Eutectoid transformations in Fe-Si Alloys for thermoelectric applications

Wade A. Jensen a,*, Naiming Liu a, Eva Rosker a,1, Brian F. Donovan b,2, Brian Foley b, Patrick E. Hopkins a, b, c, Jerrold A. Floro a

a Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA, 22904, USA
b Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA, 22904, USA
c Department of Physics, University of Virginia, Charlottesville, VA, 22904, USA

ABSTRACT

Semiconducting β-FeSi2 is a candidate thermoelectric material whose constituents are abundant and eco-friendly, but significant improvements in the relevant properties are needed. This work investigates eutectoid decomposition, z-FeSi2 → β-FeSi2 + Si, as a means to modify microstructure and control thermal transport. Process conditions are adjusted to strongly affect both the microstructural length-scales and morphology, and hence the thermal conductivity. Low temperature annealing of a hypoeutectic sample produces cooperatively-grown Si lamellae, which then decompose into Si nanowires by Rayleigh instability upon further aging. We show that nucleation of eutectoid colonies occurs preferentially on cracks, while at smaller undercooling, nucleation also occurs on eutectic Si particles. The growth velocity, \( v \), and interlamellar spacing, \( \lambda \), of the pearlitic colonies obey a relation of the type \( v^2 = f(\lambda) \). This sets the bounds of the activation energy for the diffusion mechanism, although the exact mechanism cannot be specified. Nanostructuring of eutectoid Si increases heterointerface density by 40x, with a concomitant reduction in thermal conductivity of 2x. The thermal boundary conductance is determined for the β-FeSi2/Si heterointerface, which shows that this interface only weakly scatters phonons.

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1. Introduction

The majority of energy produced for electrical power is rejected into the environment as waste heat [1]. With the current push for increased efficiency in energy production and consumption, harvesting waste heat could recover significant amounts of energy from current infrastructure. Thermoelectric materials provide a means for converting waste heat into electricity; however, current materials are too expensive and inefficient for usage at scale. β-FeSi2 is one of only a few semiconducting transition metal silicides and is a promising candidate thermoelectric material. The compound has a naturally high Seebeck coefficient, a low thermal conductivity, and is thermally stable between 500 and 900 K [2]. It is more attractive since the chemical components are inexpensive and abundant. However, its low electrical conductivity limits the thermoelectric figure of merit, \( zT = \frac{S^2 T}{\kappa} \), with the best reported value being \( zT = 0.4 \) for Co-doped FeSi2 [3].

One approach to enhancing the thermoelectric performance for the Fe-Si system is to exploit the eutectoid [4–9], \( z-\text{FeSi}_2 \rightarrow \beta-\text{FeSi}_2 + \text{Si} \), shown in Fig. 1 [10]. The \( z \)-phase contains a large Fe vacancy concentration [11] having the more Si-rich composition relative to \( \beta \), which is a stoichiometric (Cmca) structure whose unit cell contains 16 formula units. Eutectoid decomposition results in a pearlitic microstructure consisting of diamond cubic Si lamellae in a β-FeSi2 matrix. Manipulation of the pearlitic microstructure provides a route for hierarchical structural control determined by composition, processing methodology, and aging parameters. By controlling the eutectoid decomposition kinetics, we can vary length scales and morphology of the Si phase. This allows for the modification of phonon scattering by tailoring the β-FeSi2/Si heterointerface density and the β-FeSi2/Si grain size distribution. Furthermore, the Si itself can be independently doped, and may
provide higher overall carrier mobility, depending on the phase morphology and connectivity. β-FeSi₂ itself is a well-studied material, and its thermoelectric properties are well documented [2,3,6,12].

This work reports an investigation of the microstructure in the Si-rich, Fe-Si system, in the context of well-known mechanisms for development of pearlitic microstructures. The kinetics of eutectoid decomposition in this system has been previously examined, resulting in several time-temperature-transformation (TTT) diagrams [13–15]. The goal of the present work is to investigate how the pearlitic structural length scales depend on processing conditions, relevant to thermoelectric properties control. In a hypoeutectic (Fe₂₇Si₇₃) sample, we examine the effect of isothermal annealing conditions on nucleation and growth of pearlitic colonies, the interlamellar spacing, and the subsequent evolution of morphology as the transformation proceeds. A Fe₂₈.₄Si₇₁.₆ sample, on the eutectic composition, is also examined. This sample contained a low level of adventitious Cu impurities, which greatly enhanced the overall transformation rate [16]. We report the room-temperature thermal conductivity in two samples with extremal two-phase microstructures at this composition. This is not intended to be a complete, temperature-dependent examination of transport properties relevant to thermoelectrics, but provides some insight into the potential efficacy of eutectoid structuring on thermal transport.

2. Materials and methods

Bulk samples were prepared by arc-melting high purity Fe (99.99%) and Si (99.999+%) in an argon atmosphere, after evacuating the arc-melter to a pressure of 6.0 × 10⁻⁹ Torr. The arc was initially struck on a Ti getter in order to minimize residual oxygen background. Buttons of approximately 50 g were produced, with grain sizes of order millimeters. These buttons were melted successively from both sides with extensive stirring. Compositional analysis was performed by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). For both samples ~40 mg of material were digested in a 3:2 solution of HNO₃ and HF; each solution was analyzed three times in order to determine error. The solutions were compared against Fe, Si, Cu, Ti, and W standards, where Cu, Ti, and W are possible contaminants from arc-melting. The hypoeutectic melt was near the eutectic composition, with a final composition of 73.0 ± 1.0 at% Si (Fe₂₇Si₇₃) and negligible metallic contamination. The on-eutectoid melt and was determined to be 71.6 ± 1.0 at% Si (Fe₂₈.₄Si₇₁.₆), near the published eutectoid composition, but it was found to contain small amounts of Cu (0.07 at%) and W (0.02 at%) contaminants.

Samples were subjected to isothermal aging to foster eutectoid decomposition. Pieces were cut from the button and encapsulated in fused quartz ampoules that were evacuated to 5 mTorr, then backfilled with Ar. This was cycled three times, with the second to last including a slight heating of the quartz tube, in order to remove any residual water vapor. The final Ar backfill was to a pressure of ~180 Torr. The ampoules were aged in a tube furnace and then quenched to room temperature in water. Prior to structural characterization, the samples were polished to mirror finish with 0.05 μm diamond spray. Roughly 1 mm of material was removed for each polish, to ensure that only transformations occurring in the bulk of the material were observed. After polishing the microstructure was characterized using scanning electron microscopy (SEM) and x-ray diffraction (XRD). SEM was performed in a FEI Quanta 650, operated at 10 kV, primarily in backscatter detection mode (BSE) for its enhanced compositional contrast. Select samples were further examined using electron backscatter diffraction (EBSD) to obtain grain size and crystallographic orientation. To remove surface deformation prior to EBSD scans, these samples were mounted into epoxy mixed with conducting Ni powder, and were polished and finished with a vibratory polish with 5 μm colloidal silica. Powder XRD samples were prepared via mortar and pestle, and small particles were removed via a 45 μm wire sieve. XRD data was obtained from the PANalytical X’Pert Pro MPD for phase identification.

Thermal transport was measured via time domain thermoreflectance (TDTR) [17–19] at room temperature. TDTR is an optical pump-probe measurement technique that utilizes a train of ultrafast laser pulses to induce a modulated heating event and measure the temporal temperature dependent change in reflectance of the sample surface between pulses. Sub-picosecond pulses emanate from a Ti:Sapphire oscillator at 80 MHz; the thermal decay is monitored for 6 ns after the pump pulse arrival on the sample surface. A thin Al film (89 ± 5 nm) was e-beam evaporated onto the sample surface to act as a thermal transducer. Thermal conductivity is determined by fitting a cylindrically symmetric, multilayer thermal model thermal model to the TDTR decay curve, assuming a reduced thermal conductivity of the Al film given by four-point-probe measurements and literature values of the heat capacity of Al [20]. The heat capacity of the two-phase material was determined by a weighted sum of β-FeSi₂ [21] and Si [20], according to their volume fractions. The small spot size and shallow penetration depth of the incident beam make it an ideal technique for thermal conductivity measurements while avoiding native fractures in the sample.

3. Results and discussion

As-cast, the hypo-eutectic sample contains coarse bands of proeutectic α interleaved with eutectic α+Si, as shown in the inset of Fig. 1. The sample exhibits cracking due to stresses associated with thermal gradients during cooldown. Samples of this specimen were
aged at four different temperatures (Table 1), with aging times adjusted so that the nascent stages of transformation could be characterized. Two preferred nucleation sites for the pearlitic colonies were observed. At 587 and 680 °C, β-colonies only nucleate at cracks, while at 800 and 910 °C, nucleation occurs on both cracks and on eutectic Si particles. Extensive areal surveys in the SEM confirm the nucleation mechanism for each case; Fig. 2 shows examples.

In many eutectoid reactions, colony nucleation is found to occur at grain boundaries, e.g., in austenite for the Fe-C archetypal system. In the current specimens, however, the grain size (~1 mm) is much larger than either the mean crack spacing (~17 μm), or the spacing between eutectic Si particles (~5 μm). Hence it is not surprising that internal free surfaces due to cracks act as alternative potent nucleation sites. The transition at higher temperatures to nucleation on eutectic Si, which has a much larger interfacial area per volume than the cracks, is explained as shown in Fig. 3. At temperatures closer to the eutectoid isotherm, aging occurs in the regime where, according to simple linear extensions of the solidi (Fig. 3a), diamond cubic Si has the larger driving force to form. High temperatures allow Si atoms in the metastable α-phase to rapidly diffuse to nearby eutectic Si particles and attach epitaxially. The local Si composition of the adjoining α-phase is reduced, as indicated in Fig. 3b). While the overall energy gain in transforming to the equilibrium β-Si is given by the distance XX (for any particular composition), the driving force to nucleate the first β particles is actually given by the distance YY. As the composition of α becomes more Fe-rich, the driving force rapidly increases, causing homogeneous nucleation of β-phase. Cooperative growth of Si lamellae in the β-phase then ensues in a fashion similar to that discussed for Fe-C pearlites [22].

The pearlitic colonies are composed of Si lamellae in the β-phase, as shown in the images of the growth fronts in Fig. 4. Confirmation of the morphology for Si was obtained by examining cross-sections cut with an ion mill. Isothermal aging at lower temperatures produces lamellae that are extended in length vis-à-vis their thickness, and locally parallel. With increasing aging temperature, the lamellae become more compact and assume a wider range of local orientations. Both the lamellar thickness and the interlamellar spacing (λ) increase with increasing aging temperature; the latter was measured for each temperature at the boundaries of growing colonies (e.g., Fig. 4), using the method of linear intercepts. This was specifically done for regions at the boundaries where the interlamellar spacing was smallest, to crudely account for the orientation of the lamellae relative to the 2D section. Growth rate (ν) was measured for each sample by measuring the diameter of the five largest β colonies in each sample (e.g., see the blue arrows in Fig. 2a) and dividing by the total aging time. This will clearly underestimate the true interfacial velocity, since we do not account for any incubation time and we ignore growth in the third dimension. Results of these measurements are summarized in Table 2.

Eutectoid decomposition can be controlled by different kinetic processes including volume diffusion in either the parent or product phases [23–26], or it can be controlled by diffusion in the advancing interphase interface [27,28]. Many treatments of eutectoid decomposition arrive at a relation between the interfacial velocity and interlamellar spacing of the form \( \nu \lambda^2 = QD \). It is usually necessary in deriving this to assume an “optimization
condition” such as a relation to the minimum thermodynamic spacing or to maximum entropy production. Shapiro and Kirkaldy [29] (S-K) argued for a relation of the form [s-k]:

\[ v^3 = A(T)D(T)(K - 1) \]  

(1)

The coefficient \( A \) will in general contain terms related to the driving force (or undercooling), the relevant solidi in the binary phase diagram, local concentrations, phase volume fractions and interfacial energies. \( D \) is the effective diffusivity and \( K \) is a constant >1 related to choice of optimization condition. S-K gave specific form to Eqn. (1) for kinetics controlled by diffusion in the growth interface, and assuming a simple symmetric eutectoid. S-K suggested that the temperature dependence of the diffusion kinetics could be obtained from Arrhenius plot of \( \ln(v^3) \) vs. \( 1/T \), but that the resulting value would overestimate the real activation energy if the temperature dependence of \( A \) is ignored. As such, Fig. 5 shows Arrhenius plots for \( v^3 \) and \( v^2 \) which should effectively bound the activation energy of the dominant kinetic mechanism. The result gives an activation energy bounded by 2.03 eV and 2.73 eV.

These values do not definitively identify the dominant kinetic mechanism, but are reasonable in magnitude. The observation discussed above that Si diffuses through the \( \alpha \)-phase to grow on the eutectic Si indicates that volume diffusion can occur at these temperatures. Diffusivities of Si in the \( \alpha \) and \( \beta \) phases are not known. d’Heurle and Gas noted in a review that Si diffusion in metal silicides has relatively low activation energy compared to metal self-diffusion of similar homologous temperature. This may result either from grain boundary diffusion or due to intrinsically large vacancy concentrations associated with structure or stoichiometry [30]. For example, silicon diffusion in MoSi\(_2\) (\( T_m = 2600 \) K) has an activation energy of only 2.2 eV, whereas the activation energy for self-diffusion of Mo in Mo (\( T_m = 2900 \) K) is 4.4 eV. The \( \alpha \)-FeSi\(_2\) phase has a very high level of intrinsic vacancies (~14%) attributed to the Fe sublattice, associated with the off-stoichiometry composition (see Fig. 4) [11,31]. However, we cannot rule out boundary diffusion. Taking the activation energy of grain boundary self-diffusion in Si as a proxy, this has been reported as 2.4 eV [32], also within the bounded range from Fig. 5. In Fig. 5, potential systematic errors in the measurement of \( v \) and \( \lambda \) will affect the activation energies as follows. The most likely systematic error in measuring \( \lambda \) would be to overestimate the spacing, but this is not likely to be an error much larger than the random error noted in Table 2, hence we do not consider this further. The most likely systematic error in measuring \( v \) is to underestimate the velocity, as described above. This is not likely to be significant at large undercooling, but could be significant in the sample aged at 910 °C, where the uncertainty in the start time is largest. For example, if we

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**Table 2**

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( \lambda ) (nm)</th>
<th>( v ) (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>567</td>
<td>54 ± 4</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>680</td>
<td>107 ± 22</td>
<td>433 ± 22</td>
</tr>
<tr>
<td>800</td>
<td>157 ± 12</td>
<td>2217 ± 130</td>
</tr>
<tr>
<td>910</td>
<td>1246 ± 80</td>
<td>115 ± 61</td>
</tr>
</tbody>
</table>

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**Fig. 4.** \( \beta \)-FeSi\(_2\) + Si colony reaction front for Fe\(_{27}\)Si\(_{73}\) samples aged at a) 567 °C, b) 680 °C, c) 800 °C, and d) 910 °C.

**Fig. 5.** Arhenius plot of \( \ln(v^3) \) vs \( 1/T \), where \( n = 2 \) or 3 for interface or volume limited growth kinetics.
arbitrarily increase \( v \) by an order of magnitude at 910 °C, the resulting bounds on activation energy change to 2.51–3.2 eV. These bounds on activation energies are larger than what seems likely given the mechanisms described above, hence we believe our error in the velocity is not nearly as large as an order of magnitude.

Examining the data in Table 2, it is apparent that the sample aged at 910 °C behaves quantitatively rather differently from samples aged at lower temperatures. The velocity increases with aging temperature until 910 °C, where there is a marked decrease. At the same time, the interlamellar spacing increases by an order of magnitude compared with aging at 800 °C. The lamellae at this temperature tend to be very coarse and rather short. Furthermore, inspection of colonies at this temperature, unlike those formed at lower temperatures, shows significant heterogeneity. As shown in Fig. 6, near the center of the colony, where nucleation is presumed to have occurred, the microstructure is much finer and more equiaxed. This is not due to breakup of lamellae due to an instability, as is discussed next, which leads to coarser structures.

This fine-scale, spheroidal microstructure is attributed to transient degenerate pearlite, arising from initially uncoupled, competitive growth of microconstituents in the early stage of colony development [33–35]. Si spheroids nucleate with small spacings and are occluded by faster \( \beta \) phase growth. Screening the particles from the \( \alpha \) phase initially limits the transformation lengthscales [36], and requires Si to repeatedly nucleate at the reaction front. This may explain the apparent decrease in colony growth rate observed at 910 °C, as the growth rate is only a maximum when cooperative growth is achieved. The degenerate microstructure depends on the ratio of the growth rate of \( \beta \) and Si, \( V^\beta \) and \( V^Si \) respectively. When \( V^\beta /V^Si \) is much greater than unity, the decomposition produces fine spheroids whose spacing can be an order of magnitude smaller than that arising from lamellar growth [36]. Uncoupled growth is a transient mode, and as the interlamellar spacing increases and \( V^\beta \) decreases, the microstructure evolves from spheroid to truncated lamellae to lamellae (cooperative growth). The change from fine lamellae at high undercooling to ribbons at low undercooling suggests either \( V^\beta \) is inherently greater at high temperatures or the colonies had yet to reach steady state.

Diffusion of Si in the \( \beta/Si \) interface also clearly occurs. Fig. 7 shows micrographs obtained both at the growth interface and far behind the interface. The lamellae break up into wirelike structures behind the propagating interface, and eventually spheroidize. We emphasize that this must occur after the growth front has passed and is not the result of a divorced eutectoid. The fragmented lamellae are thicker than those at the growth front, and measurements of the eutectoid Si microconstituent show a decrease in the area fraction. In an extension of Lord Rayleigh’s instability theory for wires [37], Werner showed that surface area can decrease when finite and semi-infinite lamellae disintegrate into narrow ribbons [38]. SEM inspection shows that this process occurs across the range of investigated temperatures on the same timescale as the eutectoid decomposition itself. At shorter timescales, there does not appear to be Ostwald ripening, i.e., there is not a decrease in the number density of features via competitive coarsening. This implies that Si diffusion along the \( \beta/Si \) interface is faster than diffusion through the \( \beta \)-matrix, which would foster ripening.

A second arc-melted boule had an on-eutectoid composition (Fe\(_{28.4}\)Si\(_{71.6}\)), with no evidence of any as-cast eutectic microconstituents. However, the sample was found to contain 0.07 at% Cu impurities. Cu has a profound effect on accelerating the eutectoid decomposition process [13]. We also found a similar but more potent effect, producing full transformations for times and temperatures reported for 0.2 at% Cu by Yamauchi et al. [7], but here with only 0.07 at% Cu. There is also a small amount of W in this sample, but the effect of W on decomposition has not been explored in the literature. One sample was aged at 567 °C for 56 h, which resulted in complete eutectoid transformation, whereas the hypoeutectoid sample was only 3% transformed under the same conditions. Annealing at 910 °C for 104 h deeply overaged the sample, resulting in heavily spheroidized and coarsened Si. Fig. 8 compares the two samples; the low-temperature aging produced Si nanowires with mean diameter of 29 ± 5 nm and mean spacing 106 ± 20 nm. The mean \( \beta \)-grain size was 16 µm while the sample overaged at high temperatures had grain size of 30 µm. In both samples, the grain size distributions show a large positive skew, almost tending to bimodality. The grain size distributions were obtained using EBSD and the method of linear intercepts.

Given the large differences in the lengthscales and morphology of the microstructures, these two samples were subjected to time domain thermoreflectance measurements of the thermal conductivity. The Fe\(_{28.4}\)Si\(_{71.6}\) sample aged at 910 °C for 5 days had a thermal conductivity of 23 ± 5 W/m/K. For the sample aged at 567 °C for

![Fig. 6. SEM micrograph of the transient degenerate pearlite (fine spheroids) prior to achieving steady state lamellae propagation, in the Fe\(_{27}\)Si\(_{73}\) sample aged at 910 °C.](image69x75 to 267x214)

![Fig. 7. Fe\(_{27}\)Si\(_{73}\) sample aged at 800 °C for 1 h taken a) at the reaction front and b) in the coarsened region far from the reaction front.](image338x467 to 536x727)
The thermal conductivity of the 910 °C sample provides two equations with two variables, the thermal conductivity and the thermal boundary conductance, and the thermal conductivities of the two samples were determined by the linear intercepts method and was found to be $\rho_{\text{int}} = 0.3$ and 11.0 interfaces/µm for the 910 °C and 567 °C samples, respectively. The low temperature exhibits a roughly 40-fold increase in β/Si interfaces per unit distance, and a twofold decrease of the thermal conductivity, vis-à-vis the high temperature aging. The only unknowns are the thermal conductivity of the β phase and the thermal boundary conductance of the interface. Using data from both 910 °C and 567 °C samples provides two equations with two variables to be solved simultaneously. The result gives $\kappa_T = 20 \pm 4$ W/m-K and $h_0 = 268 \pm 64$ MW/m²-K. The thermal conductivity of β is larger than other reported values [9,39]. These investigations used powder processing and created significantly smaller β grain sizes that may reduce the overall thermal conductivity. The thermal boundary conductance is near the upper end of the phonon-dominated thermal conductance regime [40], implying that the β/Si interface is an inefficient scatterer of phonons. This is unsurprising given the relatively small difference in mean molecular weight and bonding between the two phases.

The detailed mechanism of Cu in enhancing the eutectoid transformation is not well understood. However, in comparing the β grain size of the samples with and without Cu, the grain size in the latter is much larger, even in early stages of transformation, since the nucleation density is low. This suggests that Cu has a potent effect on enhancing the nucleation rate of the pearlitic colonies. Furthermore, since Cu does not appear to affect lamellae spacing and size, we rule out a major effect of Cu on growth rates and/or coarsening.

4. Conclusions

We examined the mechanisms for the $\alpha$-FeSi$_2 \rightarrow \beta$-FeSi$_2 +$ Si eutectoid transformation. Nucleation of pearlitic colonies occurs only on cracks at low temperatures, while at high temperatures nucleation also occurs on eutectic Si, associated with facile diffusion of Si that creates a large driving force for β nucleation. The temperature-dependence of the interlamellar spacing and colony growth rate were obtained, setting bounds on the activation energy for Si diffusion. Since these bounds are consistent with either (anticipated) volume diffusion of Si in $\alpha$, or boundary diffusion, we cannot be more specific on mechanism without further information. At temperatures well below the eutectoid isotherm, the transformation proceeds cooperatively producing parallel wavy lamellae of Si in the β -matrix. At small undercooling there is indication that growth is close to becoming decoupled. Facile diffusion of Si at the β/Si interface leads to coarsening of Si lamellar into rods and spheroids behind the growing decomposition front. A 2x reduction in thermal conductivity is associated with a 40x reduction in eutectoid length scales; and we showed that the β/Si interface is a relatively inefficient scatterer, therefore requiring a high interface density in order to significantly reduce the thermal conductivity.
conductivity of the nanocomposite. The transformation kinetics observed here are consistent with the literature, including the powerful effects of trace Cu impurities in accelerating the decomposition kinetics.

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