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In situ energy dispersive X-ray diffraction study of iron disilicide thermoelectric materials

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Abstract

The dynamic phase transformation and structure of rapidly solidified $Fe_{1-x}Co_xSi_2$ ($0.02 \leqslant x \leqslant 0.06$) thermoelectric materials were *in situ* investigated under high temperatures and high pressures by energy dispersive X-ray diffraction using synchrotron radiation. The $FeSi_2$ alloys which solidified as α-Fe_2Si_5 and ε-FeSi eutectic structures, were transformed to the semiconducting β-$FeSi_2$ phase upon heating by the main reaction $\alpha+\varepsilon\rightarrow\beta$ and the subsidiary reaction $\alpha\rightarrow\beta+Si$. The low heating rates and Co contents were found to be beneficial for the β phase formation. The decomposition temperature of $\beta\rightarrow\alpha+\varepsilon$ was weakly dependent on heating rate, but significantly suppressed by the high pressures.

Keywords: A. Inorganic compounds; A. Semiconductors; C. High pressure; C. X-ray diffraction; D. Phase transitions

1. Introduction

Semiconducting iron disilicide (β-$FeSi_2$) has received much attention for potential applications in power generators [1], thermal sensor [2], and optoelectronic devices [3]. Compared to $ZT\approx 1$ for the state-of-the-art Bi_2Te_3 and PbTe based thermoelectric alloys [4], despite the high Seebeck coefficient α, the low electrical conductivity σ and the high thermal conductivity κ of β-$FeSi_2$ lead to a much lower thermoelectric dimensionless figure of merit $ZT\approx 0.2$ ($ZT=\alpha^2\sigma T/\kappa$, T is temperature in Kelvin). However, it is still attractive for thermoelectric interest because of low cost of raw materials, high oxidation resistance, chemical stability and environmental friendliness [5,6]. By doping with different elements, the conduction type and thermoelectric properties of β-$FeSi_2$ could be modified and improved. Mn-, Cr-, Zr- or Al-doped $FeSi_2$ shows p-type conduction [7–10], while Co-, Ni-, or B-doped $FeSi_2$ shows n-type conduction [7,11,12]. Many research efforts such as composition optimization [7–12], fine particle dispersion [13], and grain refinement [14] have been made to improve the figure of merit of β-$FeSi_2$ based materials.

According to the Fe–Si binary phase diagram in Fig. 1 [15], three reactions will take place during solidification of a stoichiometric alloy $FeSi_2$: the eutectic solidification of the liquid (L) at 1212 °C, $L\rightarrow\alpha$-$Fe_2Si_5+\varepsilon$-FeSi, the peritectoid reaction of the solidified α and ε phases to the semiconducting β-$FeSi_2$ phase at 982 °C, $\alpha+\varepsilon\rightarrow\beta$, and the eutectoid decomposition of the possibly remained α phase at 937 °C, $\alpha\rightarrow\beta+Si$. A long annealing duration is generally needed to obtain the complete β phase due to the slow peritectoid reaction. Rapid solidification is an effective method for producing fine grained structures, and improving phase transformation rates and thermoelectric properties of iron disilicides, as demonstrated in our previous work [16–18]. However, when the submicron eutectic structures in rapidly solidified iron disilicides transform to the β phase, the grain size increases rapidly during hot pressing [18,19]. The phase transformations and structural evolutions during the process of rapid solidification, hot

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pressing and annealing are complicated [20]. A systematic study on the dynamic phase transformations during high temperature and high pressure (HTHP) is highly desirable in order to optimize the process and improve thermoelectric properties of rapidly solidified iron disilicides.

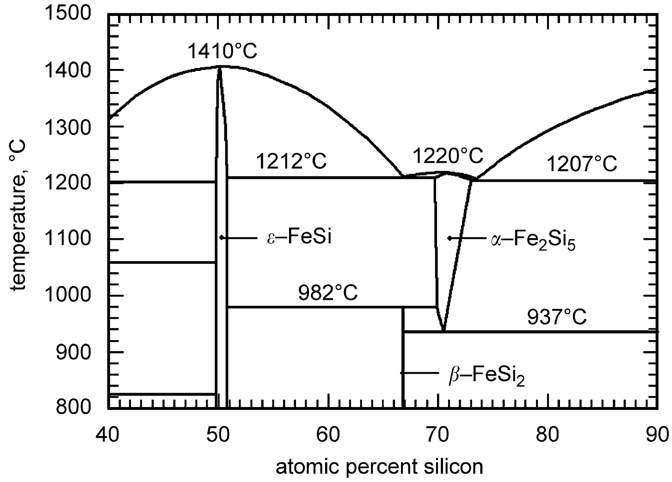

Fig. 1. Equilibrium Fe–Si binary phase diagram.

In this work, *in situ* energy-dispersive X-ray powder diffraction (EDXRD) measurements using synchrotron radiation were performed to investigate the dynamic process of phase transformations in the rapidly solidified Co-doped $FeSi_2$ alloys under high temperatures and high pressures. The effects of Co content, heating rate and applied pressure on β phase transformations are presented.

2. Experimental

Mixtures of iron (>99.3%), silicon (>99.999%), and cobalt (>99.5%) with the desired compositions of $Fe_{1-x}Co_xSi_2$ ($0.02 \leqslant x \leqslant 0.06$) were melted by levitation melting using a copper crucible. The obtained ingots were re-melted in an arc-furnace, then rapidly solidified by spilling the melt to the edge of a chilled rolling molybdenum wheel with a linear speed of about 27.5 m s^{-1} at the edge. Both levitation melting and melt spinning were carried out under a high-purity argon atmosphere.

Table 1
Different heating rates during EDXRD measurement under various pressures for Co-doped rapidly solidified $FeSi_2$ powders

External hydraulic press (ton)	Actual pressures on samples (GPa)	RT (°C/min)				
		600 °C	600–700 °C	700–900 °C	900–1000 °C	1000–1200 °C
1	~0	10	2.5	2.5	2.5	–
15	~2.5	15	2.5	5	10	10
30	~4.7	15	2.5	5	10	10

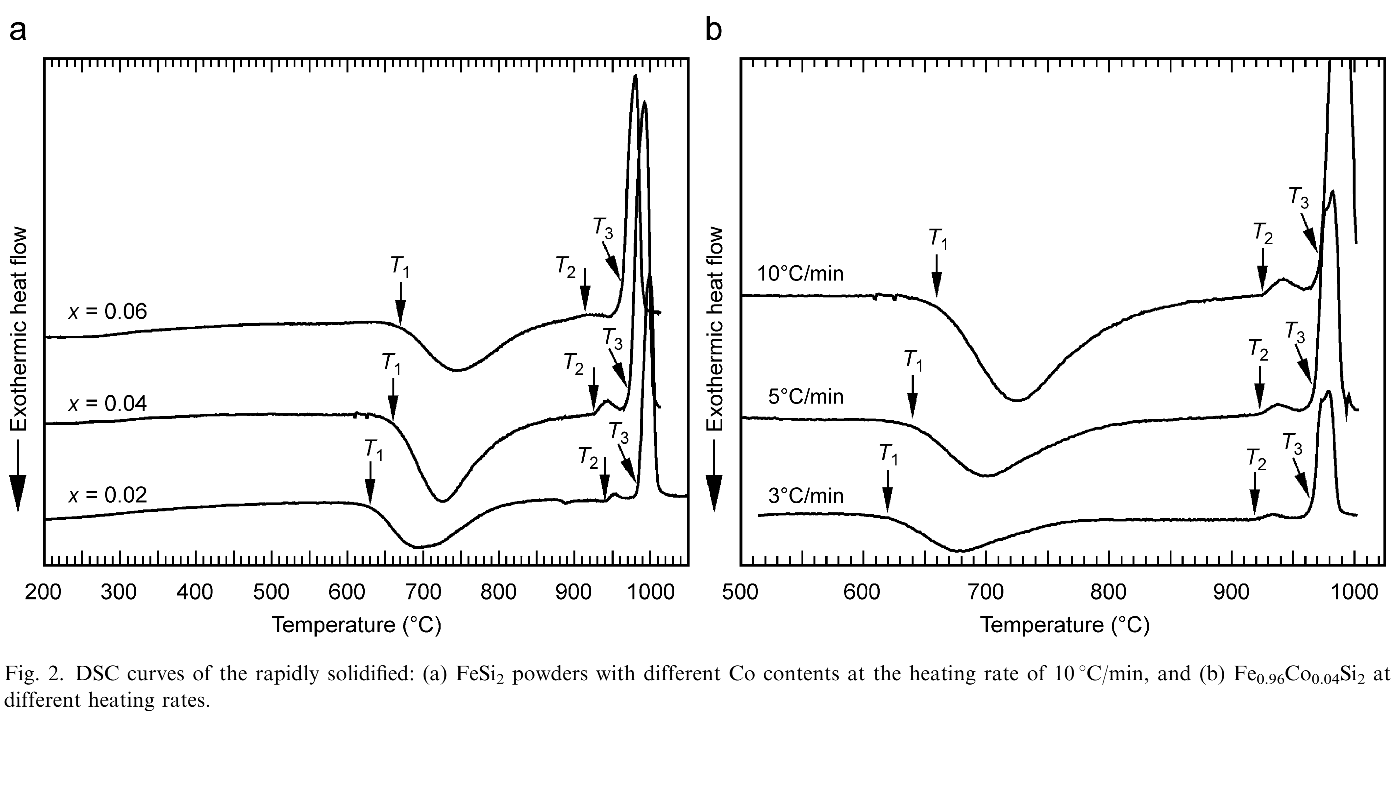

Fig. 2. DSC curves of the rapidly solidified: (a) $FeSi_2$ powders with different Co contents at the heating rate of 10 °C/min, and (b) $Fe_{0.96}Co_{0.04}Si_2$ at different heating rates.