 K for 3 h. A large amount of the α -phase remained in the 1143 K specimen, as shown in Fig. 5(a), because the peritectoid reaction of $\alpha + \epsilon \rightarrow \beta$ mainly occurred but was not completed due to the slow diffusion through the β -phase. In the 1103 K specimen, many silicon grains were dispersed in the β -phase, as shown in Fig. 5(c). It is obvious that the eutectoid reaction mainly occurred, and the subsequent reaction was not completed. Based on Fig. 5(b), it is thought that the eutectoid reaction $\alpha \rightarrow \beta + \text{Si}$ and the subsequent reaction $\epsilon + \text{Si} \rightarrow \beta$ mainly occur at 1123 K. Accordingly, the critical temperature, T_c , is between 1123 and 1143 K. These results are in agreement with the XRD results.

Fig. 5. Reflection electron images of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ annealed at T_{anl} for 14 h. (a) $T_{\text{anl}} = 1143$ K, (b) $T_{\text{anl}} = 1123$ K, (c) $T_{\text{anl}} = 1103$ K.

The β -phase ratios of the specimens annealed at various temperatures are shown in Fig. 6. It is obvious that 1123 K is the optimum annealing temperature for the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ specimen. Thus, the annealing conditions were determined to be at 1123 K for 14 h. The β -phase ratio of $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ is larger than that of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$, because the transformation to the β -phase for the $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ specimen is faster than that for the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ ^{13),14)} specimen. The β -phase ratio of the $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ specimen annealed at 1143 K is larger than that of the specimen annealed at 1123 K. This is because T_c for $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ is independent of the amount of dopant (x), although T_c for $\text{Fe}_{1-y}\text{Mn}_y\text{Si}_2$ decreases with increasing amount of dopant (y).^{8),13),14)}

Fig. 6. β -phase ratios of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ and $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ annealed for 14 h.

Table 1. Comparison of Relative Density Among Different Forming Methods. All Samples Were Sintered at 1443 K

Forming Method	$\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$	$\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$
	Relative Density (%)	Relative Density (%)
Slip Casting	95	91
Cold Isostatic Pressing	95	90
Uniaxial Pressing	92	87

3.3 Comparison of productivity of slip casting with that of other forming methods

The relative green density was 54%. The shrinkage of the specimen during sintering was $17.1 \pm 0.3\%$, and was independent of both powder concentration and starting material ($\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ or $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$). The sintered specimens did not have cracks and strains, and thus uniform green bodies were obtained.

Table 1 shows the relative density of the sintered sample formed by slip casting, CIP or uniaxial pressing. The difference in the relative density among the forming methods is mainly caused by the difference in the green density. Compared with uniaxial pressing, a denser green body without cracking can be formed by CIP, because the powder is isostatically compacted at high pressure. The green density of the specimen formed by slip casting is almost the same as that of the CIP specimen. Slip casting enables the green density to be higher without pressing. Figures 7(a) and 7(b) show the XRD patterns of CIP and slip casting specimens ($\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$) annealed at 1123 K for 14 h after sintering at 1443 K for 3 h. The peaks without marks represent the β -phase. The peaks of the CIP specimen are almost the same as those of the slip casting specimen.

Fig. 7. XRD patterns of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ annealed at 1123 K for 14 h. (a) slip casting, (b) CIP.

Fig. 8. Temperature dependence of the thermoelectric properties of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$.

Figures 8 and 9 show the temperature dependence of the thermoelectric properties of the $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$ and $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ specimens formed by slip casting or CIP. Annealing was carried out at 1123 K for 14 h. There are no significant differences in the thermoelectric properties. In view of the complicated process and the high cost of equipment, CIP is not a suitable forming method for iron-disilicide thermoelectric materials. Thus, it is concluded that slip casting is superior in productivity to CIP.

4. Conclusions

The optimum sintering and annealing conditions of iron disilicide were determined, and the properties of the specimen produced by the slip casting method were compared with those produced by conventional methods.

(1) The optimum sintering temperature is 1443 K. In the case of $\text{Fe}_{0.91}\text{Mn}_{0.09}\text{Si}_2$, the transformation to the β -phase for the 1453 K specimen is much slower than that for the 1443 K specimen, though a higher density is obtained. The optimum annealing temperature is 1123 K.

(2) The density and thermoelectric properties of the specimens formed by slip casting are almost the same as those of the specimens formed by CIP. Slip casting is regarded as the best production forming method.

Fig. 9. Temperature dependence of the thermoelectric properties of $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$.

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