Preparation of Thermoelectric $\beta$-FeSi$_2$ Doped with Al and Mn by Mechanical Alloying (Overview)

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MA has been applied to the Fe-Si system near the composition FeSi$_2$ starting from elemental powders using a horizontal ball mill. Powders were examined by means of XRD and DSC. After substantially long time milling, the pre-mixed powder of nominal composition Fe$_{80}$Si$_{20}$ was found to transform to a homogeneous $\beta$-FeSi$_2$ phase in the as milled condition. The appropriate milling time of a powder for sintering was considered to be 720 ks. At this stage the powder consists of very fine Fe and Si crystals in the as milled condition. This transforms into a homogeneous $\beta$ phase with an exo-thermic reaction at around 720 K. The transformation rate from ($\alpha$+e) to $\beta$ in the MA powder was found to be faster than that in the specimen prepared from an eutectic alloy ingot. Specimens prepared by hot pressing from MA powder showed smaller grain size and lower thermal conductivity than those prepared by ingot metallurgy. The p-type thermoelectric properties were measured for $\beta$-FeSi$_2$ hot-press sintered specimens doped with both Al and Mn. Due to a small grain size, the specimen prepared from the MA powder showed a higher figure of merit and hence is, higher in conversion efficiency than that prepared by ingot metallurgy. The sequence of phase formation by mechanical alloying and post-milling annealing is considered. The effects of grain size on the thermal conductivity and Seebeck potential are discussed.

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I. Introduction

Thermoelectric power generator has become a subject of great interest to meet the modern requirements for a reliable source of electric power. A number of materials have been tested for utilization in a thermoelectric generator. $\beta$-FeSi$_2$ is one of the promising materials useful for energy conversion in the temperature range 200 to 900°C. The material is nonpoisonous, good resistant against oxidation and can be operated in air without any protection, exhibits high electrical conductivity and large thermoelectric power(10-46). A great advantage is that both p- and n-type of the $\beta$ phase can be instantaneously obtained by doping with Mn(104) or Al(123) and with Co(24-6) respectively. Thus, both legs of thermocouple can be constructed of the same basic material, thus eliminating problems of differential thermal expansion.

However, a great disadvantage is that the as-cast materials are brittle and porous. Furthermore, the eutectic and peritectoid reactions from liquid to $\beta$ phase cause difficulties to form a bulk material with a homogeneous $\beta$ phase. Thus, in a conventional process, ingots were ground to fine particles and long time homogenization have been carried out to eliminate segregation as shown in Fig. 1. Mechanical alloying (MA) is a solid state alloying process which is suitable for the production of segregation free material with a very fine microstructure. It is to be expected that a homogeneous $\beta$-FeSi$_2$ phase can be produced by the MA process in a much simpler way than by conventional melt and cast processes as is shown in Fig. 1(58).

The thermoelectric performance of materials is represented by effective maximum power ($P_{\text{eff}}$) and conversion efficiency ($h_{\text{max}}$). Both factors should be large for the material used in a thermoelectric generator. The improvement of these factors can be achieved by the reduction of thermal conductivity. The thermal conductivity of the semiconductor like $\beta$-FeSi$_2$ mainly arise from the lattice wave (phonons). Thus, it can be expected that grain size refinement reduces the thermal conductivity by increasing the phonon scattering by grain boundaries. Mechanical alloying is well known as one of the ideal processes to obtain a fine grained material.

In this paper, an improved fabrication process for $\beta$-FeSi$_2$ thermoelectric material by MA is described. It will be shown that MA can produce homogeneous $\beta$-FeSi$_2$ with a fine grain size, and that a long time homogenizing treatment or a long time annealing, which is usually required for the powders made from alloy ingot, can be eliminated. Moreover, because of the low thermal conductivity due to the fine grain size, a higher figure of merit and hence higher conversion efficiency can be obtained by the MA process.

II. Thermoelectric Properties and Their Improvement

The thermoelectric properties can be expressed explicitly by the two factors; effective maximum power ($P_{\text{eff}}$) and conversion efficiency ($h_{\text{max}}$). The effective maximum power ($P_{\text{eff}}$) depends upon the Seebeck potential ($E_s$)
and mean electrical resistivity \( (\rho_m) \) and is given by

\[
P_{\text{eff}} = E_0 / (4\rho_m) \]

\( E_0 \) depends on the temperature difference over which the device operates. In most of the practical cases, the temperatures of heat source and coolant for thermoelectric generator will be fixed. Thus, the attainable temperature difference in the device depends on the thermal conductivity of the material. If the thermal conductivity of the material is large, the obtainable \( P_{\text{eff}} \) will be small even if the Seebeck coefficient is large. For instance, pure Cu or Ag show higher \( P_{\text{eff}} \) than FeSi₂ doped with Al or Mn when given the same temperature difference in the material. This is because \( \rho_m \) of Cu and Ag is 3 orders of magnitude smaller than that of FeSi₂, even if the Seebeck potential is about 1 order of magnitude smaller than that of FeSi₂. However, the thermal conductivity of Cu or Ag is about 50 times larger than that of FeSi₂, the attainable temperature difference in Cu or Ag under normal condition is several % of that of FeSi₂. Because of this small temperature difference in Cu or Ag, the \( P_{\text{eff}} \) of these materials turns out to be less than 1% of that of FeSi₂. This indicates that practical \( P_{\text{eff}} \) can be increased by the reduction of thermal conductivity.

The maximum conversion efficiency \( (h_{\text{max}}) \) of a thermocouple depends upon the temperature difference \( (T_h - T_c) \) over which it operates, its average temperature \( (T_a) \), and the figure of merit \( (Z) \) for the thermocouple material, and is given by

\[
h_{\text{max}} = (T_h - T_c) (m_0 - 1)/(T_a (m_0 + T_c/T_h)) \]

where

\[
m_0 = (1 + ZT_a)^{1/2} \]
\[
T_a = (T_h + T_c)/2 \]
\[
Z = (E_0/DT)^2/(\rho_m K). \]

The conversion efficiency expression can be separated into two terms, one representing the Carnot cycle efficiency and the other governed by the factor \( Z \), a material parameter. The Seebeck potential and electrical conductivity depends on carrier density as is shown in Fig. 2. Thermal conductivity \( K \) is the sum of the contribution arising from the lattice waves (phonons) \( K_L \) and a contribution \( K_e \) from the charge carriers present. All three

![Fig. 2 Seebeck coefficient, electrical conductivity and thermal conductivity as a function of carrier concentration (schematic).](image-url)
parameters in the figure of merit, $E_0$, $r_0$, and $K$, vary with the carrier concentration and $Z$ is optimized at around $10^{26}$ m$^{-3}$. At this high carrier concentration $K_L$ still account for more than 75% of the thermal conductivity\textsuperscript{(9)}. To increase the conversion efficiency or the figure of merit, thermal conductivity should be decreased.

As mentioned in the previous section, the thermal conductivity can be reduced by decreasing the grain size and thus increasing the phonon scattering. At the same time one has to consider the effect of reduction in grain size on the electrical conductivity and Seebeck potential as well. This is because $P_{dd}$ and $Z$ depend on the electrical conductivity and Seebeck potential. These factors are discussed in detail in Section VI. 2.

III. Iron Silicide and Effect of Doping Elements on $\beta$-FeSi$_2$

Figure 3 shows the phase diagram of FeSi-Si system\textsuperscript{(10)}. FeSi melts congruently at 1683 K and shows a homogeneity region extending from 49.0 to 50.8 at%Si at 1400 K. Stoichiometric iron disilicide, $\beta$-FeSi$_2$, possesses stable semiconducting properties below 1255 K. Above this temperature, however, it transits to the metallic phase\textsuperscript{(11)-(14)} which is a eutectic alloy composed of $\varepsilon$-FeSi\textsuperscript{(15)} and $\alpha$-FeSi\textsuperscript{(16)-(17)}. The high temperature $\alpha$-FeSi$_2$ phase deviates from the stoichiometric composition, has a tetragonal structure with about 13% Fe vacancies. As shown in the phase diagram of Fig. 3, the silicon content in the eutectic alloy at the eutectic point corresponds to that of FeSi$_2$, and the semiconducting phase is obtained by annealing the eutectic alloy below 1255 K. The crystal structure of $\varepsilon$-FeSi, $\alpha$-FeSi$_2$ and $\beta$-FeSi$_2$ are shown in Fig. 4. $\varepsilon$-FeSi consisting of a cubic structure with 8 atoms in a unit cell\textsuperscript{(19)}, $\alpha$-FeSi$_2$ is a tetragonal structure with 2.87 atoms in a unit cell\textsuperscript{(16)-(17)} and $\beta$-FeSi$_2$ presents an orthorhombic structure with 48 atoms in a unit cell\textsuperscript{(11)}.

It has been found possible to dope FeSi$_2$, resulting in both n and p types semiconductor\textsuperscript{(2)}. The replacement of iron by an element to its left in the periodic table, e.g. Mn\textsuperscript{(18)}, Cr\textsuperscript{(18)}, V\textsuperscript{(18)}, Ti or other elements from this group, produces p-type material and right in the periodic table, e.g. Co\textsuperscript{(21)-(23)}, Ni\textsuperscript{(18)(19)} or other elements from this group, produces n-type material. Substitution of a Group 3 element for silicon produces p-type material. Of a wide range of doping elements investigated, the optimum thermoelectric properties were formed using Co for n-type doping and Al or Mn for p-type. Matsubara et al.\textsuperscript{(20)(21)} observed high thermoelectric power in partially oxidized FeSi$_2$ films prepared by the ionized cluster beam (ICB) method and other ion-based film deposition methods.

Huge thermoelectric power was obtained in some p-type or n-type semiconducting films in which selective oxidation of either silicon or iron was expected. The selective oxidation creates many dangling bonds and/or defects introducing varieties of localized electronic states. The huge thermoelectric power is considered to be associated with such states in the disordered system.

IV. Experimental Procedure

Powders of elements Fe (>99.9% purity, <150 µm), Si (>99.9% purity, <10 µm), Mn (>99.9% purity, <75 µm) and Al (>99.9% purity, <180 µm) were used as starting materials. Mixtures of these powders were pre-
pared in atomic percentage Fe₅Siₓ₋ₓ (10 ≤ x ≤ 50) and Feₓ₂MnₓSi₇₀₋ₓAlₓ (2 ≤ x ≤ 4). Mechanical alloying was carried out in conventional laboratory ball mills, using SUS304 stainless steel vials (1700 ml, 128 mm diameter) and balls (9.6 mm diameter). A ball-to-powder weight ratio of 100:1 was used in all cases, with the mills rotation at 95 rpm. The powder charge was 36 g and the milling was performed with the addition of 2 mass% methyl alcohol. After MA processing, powders were first cold compacted under an argon atmosphere into discs of 13 mm diameter and 1 mm height, by applying a pressure of 300 MPa. A set of these samples were annealed in a furnace with a protective atmosphere of argon gas. The mechanically alloyed powders and the cold compacted and annealed samples were characterized by means of X-ray diffraction (XRD) and differential scanning calorimetry (DSC). To study the transformation rate of (α + ε) phase to β phase, Fe₅₀Si₃₀ samples heat treated at 1273 K for 0.6 ks were annealed at various temperatures between 873 and 1173 K for 3.6 ks. The thermoelectric properties of α-type Fe₅Si₃₀ were measured using the MA powders of nominal composition Feₓ₂MnₓSi₇₀₋ₓAlₓ (2 ≤ x ≤ 4) milled for 720 ks. MA powders were hot press sintered at 1353 K for 1.8 ks under a pressure of 36 MPa into a disk of 60 mm diameter followed by annealing at 1033 K for 360 ks to transform to β phase. Thermoelectromotive force Eₑ, effective mean resistivity were measured using specimens of 5 × 5 × 40 mm cut from a hot press sintered disk sample with ordinary d.c. method as a function of temperature difference ΔT (0 ≤ ΔT ≤ 800 K). The thermal conductivity was measured using laser flash method. The electron-microscopic observations were carried out in a Hitachi electron microscope operated at 200 kV.

V. Experimental Results

1. XRD analysis of mechanically Alloyed Powder

The XRD patterns for mixtures of the composition 10 ≤ Fe ≤ 50 at% milled for 720 ks are presented in Fig. 5. The diffraction peaks corresponding to only Fe and Si are seen for the mixtures of Fe ≤ 30 at% and those corresponding to ε phase and Fe are seen for the mixtures of Fe ≥ 40 at%. The SEM observation of as milled powders revealed that the size of MA powder is very fine at around 1 μm after 360 ks of milling and it does not change with further milling. The composition dependence of the powder particle size is small and the fraction of a little large particles of around 5 μm increases slightly with the increase in Fe content. Because of broadening of diffraction peaks, the formation of amorphous phase is not clear. The formation of amorphous phase by MA in the Fe-Si system near the composition Fe₃₀Si₅₀ was reported by Malhouroux-Gaffet and E. Gaffet and at the composition Fe₃₀Si₅₀ by Escorial et al. as will be mentioned later. The chemical composition of the powder milled for 720 ks measure by EPMA was Fe₀₃₄Si₆₆₅₁Cr₀₁₈₀Ni₀₉₆. The small increase in Fe content and the existence of Cr and Ni are due to the contamination from the vial and balls.

The XRD patterns for the mixture of the composition Fe₃₀Si₇₀ milled for various times are presented in Fig. 6. The diffraction peaks corresponding to only Fe and Si are seen for the mixtures milled for 720 ks or shorter and those corresponding to β phase are seen for the mixtures milled for 1800 ks.

2. DSC results of MA powder

Figure 7 shows the DSC traces of the 720 ks milled powders with nominal composition Feₓ₅Si₁₀₀₋ₓ (10 ≤ Fe ≤ 50). A large exothermic peak is seen in the specimen of Fe₂₀Si₵₀ and Fe₅₀Si₇₀. The size of exothermic peaks are smaller in other composition of specimens. From the XRD analysis the exothermic peak was found to correspond to the formation of β-FeSiₓ by the reaction of Fe and Si. The small exothermic peak in the powder of
that with milling time 720 ks consists of $\beta$ phase. No significant change in diffraction pattern by heating was observed in the 1800 ks milled Fe$_{50}$Si$_{70}$ powder. From the DSC and XRD analysis it is clear that $\beta$ phase formation takes place after 720 ks of milling. Thus, suitable MA time for the production of $\beta$ phase bulk material by sintering is considered to be 720 ks.

3. Phase transformation of MA powders by heat treatment

The phase transformation in the MA powder milled for 720 ks by heat treatment was examined using cold compacted specimens made of various composition of MA powders. Specimens were heated to various temperatures and kept for 600 s and air cooled. Figure 9 shows the XRD of the specimens of Fe$_{50}$Si$_{70}$ heated to 1173, 1223 and 1273 K. $\beta$, $\beta+\alpha$ and $\alpha+\varepsilon$ phases are seen in the specimens heated to 1173, 1223 and 1273 K, respectively. These results well corresponds to the phase diagram of Kubaschewski$^{100}$ (see Fig. 3).

The phases in the cold compacted specimens made of MA powders of the composition range Fe$_{\leq50}$ at% milled for 720 ks were examined after heat treated at temperatures 1173 – 1273 K. The observed phases were summarized on the phase diagram and shown in Fig. 10. The observed phases in each specimen is indicated at the location corresponding to the respective nominal composition and heat treated temperature. Although a little increase in Fe content in MA powders shifts the $\varepsilon$ phase formation range slightly to the Si-rich side, the observed phases basically agreed with those expected from the phase diagram over the composition range studied.

4. Hot-press sintered specimen

MA powders with composition Fe$_{x}$Si$_{100-x}$ ($x=20-33$) were hot press sintered at various temperatures and examined by XRD. In most of the cases the observed phases in
the sintered specimens were those expected from the reported phase diagram, but the ε phase with supersaturated Si was observed in some cases. Figure 11 shows the XRD patterns taken from the compacted specimens prepared from 720 ks milled powder with composition Fe₉₀Si₇₀. The pattern shown above is taken from the specimen after heating to 1223 K and air cooled. The pattern shown below is taken from the specimen hot press sintered at 1273 K. The pattern below is identified to be mostly ε phase with small fraction of α. According to the phase diagram (10), (α + ε) with a predominant α phase is expected at this temperature and composition as is observed in the XRD pattern shown above. These results indicate that when the specimen with the β phase is heated under compressive stress, β to the ε phase transformation takes place just above the peritectoid temperature. The composition of ε phase thus formed is close to that of β. The formation of larger fraction of ε phase can be explained as follows. The tetragonal α phase has 20% vacancies in the iron sublattice (106) and about 4% of volume expansion is expected to occur associated with the β to (α + ε) phase transition. While the β to ε phase transition with an identical composition with the β phase is associated with about 10% volume contraction. It is considered that applied compressive stress suppresses the β to α phase transition and instead induces β to ε transition.

5. β phase formation from (α + ε) phase

The transition rate from (α + ε) to β was examined using the cold compacted MA powders with composition Fe₉₀Si₇₃ milled for 720 ks. Compacted specimens were initially heated at 1273 K for 0.6 ks to produce (α + ε) structure and annealed at various temperatures between 873 and 1173 K for 3.6 ks in vacuum to transform to β phase. The XRD patterns from the annealed specimens were shown in Fig. 12. The fraction of β-FeSi₂ was estimated using the XRD peak intensities of (202) β-FeSi₂ (I₄) and (101) α-FeSi₂ (I₆). The values of I₄/(I₄ + I₆) were plotted as a function of annealing temperature and shown in Fig. 13. It is seen that the volume fraction of β phase has two maxima at around 1153 K and 1000 K. Nishida et al. (104) reported that in a powder made from an ingot of Fe₃Si, alloy, the formation rate of β phase shows a minimum at around 1128 K as observed in the present investigation. However, the powder prepared from an alloy ingot show a gradual decrease of β phase formation rate with the decrease in annealing temperature below 1128 K in contrast to the present result. This difference in the transformation rate of the β phase is considered to be caused by
the much finer grain size in the MA powder.

6. Internal structure of β-FeSi₂

The internal structure of β-FeSi₂ in the sintered specimen was investigated by transmission electron microscopy. Mechanically alloyed (for 720 ks) powders of Fe₃₀Si₇₀ were hot press sintered at two different temperatures. One is at 1273 K which is in the (α + ε) two phase range. The other is at 1173 K at which β phase is stable. The specimen hot press sintered at 1273 K was annealed at 1073 K for 36 ks to obtain a single β phase. In the specimen sintering at 1173 K, β phase is considered to be formed directly from the mixture of Fe and Si phase. TEM specimens were prepared by ion milling. Figure 14 shows the TEM micrographs of sintered samples (a) sintered at 1273 K and (b) sintered at 1173 K. The grain size is about 1 μm in the specimen sintered at 1273 K and 0.2 μm in the specimen sintered at 1173 K. A high density of planar defects was seen in both specimens although the formation process of the β phase was different.

Matthes et al. (25) and Sumida et al. (26) studied the internal structure of β-FeSi₂ by electron microscopy. Both of them found that most of the grains in the β phase have lamellae. It was suggested (26) that the lamellae are not thin precipitates but stacking faults on the plane parallel to the (100) plane with the [011] displacement vector. This microstructure is considered to be related with the phase transformation from α to β-FeSi₂ (26). Matthes et al. (25) considered the possibility of martensitic transformation from the similarity of lamella structure with those observed in Cu-Zn alloys. However, from the absence of surface relief and the observed slow growth rate, they concluded this transformation is diffusional.

The present results suggest that the planar defects may not be associated with the formation of the β phase from the α and ε phases since the planer defects were also observed in the β phase directly formed from the Fe and Si phases. To make this point clear, the intermediate stage of transformation should be studied in detail.

7. Thermoelectric properties of Fe-Si-Al-Mn alloys

Tokita et al. (27) showed that β-FeSi₂ doped with Mn and Al near the composition Fe₁ₓMnₓSi₇₀Al₁ exhibits larger effective maximum power than those doped with either Mn or Al. Referring to their results and considering the composition deviation by MA, the nominal Fe and Mn contents were taken as 28 at% and 2 at% respectively in the present study. The 720 ks milled MA powders of nominal composition Fe₃ₓMnₓSi₇₀₋ₓAl₁ in the range 2 ≤ x ≤ 4 were prepared. The addition of Mn and Al did not show any detectable change in the XRD pattern nor DSC traces. The milled powders were hot press sintered at 1353 K for 1.8 ks and thermoelectric properties were measured. The measured effective maximum power are plotted in Fig. 15 as a function of Al content. In the specimens prepared from ingot metallurgy (IM) the maximum of $P_{\text{eff}}$ was observed at around 2 at%Al. However, in the specimens prepared from MA, the maximum $P_{\text{eff}}$ was observed at around 3 at%Al. This difference in the optimum Al content for $P_{\text{eff}}$ is considered to be due to the reduction of Al content in solution by oxidation. Comparable value of $P_{\text{eff}}$ was obtained in the specimen prepared by MA.

The measured thermal conductivity of the specimens which showed the largest effective maximum power prepared by MA and IM is plotted as a function of temperature in Fig. 16. It is seen that the thermal conductivity of the specimen prepared by MA is about 30% lower than
that prepared by ingot metallurgy. The grain size of the MA specimen measured from the TEM observation was about 0.2 μm which is much smaller than the grain size of 15 μm reported in the case of the IM specimen by Kojima et al.\(^{(26)}\)

The calculated figure of merit and maximum conversion efficiencies were listed in Table 1 together with all the measured thermoelectric properties used for such calculation. It is seen that the figure of merit and maximum conversion efficiency is higher in MA specimen than IM specimen. This high figure of merit and conversion efficiency is attributed mainly to the low thermal conductivity of the specimen prepared by MA. This low thermal conductivity is attributed to the small grain size in the specimen prepared by MA. Thus, it can be concluded that grain refinement by MA is an effective method to improve the figure of merit or conversion efficiency of thermoelectric material.

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**Table 1** Thermoelectric properties of the specimens prepared from ingot metallurgy (IM) and MA process. \(\Delta T=720\,\text{K}\).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>IM (\text{Fe}<em>{58}\text{Mn}</em>{12}\text{Si}<em>{14}\text{Al}</em>{12})</th>
<th>MA (\text{Fe}<em>{70}\text{Mn}</em>{12}\text{Si}<em>{14}\text{Al}</em>{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seebeck potential (E_0) (mV)</td>
<td>(1.5 \times 10^5)</td>
<td>(1.9 \times 10^5)</td>
</tr>
<tr>
<td>Seebeck coefficient (\alpha) (mV/K)</td>
<td>0.21</td>
<td>0.27</td>
</tr>
<tr>
<td>Average specific resistance (\rho_s) (mV/K)</td>
<td>5.7</td>
<td>1.1 \times 10</td>
</tr>
<tr>
<td>Thermal conductivity (K) (W/m·K)</td>
<td>6.9</td>
<td>(= 5)</td>
</tr>
<tr>
<td>Figure of merit (Z) (1/K)</td>
<td>(1.1 \times 10^{-4})</td>
<td>(1.3 \times 10^{-4})</td>
</tr>
<tr>
<td>Effective maximum power (P) (W/cm(^2))</td>
<td>0.97</td>
<td>0.86</td>
</tr>
<tr>
<td>Maximum conversion efficiency (\eta) (%)</td>
<td>1.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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**VI. Discussion**

1. **Mechanical alloying in the Fe–Si system and phase change by annealing**

Ball milled samples of Fe–Si has been examined by several researchers\(^{(22)(23)(29)}\). Caer et al.\(^{(25)}\) studied the formation of various carbides and silicides by ball milling. Starting from elemental powders of the nominal composition \(\text{Fe}_{70}\text{Si}_{30}\) they found that the final milled powder is a mixture of \(\beta\)-FeSi\(_2\), \(\alpha\)-FeSi\(_2\) and \(\varepsilon\)-FeSi. In their paper the volume fractions of these phases are not specified. Escorial et al.\(^{(23)}\) studied the ball-milled samples of nominal composition \(\text{Fe}_{60}\text{Si}_{40}\) \((x = 5 \sim 50)\). From XRD analysis, they found \(\alpha\)-Fe and \(\varepsilon\)-FeSi and traces of \(\text{Fe}_2\text{Si}\), \(\text{Fe}_3\text{Si}_2\) and \(\alpha\)- and \(\beta\)-FeSi\(_2\) phases in the as milled sample of \(\text{Fe}_{50}\text{Si}_{50}\). From the measured Curie temperatures of 598 and 903 K in as milled \(\text{Fe}_{50}\text{Si}_{50}\), they concluded the formation of amorphous phase (22%) and solid solution of Si in \(\alpha\)-Fe as being \(\text{Fe}_{70}\text{Si}_{2}\) (5%).

Malhouroux-Gaffet and E. Gaffet\(^{(22)}\) studied ball milled powder of Fe–Si. From the experiment using the premixed powders with composition around \(\text{Fe}_{70}\text{Si}_{30}\), they observed that as-milled powder corresponds to an \(\alpha\)-Fe, Si, FeSi and \(\alpha\)-FeSi\(_2\) crystalline phase mixture added to an amorphous phase. It is interesting to note the formation of \(\alpha\)-FeSi\(_2\) was observed by ball milling instead of the formation of stable \(\beta\)-FeSi\(_2\) under the experimental condition they studied. The sequence of phase transitions from the mixture of Fe and Si powder induced by ball milling was suggested as follows; (1) amorphous Si, (2) amorphous Fe\(_{50}\text{Si}_{50}\), (3) \(\varepsilon\)-FeSi, (4) \(\alpha\)-FeSi\(_2\).

Regarding the solid-state reaction induced by annealing of multilayer systems, two rules were postulated; the Walter and Ben rule\(^{(30)}\) related to the prediction of the first crystalline phase formed, and the rule of Tsaur et
Concerning the second crystalline phase formed. The first crystalline phase nucleated will be the congruently melting phase next to the lowest-temperature eutectic. The second phase formed is the compound with the smallest $\Delta T$ that exists in the phase diagram between the composition of the first phase and the unreacted element. According to such rules, the first phase expected to form is $\varepsilon$-FeSi. This has been observed by Malhroux-Gaffet and Gaffet (22) and in the present study as well. However, there is a discrepancy in the observed second phase. It is interesting to note that the rules on the formation of the second phase were made after studies on thin films/diffusion couples and many systems found to follow the rule. However, the Fe-Si system seems to be an exception from the studies of Zhu et al. (23) and Wallart et al. (23) on the thin films. By the reaction (after deposition and annealing) of a thin film of Fe on the silicon substrate, they found that $\varepsilon$-FeSi forms first. This is followed by the formation of $\beta$-FeSi$_2$. This indicates that the Fe-Si system may not follow the rules of formation of the second phase strictly. A close look at the phase diagrams of all the systems listed by Tsaur et al. (24) shows that the second phase formed is stable at the lowest temperature indicated on the phase diagram. We presume that this holds good at room temperature as well. If we consider this aspect the Fe-Si system differs in that $\alpha$-FeSi$_2$ is not a stable phase at room temperature and it is $\beta$-FeSi$_2$ which is stable at room temperature. If the requirement that the second phase to be formed should be stable at room temperature, then one can expect $\beta$-FeSi$_2$ to form and not $\alpha$-FeSi$_2$.

When the rule for the formation of the second phase is violated in the studies of thin films of iron-silicon, it is not clear that how far these rules are applicable to mechanical alloying cases. This is because the two situations are different. In the case of deposition of films any heat evolved during reaction is absorbed by the substrate. In the case of mechanical milling the heat evolved during milling is retained within the powder particle. This can give raise to a local increase in temperature. This may be the reason for observing the high-temperature $\alpha$-FeSi$_2$ phase by Malhroux-Gaffet and Gaffet (22), who used high energy mills. Thus, the formed $\alpha$-FeSi$_2$ phase might not have transformed to the $\beta$-FeSi$_2$ phase as the reaction of $\alpha$ to $\beta$ and Si is sluggish and that the duration of milling may not be sufficient to bring about the transformation.

2. The effect of grain size on the thermoelectric properties

In the present study the improvement of thermoelectric properties of $\beta$-FeSi$_2$ was achieved by grain refinement through MA. The effect of grain refinement on thermoelectric properties will be discussed regarding the thermal conductivity and Seebeck potential.

Since the lattice thermal conductivity is the dominating factor in thermoelectric semiconducting material, the effective thermal conductivity can be reduced by reducing the lattice thermal conductivity. Lattice thermal conductivity is reduced mainly by the scattering of phonons. Phonons get scattered by lattice defects, charge carriers, etc. The scattering of phonons by grain boundaries is effective when heat is transmitted by phonons whose mean free path is comparable with the grain diameter. This is analogous to the kinetic theory of gases and thermal conductivity can be expressed as

$$K = nC_v
$$

where $\lambda$ is the mean free path of the phonons, $C_v$ is the specific heat at constant volume, $V$ is the velocity of the phonons and $n$ is the density of phonons.

The above expression shows that the lattice thermal conductivity $K_{\lambda}$ is directly proportional to the mean free path. When the grain diameters are comparable with the phonon mean free paths, they are scattered by the grain boundaries. Thus, the lattice thermal conductivity will be directly affected by the grain diameter ($d$) in such cases. Therefore, one can write

$$K_{\lambda} = \text{constant} \cdot d.$$  

Many theories have been proposed which takes into account the effect of grain size on thermal conductivity. The basic idea behind all these theories is to consider the ratio between the thermal conductivity of a polycrystalline material ($K$) and thermal conductivity of a single crystal ($K_c$) of the same material. The deviation of the ratio $K/K_c$ from unity describes the effectiveness of the boundary scattering.

Parrott has proposed a theory for thermal conductivity of sintered semiconductor alloys by taking grain size into consideration. He has included the grain size in the expression for the combined relaxation time ($\tau_c$) and uses this in estimating the thermal conductivity of the polycrystalline material $K$. By taking the ratio of $K/K_c$ into account, he has shown that the thermal resistance increases by 9% for a grain diameter of 40 $\mu$m and by 26% for a grain diameter of 4 $\mu$m.

Following Bhandari and Rowe have also proposed a theory by considering separately longitudinal and transverse phonon modes and their scattering by grain boundaries. They have considered the phonon relaxation time due to scattering by charge carriers also. This theory predicts that there will be 20-30% reduction in the thermal conductivity of the materials with grain size $< 1$ $\mu$m.

In the light of the above discussion it is interesting to summarize the effect of grain size on the lattice thermal conductivity from the available literature. The experimental values of lattice thermal conductivity of Savvides and Goldsmid on samples of silicon film agrees quiet well with the theoretical predictions of Bhandari and Rowe. Rowe and Shukla studied the temperature variation of lattice thermal conductivity with grain size in $\text{Si}_{63.5}$:Ge$_{36.5}$ alloy. Starting from a single crystal with $K_l = 4.31$ W m$^{-1}$ K$^{-1}$, they found that lattice thermal conductivity to decrease with grain size and with a grain size $< 5$ $\mu$m, $K_l = 3.1$ W m$^{-1}$ K$^{-1}$ at room temperature. This amounts to a total reduction of 28% compared to the single crys-
tal. With increase in temperature lattice thermal conductivity further decreased and at 1000 K a total reduction of 35% was observed.

After considering the positive effects of smaller grain size in reducing the lattice thermal conductivity and increasing $P_{\text{eff}}$ or $Z$, we shall consider below the effect of grain size on the electrical conductivity.

The expression for $P_{\text{eff}}$ or $Z$ indicate that it will be enhanced by reducing the electrical resistivity. This implies we have to increase the electrical conductivity to increase $P_{\text{eff}}$ or $Z$. However, by decreasing the grain size we are increasing the potential trapping sites for the charge carriers. The theories of Rai-Choudhury and Hower\(^{(39)}\) and by Kamins\(^{(39)}\) describes how charge carriers are trapped at the grain boundaries. The large number of defects at the grain boundary due to incomplete bonding trap the charge carriers and immobilize them. This not only reduces the number of charge carriers available for electron conduction but also gives rise to a potential barrier around the grain boundaries. This, further obstructs the motion of charge carriers between the adjacent grains. Based on this model, for the same amount of doping, the mobility and carrier concentration of a polycrystalline semiconducting material would be less than that of a single crystalline material. Thus, the reduction in grain size adversely affects the electrical conductivity and intern $P_{\text{eff}}$ or $Z$. This happens when the grain size is of the order of the mean free path of these charge carriers which is about 0.1 μm. Hence, this forms the limiting factor for grain size in thermoelectric materials.

The effect of grain size and the grain boundaries on Seebeck potential is important when we are trying to optimize $P_{\text{eff}}$ and $Z$ with grain size. Jerhot and co-workers\(^{(40)-(42)}\) have studied extensively on the Seebeck effect in polycrystalline semiconductors. Polycrystalline semiconductor is considered to be composed of grains separated from one another by intergrain domains (grain boundaries). Charge transport between the domains is assumed to take place by three mechanisms, namely, tunneling, thermionic emission and Ohmic transport. Jerhot and Vlcek\(^{(40)}\) have discussed in detail the effect of grain size and grain boundaries on Seebeck potential when one of the three mechanisms prevails. In the grain diameter ($d$) range observed in $\beta$-FeSi$_2$ in the present study (0.1 μm) the width of the grain boundary ($w_b$) is quite small. Then the main conclusions that can be drawn from their results is that the Seebeck potential of a polycrystalline semiconductor is given by the grain properties and that due to grain boundary is negligible unless the grain size is in the order of nano scale.

VII. Summary

In the present study, MA has been applied to the Fe–Si system to produce $\beta$-FeSi$_2$ intermetallic compound, a potential thermoelectric material, starting from elemental powders. Mechanically alloyed powders were examined using XRD and DSC in the as milled condition and also after annealing. Using hot-press sintered specimens, the thermoelectric properties of Mn and Al doped $\beta$-FeSi$_2$ specimens were measured. The grain size and internal structure of $\beta$-FeSi$_2$ of sintered samples were examined by TEM. The main results are summarized as follows:

1. The $\beta$-FeSi$_2$ phase can be synthesized in the as milled condition from an elemental powder mixture of nominal composition Fe$_{30}$Si$_{70}$ after long milling times. The appropriate milling time for sintering was considered to be about 720 ks. At this stage the powder consists of very fine Fe and Si crystals in the as milled condition. This transforms into a homogeneous $\beta$ phase by an exothermic reaction at around 720 K. These results indicate that long time homogenizing treatment applied to the specimens prepared by conventional ingot metallurgy can be eliminated by using the MA process for the formation of $\beta$-FeSi$_2$.

2. XRD analysis revealed that heat treated MA samples show the phases corresponding to the Fe–Si phase diagram. The transformation rate of MA powder from the $\alpha+\epsilon$ to the $\beta$ phase showed maxima at two temperatures as observed in the conventional powder prepared from an alloyed ingot. However, the decrease of transformation rate starts at much lower temperature in MA powder than that in the conventional powder. This is considered to be due to grain refinement.

3. The high density of planar defects were observed in the $\beta$-FeSi$_2$ phase transformed either from the $\alpha+\epsilon$ phase or a Fe and Si mixture.

4. The p-type $\beta$-FeSi$_2$ thermoelectric material doped with Mn and Al prepared by MA process and hot press sintering showed higher figure of merit and higher conversion efficiency than that prepared by conventional ingot metallurgy. The improvement is mostly due to the lower thermal conductivity associated with the fine grain size produced by MA.

The advantages of using MA technique for the synthesis of $\beta$-FeSi$_2$ thermoelectric material has been discussed. The improved properties of the thermoelectric materials are attributed to the refinement in grain size. This is the inherent advantage of using mechanical alloying for processing. It is suggested that not only this advantage of MA but other advantages of MA also should be put to practical use. In this respect MA is advantageous for adding suitable alloying additions which cannot be done by other processes. The enhanced thermoelectric properties of selectively oxidised Fe or Si requires more studies to improve the ways to control oxidation and at the same time employing MA for synthesising the alloys such that the advantages of MA are not lost.

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