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Synthesis and thermal transport of eco-friendly Fe-Si-Ge alloys with eutectic/eutectoid microstructure

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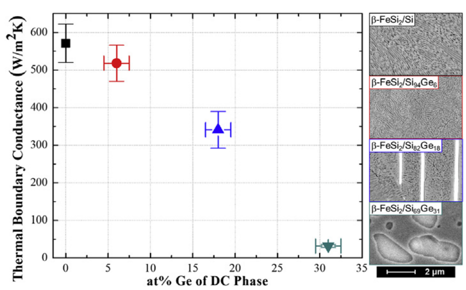
HIGHLIGHTS

- Eutectic/Eutectoid processing strategy to produce novel hierarchical microstructure.
- Thermal conductivity of β-$FeSi_2$+Si nanocomposite can be reduced with a few at% Ge.
- Local Ge incorporation into $Si_{1-x}Ge_x$ nanoinclusions can be controlled via processing.
- Ge incorporation can reduce the β/$Si_{1-x}Ge_x$ thermal boundary conductance by 91%.
- Local composition can supersede lengthscales, and may enhance thermal stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The β-$FeSi_2$/Si semiconducting nanocomposite is a promising thermoelectric system with eco-friendly materials. We show that small quantities of Ge can enhance the thermoelectric properties and widen the design space, if Ge content and spatial disposition can be controlled. We investigated the use of solidification combined with solid-state transformations to reduce the thermal conductivity via hierarchical modification of microstructure. Solidification of $Fe_{28}Si_{68}Ge_4$ alloys leads to eutectic lamellar microstructure comprised of hyperstoichiometric α-$FeSi_{2+\delta}$ phase and diamond cubic $Si_{1-x}Ge_x$. The eutectic lengthscales can be varied over two orders of magnitude depending on solidification rate. Subsequent aging of the eutectic produces eutectoid decomposition, α-$FeSi_2$ → β-$FeSi_2$ + $Si_{1-y}Ge_y$, where the additional diamond cubic product is interleaved with the eutectic lamellae. By controlling both the frequency of β-$FeSi_2$/diamond cubic heterointerfaces, as well as the degree of Ge segregation into the eutectoid microconstituent, the thermal conductivity of the composite was varied from 22.8 W m^{-1} K^{-1} down to 8.3 W m^{-1} K^{-1}. We analyze the thermal conductivity in terms of a series thermal resistance model, including thermal boundary conductances at the heterointerfaces, and show that the thermal boundary conductance is reduced by at least an order of magnitude when the diamond cubic microconstituent is enriched from 0 to 30 at% Ge. Avenues for additional microstructural improvements towards thermoelectric applications are discussed.

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1. Introduction

Current means of energy production are highly inefficient and the majority of the energy produced is released into the environment as waste heat [1]. Recapturing even a trivial percentage of this waste heat would equate to a significant amount of energy annually. Thermoelectrics are solid state materials capable of converting a thermal gradient into an electrical current. A material's thermoelectric efficiency is quantified by a dimensionless figure of merit, $zT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, $S^2\sigma$ is the power factor, κ is the thermal conductivity, and T is the temperature. Optimizing these parameters is nontrivial, as they are intricately interconnected. While modern thermoelectric materials have advanced zT in recent decades by exploiting complex crystal structures, nanoinclusions, and small grain sizes [2], current materials remain costly and inefficient, and thermoelectrics are still largely used only in niche applications.

This paper will investigate a potential approach to improve the thermoelectric properties of the β-$FeSi_2$ system. This is motivated by the inexpensive, abundant, and non-toxic constituents providing the potential for an economical, and eco-friendly, thermoelectric materials system for harvesting waste heat. β-$FeSi_2$ is one of the few semiconducting transition metal silicides ($E_{gap} = 0.78$ eV) [3], with a complex Cmca crystal structure that contributes to a naturally high Seebeck coefficient and low thermal conductivity [4]. It is oxidation resistant to 900 K and has a high operational temperature that makes it ideal for hot environments. However, the thermoelectric performance is limited by the poor electrical conductivity [5]. Together these properties contribute to only a modest zT, with the highest reported value being $zT = 0.4$ at 700 K for Co-doped β-$FeSi_2$ [6]. In the binary Fe-Si system, the metallic α-$FeSi_{2+\delta}$ ($\delta \approx 0.3$) phase is stable at high temperatures, but decomposes through a eutectoid isotherm at 937 °C to stoichiometric β-$FeSi_2$ and diamond cubic (DC) Si [7].

Zhao et al. [8] suggested that hierarchical control and optimization across multiple lengthscales could significantly improve zT. Here we will show that the Fe-Si-Ge ternary system provides opportunities for creating hierarchical structures by exploiting a strategy combining both liquid and solid state processing. Eutectic solidification leads to lamellar microstructure, L → α-$FeSi_{2+\delta}$ + $Si_{1-x}Ge_x$. Subsequent eutectoid decomposition, α-$FeSi_{2+\delta}$ → β-$FeSi_2$ + $Si_{1-y}Ge_y$, results in a second level of structural inhomogeneity, interleaved within the eutectic lamellae. Length scales of the eutectic microconstituents are controlled by the solidification rate, while length scales of the eutectoid are dictated by the aging temperature and time. Inherently, there is a third structural length scale, which is the grain size, or more accurately, the pearlitic colony size. Just as importantly, the segregation of the overall Ge into the different microconstituents plays a major role in determining thermal conductivity, and likely the electrical conductivity of the system as well.

Eutectoid decomposition of the *binary* Fe-Si system (α-$FeSi_{2+\delta}$ → β-$FeSi_2$ + Si) has already been explored as a way to enhance thermoelectric performance. Kinetics of the eutectoid decomposition have been established via time-temperature-transformation (TTT) diagrams for undoped and lightly doped systems [9] [10] [11], and it has been shown that increased volume fraction of Si [12] and finer eutectoid lengthscales [13] [14] [15] appreciably improve thermoelectric performance. Our previous work [15] showed that nanostructuring of the eutectoid DC microconstituent was achieved by annealing at large undercooling, thereby increasing the β/Si interface density. This effectively reduces thermal conductivity of the nanocomposite, although the effects of two-phase decomposition on the power factor are still unknown. A new strategy that could significantly improve the performance of these materials is to create ternary Fe-Si-Ge alloys. Alloying Fe-Si with Ge provides an additional degree of freedom to enhance thermoelectric properties. Ge alloying can reduce thermal conductivity via both alloy scattering of phonons [16] and, as will be shown in this work, through modification of the thermal boundary conductance of the hetero-interfaces [17] [18] [19] [20] [21]. Ge additions to the DC phase will also reduce the bandgap [22], thereby reducing band offsets with the β phase. Mohebali et al. showed that spark plasma sintering P-doped SiGe with Co-doped β-$FeSi_2$ yields a sharp increase in power factor and κ. When compared to the control sample, the Ge additions increased zT by nearly 2× with a final value of 0.54 [23]. However, in their work, the nature of the resulting microstructure and its connection to the thermoelectric properties was not reported.

This paper discusses the hierarchical microstructures produced through process control of eutectic and eutectoid transformations and their effect on thermal conductivity. Different from the sintering approach of Mohebali et al. [23], we explore the effects of casting ternary Fe-Si-Ge alloys. In particular, we examine the microconstituent lengthscales and compositions resulting from arc melting, which produces relatively low solidification rates, and melt-spinning, which produces much higher solidification rates. We will show that the disposition of the Ge in the eutectic and eutectoid microconstituents is strongly affected by the casting conditions. Thermal conductivity was measured for the various samples and the interface thermal boundary conductance was determined as a function of Ge content in the eutectoid microconstituent, $Si_{1-z}Ge_z$. We show that carefully controlling solidification rate and eutectoid decomposition of the ternary alloy leads to microstructural and compositional control over the thermal conductivity. In particular, we show that the Ge content in the diamond cubic phase can greatly reduce the β/DC thermal boundary conductance.

2. Materials and methods

Bulk samples were prepared via arc-melting from a charge composed of Fe (99.99%), Si (99.999+%), and Ge (99.999%) in a thoroughly evacuated chamber backfilled with ~500 Torr argon atmosphere. The arc was initially struck on a Ti getter to minimize oxygen contamination. A ~50 g charge was melted consecutively via a high-current arc on different sides to ensure homogeneity. The melt was then allowed to cool slowly (cooling rate of order 10^2 °C/sec) to room temperature on a water chilled Cu crucible. In order to evaluate the effects of cooling rate on microstructure, half of this boule was sectioned off for melt-spinning. Remelting was performed in the same chamber under the same initial conditions, but where the Cu crucible was fitted with a 2 mm diameter boron nitride aperture leading to a rotating copper plate. Capillary forces contain the melt in place, sealing the aperture and effectively dividing the chamber in two. Argon gas was backfilled into the upper chamber until a pressure differential of about 380 Torr was reached, forcing the melt through the aperture onto the Cu plate, rotating at 1200 rpm, and the solidified ribbon was thrown into a collection arm. Bulk compositional analysis was performed on the slow-cool sample by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). Roughly 40 mg of the slow-cool sample was digested in a 3:2 solution of HNO_3 and HF, and was analyzed three times in order to determine error. The bulk composition was found to be $Fe_{28}Si_{68}Ge_4$. The Ge content was not explicitly varied here, although this is of interest for future work. Here, our emphasis is on controlling and determining how Ge partitions throughout the microstructure as a function of process variations.

Samples were subjected to isothermal aging to foster eutectoid