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Synthesis of β -FeSi₂ Utilizing the Combined Process of MA/SPS[†]

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and Masaaki NAKA****

Abstract

β -FeSi₂ was successfully produced by making use of the combined process of mechanical alloying (MA) and spark plasma sintering (SPS). The MA was performed under the Ar gas atmosphere using mixed powders of pure iron and silicon having the mole fraction of 1:2. The SPS process was performed at 1073 K with the heating rate of 133 K/s and a holding time ranging from 0 to 15ks. The combined process was quite effective for the production of β -FeSi₂, where the minimum SPS time required was found to depend on the MA time. The shortest SPS holding time of 0s. was achieved for the powders mechanically alloyed for 72ks. The relative density of each sinter was around 90% (4.44g/cm³) of its ideal density, and in particular the density of 97.4 gr was obtained for the sinter which was mechanically alloyed for 72ks, followed by the SPS treatment for 600 s.

KEY WORDS: (β -FeSi₂)(mechanical alloying) (spark plasma sintering) (combined process)
(thermoelectric material)

1. Introduction

Energy and ecology are the important key words which have come to be recognized as representing urgent problems for human beings. In order to solve these problems, much attention has been focused on the development of energy transferring materials which possess, for example, electro-thermal or thermo-electromotive properties. These materials are quite innovative since they can make use of the un-utilized resource like exhaust heat and enable us to be independent of fossile fuel.

In particular, β -FeSi₂ is known to be an candidate material for such demands since both iron and silicon are nontoxic, abundant in the earth's crust and widely used in modern industry. In addition, the material is quite stable at elevated temperature and shows high corrosion resistance against acids, so the β -FeSi₂ has been attracting much attention as an environment-conscious material such as in thermo-electromotive materials at high temperature¹⁾⁻⁵⁾.

β -FeSi₂ is a semiconductor which is stable below 1255K, and decomposes into α -FeSi₂ + ε -FeSi phases above this transition temperature⁶⁾. Thus the sintering

process is limited to operation below 1255K, where sound sinters with high density cannot be produced. Usually the β -transformed material has been fabricated by sintering at 1113K for 36ks. using the powders ground from an ingot made by the arc melting method⁶⁾.

Recently, Nagai et al⁷⁾ has developed a combined process of mechanical alloying (MA) and hot pressing (HP) as a highly efficient technique for the β -transition. They have succeeded in fabricating the β -FeSi₂ by the MA for 36ks followed by the HP treatment at 1173K for 1.8ks., which remarkably reduced the time for heat treatment and also omitted the arc melting process.

On the other hand, the spark plasma sintering (SPS) method has been successfully applied for many materials which are hard to be sintered⁸⁾. This method is expected to be quite useful for producing the β -FeSi₂ for short time instead of the HP method mentioned above, but no report so far has been published for the combined process of MA and SPS for the synthesis of this material.

In the present study, a combined treatment of the MA and the SPS has been examined as a new production process, and the effects of the MA time or the SPS time on the β -transition have been investigated in order to

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elucidate the best conditions for the manufacturing of β -FeSi₂.

2. Experimental procedure

Starting materials were pure iron powders (99.5mass%, 5 μ m in particle size), and pure silicon powders (99.9mass%, under 200mesh) prepared by Mitsuwa Kagaku Co.Ltd. These iron and silicon powders were mixed to the mole fraction of 1 : 2 before the MA treatment.

The MA was performed under the Ar gas atmosphere with a ball milling machine (Nissin Giken Co. Ltd, NEV-MA8). The mill pots and balls with 11mm in diameter are made of SUS304, and the weight ratio of balls / powders is 10 : 1. The milling times were 3.6, 18.0, 36.0 and 72.0ks.

The sintering was performed at 1073 K with an SPS machine (Sumitomo Sekitan Co.Ltd, SPS2050). Powders were packed in a carbon die with the diameter of 20 mm, and an uniaxial stress of 60MPa was loaded via two punches. The heating rate was 133 K/s and the holding time ranged from 0 to 15ks. It is commonly known that the specimen and die have different temperatures ranging from some 10K to 100K^{9), 10)}. In the present study the SPS system was controlled using the temperature of the die.

Phase analysis of each powder and sinter was performed by the X ray diffraction technique. Microstructural

analysis of each sinter was carried out with an optical microscope after a mechanical and a chemical etching using an aqueous solution of HF. Density of sinter was measured by means of the Archimedean method.

3. Results and discussion

3.1 Effect of MA time on the β transition

The MA process was at first investigated by means of the X ray diffraction method and the results are shown in Fig. 1. The duration of MA treatment ranged from 3.6ks to 72.0ks. Only the peaks corresponding to iron and silicon were observed for the powders mechanically alloyed for 3.6ks and 18.0ks. Small amounts of a new reaction phase, the ϵ -FeSi phase, were formed as the MA time increased to 36.0ks, but the major phases were still iron and silicon. The β -FeSi₂ phase appeared in the powders mechanically alloyed for 72.0ks, in which a stronger intensity of the ϵ -FeSi phase was also observed along with iron and silicon phases, indicating that further MA treatment will be required for the β transition.

3.2 Combined effect of SPS / MA on the β transition

SPS treatment was then performed for the mechanically alloyed powders, which were not sufficiently β transformed as shown in Fig.1. The temperature and the holding time for the SPS were 1123K and 0.6ks,

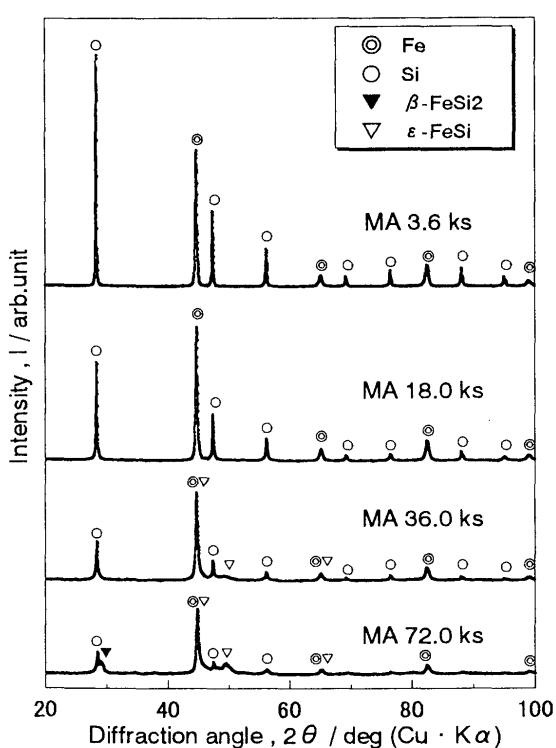


Fig. 1 XRDs of mechanically alloyed powder.

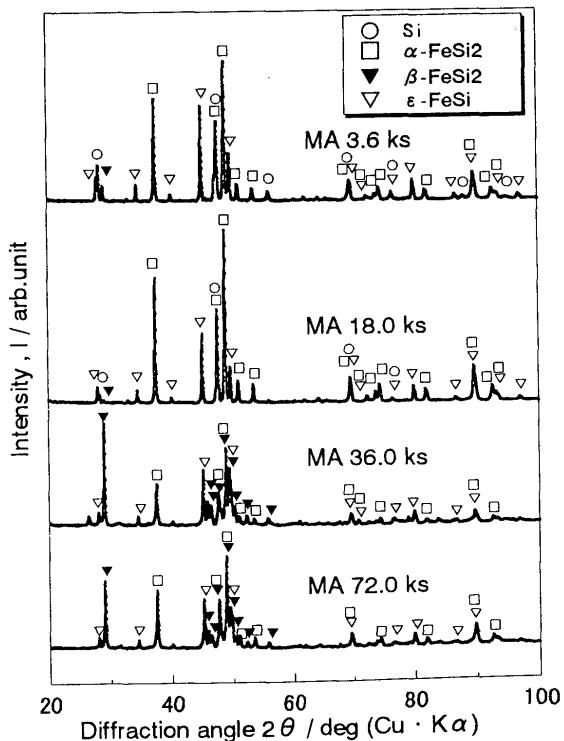


Fig. 2 XRDs of sinter, SPS-1123K, 0.6ks.

respectively. **Figure 2** shows the changes of the X ray diffraction patterns from the sinters with increasing MA time. Sintering for 3.6ks and 18.0ks. brought about decreases in the peak intensity for both iron and silicon and the appearance of both α - FeSi_2 and ε - FeSi phases along with β - FeSi_2 phase having the weakest intensity. Strong intensity of the β phase was observed in the powders mechanically alloyed for both 36.0 and 72.0ks. These successive change of phase reactions indicate that the SPS treatment is quite effective for the β transition for the mechanically alloyed powders which showed little tendency to form the β phase.

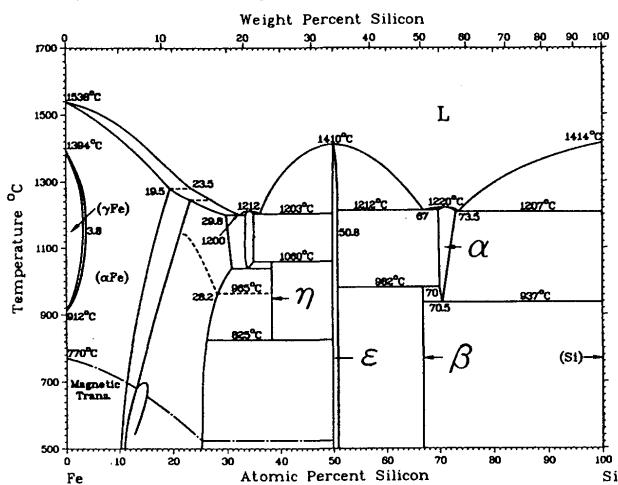


Fig. 3 Fe-Si binary phase diagram¹²⁾.

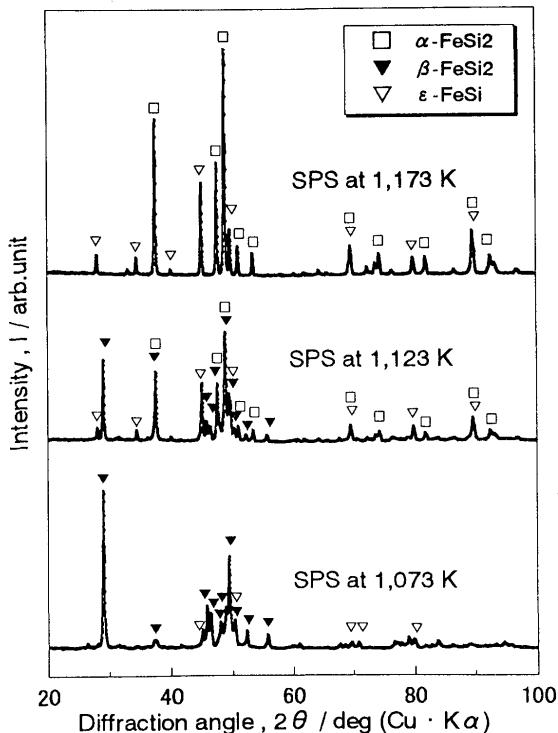


Fig. 4 XRDs of sinters, MA72.0ks and SPS 0.6ks.

However there is another difficulty in the control of the phase reactions in the powders when sintered at 1123K. The mixtures of either $(\text{Si} + \alpha + \varepsilon)$ or $(\alpha + \beta + \varepsilon)$ phase existing in the sinters are due to the high sintering temperature for producing the full β transformed phase according to the binary phase diagram of Fe-Si system as shown in **Fig.3**. The α phase is dominant at 1123K and consequently the β phase cannot increase its amount. Thus the sintering temperature is one of the important factors for the synthesis of β - FeSi_2 , and so the effect of sintering temperature on the phase formation was investigated.

Figure 4 shows X ray diffraction patterns from the sinters with different SPS temperatures. Every sinter had the same MA time as 72.0ks., and the holding time of the sintering was set to be 0.6ks. Only $(\alpha + \varepsilon)$ mixed phases were observed after the sintering at 1173K, and the β phase appeared additionally to the mixed phases at the lower temperature of 1073K. The extinction of the α phase occurred at 1023K, resulting in the mixture of $(\beta + \varepsilon)$ phases.

According to the Fe-Si binary phase diagram shown in **Fig.3**, the α , β and ε phases coexist at temperatures ranging from 1210 to 1255K. Since these three phases were observed to be formed at the sintering temperature of 1123K, the true sintering temperature should be corrected to 87 to 132K higher than the temperature of the die.

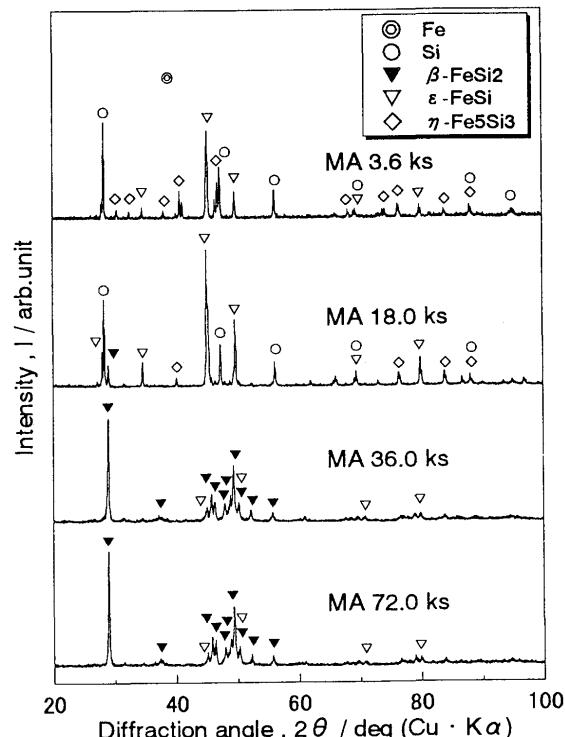


Fig. 5 XRDs of sinters, SPS 1073K-0.6ks.

Thus, the sintering temperature was set to be 1073K in order to avoid the α phase.

Figure 5 shows the changes of X ray diffraction patterns in the specimens sintered at 1073K for 0.6ks, indicating the effect of MA time on the phase formation during the SPS. No formation of the α phase was observed in each specimen sintered at 1073K. Sinters of the powders mechanically alloyed for 3.6ks. showed weak intensity of Si peaks and stronger intensity of η and ε phases but no β phase. Increasing MA time resulted in the disappearance of the η phase and promotion of the β phase as shown in the case of MA times longer than 18.0ks. Si disappeared perfectly after mechanical alloying for longer than 36.0ks., and the ε phase almost lost its intensity, indicating that the β transition was completed at this condition. From these results, the phase reaction in this powder was shown to follow the sequence $\eta \rightarrow \varepsilon \rightarrow \beta$.

The temperature regions stable for the η , ε and β phases range from 1098 to 1333K, below 1683K and below 1255K, respectively as shown in Fig.3. The α phase does not exist as a stable phase below 1210K. In the present study, the sintering temperature of 1073K shown in Fig.5 means the die temperature, and the true sintering temperature is thought to be in the range from 1160 to 1205K as discussed previously. If the phase reaction proceeds on the basis of the diffusion of iron atoms into silicon powders in this temperature range, the phase diagram can explain the sequence of phase reaction ;

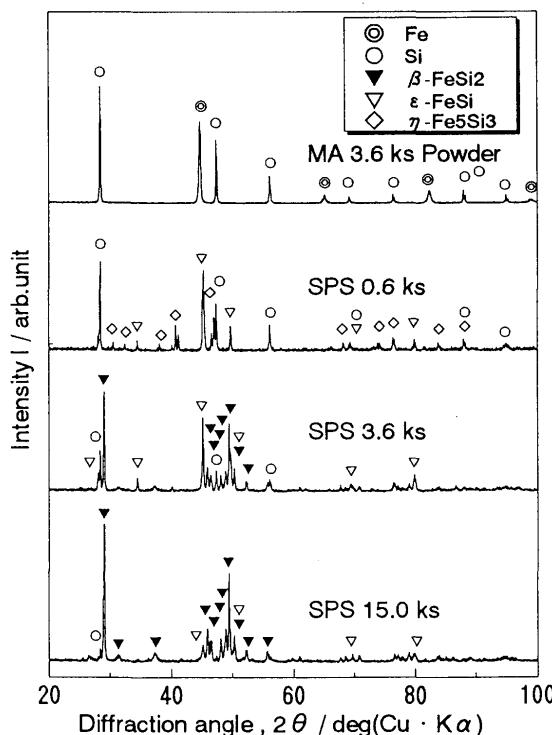


Fig. 6 XRDs of powder, MA3.6ks and SPS at 1073K.

$Fe \rightarrow \eta \rightarrow \varepsilon \rightarrow \beta$, which coincides with the present results such as shown in Fig. 5.

On the other hand, the ε - FeSi phase was always detected in every sinter. This is due to the excess amount of iron picked up from the mill pot made of stainless steel. Thus, it is possible to produce a sinter having an ideal composition of FeSi₂ by controlling the fraction of iron and silicon in the mixed powders in advance.

3.3 Effect of SPS time on the β transition

Figure 6 represents the X ray diffraction patterns from the powders and the sinters, indicating the progress of phase reaction during the SPS treatment at 1073K. Only pure iron and pure silicon existed in the powder just after the MA treatment for 3.6ks, indicating no particular phase reaction. On the contrary, both the ε - FeSi and the η - Fe₅Si₃ phases were observed to be formed after SPS treatment of 0.6ks. A longer sintering time of 3.6ks was required for the formation of the β -FeSi₂ phase with the disappearance of η - Fe₅Si₃ phase, and finally almost fully β -transformed phase came to be dominant in the sinter after 15.0ks. of the sintering

These phase reactions are attributed to the diffusion of silicon into iron powder since the amount of silicon increases with the progress of the phase reaction. Based on the diffusion of silicon into iron, the sequence of the phase reaction $\eta \rightarrow \varepsilon \rightarrow \beta$, these phases should also arise during the MA process. Thus, both the MA and the SPS processes are equivalent to each other from the view

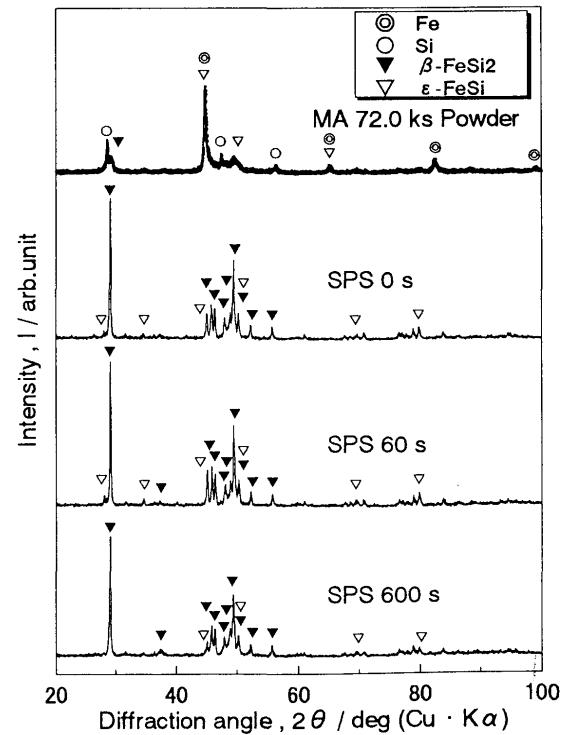


Fig. 7 XRDs of powder, MA72.0ks and SPS at 1073K.

point of diffusion mechanisms resulting in the formation of new phases.

Figure 7 represents the changes of X ray diffraction patterns from powder and sinter, showing the progress of

phase reactions during the SPS process at 1073K after the MA treatment for 72.0Ks. There exist already the ϵ and the β phases in the MA powder along with retained iron and silicon phases, suggesting that phase reaction is also

Table 1 Relation of MA time and SPS time to beta transition

MA time SPS time	3.6ks	18ks	36ks	72ks
Powder after MA	Si,Fe	Si,Fe	Si,Fe, ϵ	Si,Fe, ϵ
0 s	—	—	Si, ϵ , β (81.2)	β (93.2)
0.6ks	Si, ϵ , η (67.9)	Si, ϵ , β (68.8)	β (93.3)	β (97.4)
3.6ks	Si, ϵ (73.2)	β (89.9)		
15 ks	β (88.5)			

Die temperature : 1073K,

Heating rate : 1.33K/s

Values in parentheses : Relational density = ρ / ρ_0 [%], $\rho_0 = 4.93 \text{ g/cm}^3$

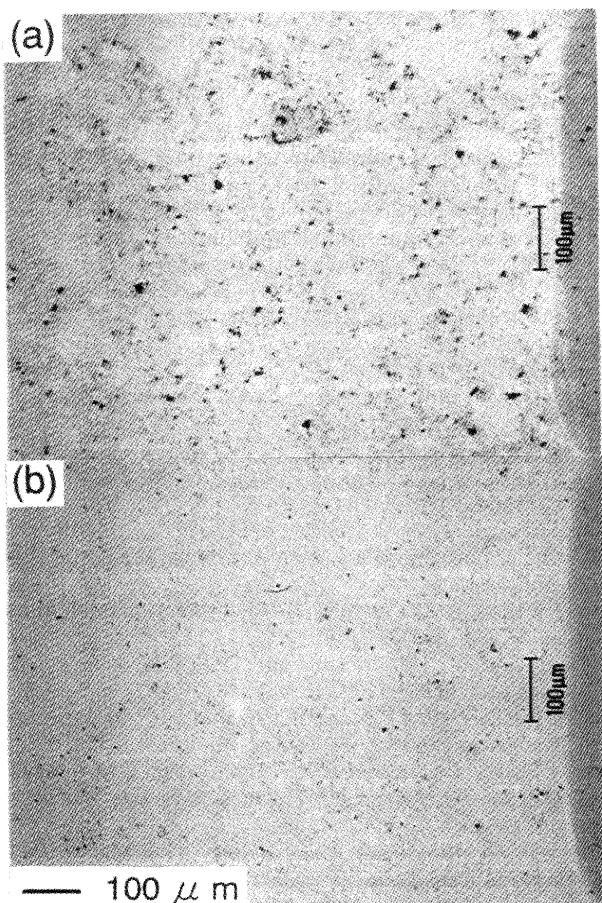


Fig. 8 Optical micrographs of sinters after polishing.
(a) MA72.0ks + SPS 1073K-0s.
(b) MA72.0ks + SPS 1073K-600s.

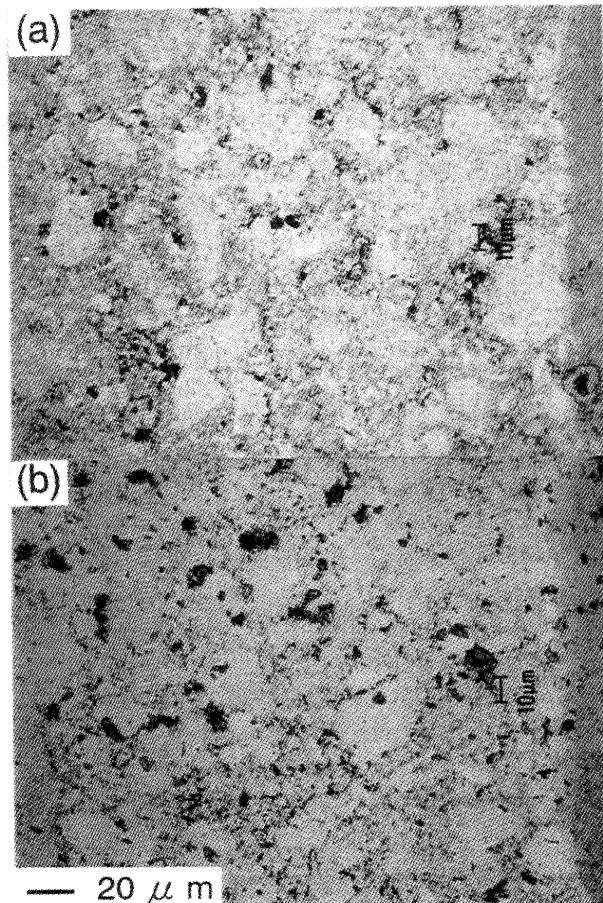


Fig. 9 Optical micrographs of sinters after etching.
(a) MA72.0ks + SPS 1073K-0s.
(b) MA72.0ks + SPS 1073K-600s.

occurring during MA process.

A formation of new phase was clearly observed immediately after the SPS treatment of 0 s. which means just heating and cooling with no holding time at 1073K of the SPS temperature. In this sinter the β phase appears as the dominant phase coexisting with the ε phase of weak intensity, and neither pure iron nor pure silicon powders was detected. As the sintering time increased the intensity of the ε phase decreased.

Table 1 summarizes the results of phase analyses and the relative density for each sinter as functions of MA time and SPS time which were revealed in the present study. As has been explained in both Figs. 6 and 7, it is clear that the time to full β transition depends on both the MA time and the SPS time, and a longer MA time resulted in the requirement for a shorter SPS time for the full β transition.

In the present study the essential process of the β transition is thought to be the diffusion process of silicon into iron powders during both MA and SPS processes. Shiga et al¹¹⁾ reported that the β -FeSi₂ was successfully produced only by MA process for 1800ks. Consequently the β transition can be realized by either “long time SPS treatment for the powders with shorter MA time” or “short time SPS treatment for the powders with long MA time”.

3.4 Density of the sinter

As shown in Table 1, dense sinters with the relative density of more than 88.5% of the ideal value for β -FeSi₂ were obtained for every fully β -transformed sinter and the maximum value of 97.4% was attained under the condition of 72.0ks. of MA followed by 0.6ks of SPS at 1073K.

Figure 8 (a) and (b) show optical micrographs of the surface of sinters produced under the conditions of (MA72.0ks + SPS 1073K-0s) and (MA72.0ks + SPS 1073K-0.6ks), respectively. Dark spots represent voids, and the number of voids is less in the sinter with longer SPS time. Grain structures in the two sinters were then examined by optical microscopy after a slight etching treatment and the results are shown in **Fig. 9**. There is observed no significant difference in grain size between the sinters, suggesting that the densification proceeded without grain growth.

Therefore, the dense and fully β -transformed sinters can be produced utilizing the combined process of MA and SPS from commercial powders of pure iron and pure silicon.

4. Conclusions

The combined process of mechanical alloying and spark plasma sintering was newly developed in order to fabricate beta-SiFe₂ and the following results were obtained.

- (1) Fully transformed bulk β -FeSi₂ was produced from the mixture of iron and silicon powders with the mole fraction of 1 : 2 by utilizing the combined process of the SPS and the MA.
- (2) Fully β transformed powders were not produced by the MA process at less than 72ks. in the present study.
- (3) The MA treatment was effective for the SPS process, and the SPS times to produce fully β transformed sinters were 15.0ks., 3.6ks. and 0.6ks. for the powders mechanically alloyed for 3.6ks., 18.0ks. and 36.0ks., respectively. The minimum SPS time of 0s. occurred for the powders which were mechanically alloyed for 72ks.
- (4) Relative densities of fully β -transformed sinters were around 90% ($\rho = 4.44\text{g/cm}^3$), and the maximum value of 97.4% ($\rho = 4.80\text{g/cm}^3$) was obtained for the specimen sintered at 1073K for 0.6ks after the MA for 72.0ks.

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