Experimental investigation and thermodynamic calculation of the Fe–Si–Sn system

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Abstract: Phase equilibrium of the Fe–Si–Sn ternary system was investigated using equilibrated alloys. The samples were characterized by means of scanning electron microscopy equipped with energy dispersive X-ray spectrometry and X-ray diffraction. Isothermal sections of the Fe–Si–Sn system at 700 °C and 890 °C each consists of 5 three-phase regions. No ternary compound was found at those two temperatures. The solubility of Sn in the Fe–Si binary phases and the solubility of Si in the Fe–Sn binary phases is limited. Furthermore, thermodynamic extrapolation of the Fe–Si–Sn system was carried out. Calculated solidification path and phase relationship agreed well with experimental results.

Keywords: Fe–Si–Sn; Isothermal section; CALPHAD; Immiscible alloys

1. Introduction

Immiscible alloys, characterized by a miscibility gap in the liquid state, are explored as potential materials for advanced bearings in automotive and mechanical fields [1–2]. Their properties depend mainly on the process of phase separation and microstructure evolution. When the physical conditions are favorable for the solidification of immiscible alloys, various macrosegregation patterns with differentiated properties are formed. However, the nature of the phase separation and solidification of immiscible alloys has remained an unsolved problem, which

limits the application of immiscible alloys. Due to broad liquid miscibility gap, solidification processes of Sn, Bi, Cu and Zr-based alloys have attracted much attention [3–7]. In the Fe–Si–Sn system, Fe₃₇Sn₃₂Si₃₁ immiscible alloy was prepared by rapid solidification, resulting in the form of droplets with 97–978 μm diameters inside a drop tube [6]. As phase constituents and microstructure evolution determined by the liquid phase separation and subsequent structural evolution have a large impact on the properties of immiscible alloy, it is important to understand the phase separation during solidification process of the Fe–Si–Sn alloys with the guidance of phase equilibrium information. However, knowledge concerning the phase relationship of the ternary Fe–Si–Sn system is restricted to the partial isothermal section at 600 °C with Si and Sn less than 10 at.% [8]. To understand the Fe–Si–Sn system and develop the thermodynamic database for designing Sn-based immiscible alloys, the present work will focus on the experimental investigation and thermodynamic extrapolation of the Fe–Si–Sn ternary system.

2. Literature information

There are three constituting binaries in the Fe–Si–Sn ternary system, Fe–Si, Fe–Sn and Si–Sn systems. The Fe–Si binary system thermodynamically assessed by Lacaze and Sundman [9] has been widely accepted in literature [10–13]. As presented in Fig. 1(a), there are five intermetallic compounds in the Fe–Si binary system: Fe₂Si, Fe₅Si₃, FeSi, FeSi₂-H and FeSi₂-L. The solution phases are: liquid, (γ-Fe) and (α-Fe). In addition, the Bcc-solid solution has two existence forms, disordered α-Fe (A2) and ordered α₁ (B2) and α₂ (D0₃).

The equilibrium phase diagram of the Fe–Sn system has been investigated intensively by many authors [14–18]. Thermodynamic descriptions developed by Nussler et al. [14] included two metastable phases Fe₃Sn and Fe_{0.565}Sn_{0.435} [14, 18], while the stable Fe₅Sn₃ phase was omitted. Kumar et al. [15] thermodynamically modeled this system and thermodynamic descriptions recently reported by Huang et al. [17] were accepted in this work. As shown in Fig. 1(b), the equilibrium phases included in this system are: liquid, α-Fe, γ-Fe, (Sn) and four intermetallic compounds: Fe₅Sn₃, Fe₃Sn₂, FeSn, and FeSn₂. The liquid phase encompasses a miscibility gap within

the composition between 31.2 at.% Si and 81.1 at.% Si. Fe_5Sn_3 is stable between 773.4 °C and 901.1 °C. The Fe_3Sn_2 phase is formed by a peritectic reaction at 801.8 °C, and it transforms into the (α -Fe) and FeSn phases by a eutectoid reaction at 601.9 °C. The FeSn and FeSn_2 phases are the products of another two peritectic reactions reacted at 751.7 °C and 502.4 °C, respectively.

The Si–Sn binary system [19] shown in Fig. 1(c) contains a eutectic reaction at 231.9 °C. The eutectic point is very close to the melting point of pure Sn. Under normal pressure, the stable phases are: liquid, the (Si) solid solution and the (Sn) solid solution. No binary compound exists in this system. More information about the crystal structure of phases in above three binary systems is shown in Table 1. No ternary compound was reported from the available literature.

Among the above three binary systems, only the Fe–Sn system has the miscibility gap characterizing formation of the immiscible alloy, so much attention should be paid to the role of Si on the solidification of Fe–Sn based alloy. In this work, phase relationship between Fe–Sn compounds and Fe–Si compounds was investigated by constructing isothermal sections of the Fe–Si–Sn systems at 700 °C and 890 °C. Vertical section of this system was established to analyze the solidification process.

3. Experimental procedure

In this study, more than 30 ternary alloys were prepared with high purity Fe (99.99wt.%) pieces, Si (99.99wt.%) pieces and Sn (99.99wt.%) blocks (Sources from Beijing Mountain Jingdian Technical Development Center, China). Proper amounts of pure elements were weighed according to nominal compositions listed in Tables 2 and 3. They were arc-melted together under a Ti-gettered argon atmosphere. The buttons were inverted and remelted 3 times to improve their homogenization. As the melting points of Fe (1535 °C) and Si (1414 °C) were much higher than that of Sn (232 °C), the electric current was set as low as possible to minimize the weight loss by volatilization of Sn. Buttons with weight loss under 1% after melting were re-sealed in evacuated quartz tubes under an argon gas atmosphere and annealed at 700 °C or 890 °C for 30 days. Due to big density differences

between Fe, Si and Sn elements, tubes containing alloys A1-A3 with more Sn content were annealed for 10 days to get equilibrium. Finally, all samples were quenched in cold water.

Microstructure and phase compositions of the annealed alloys were examined by a JSM-6510 Scanning Electron Microscopy (JEOL, Japan) equipped with Energy Dispersive X-ray Spectrometer (Oxford instrument, UK) (SEM-EDS), with probe diameter of 1 mm, accelerating voltage of 20 kV. The compositions reported in this study were the average value of at least five measurements. Moreover, some crucial samples were further characterized with X-ray diffraction (XRD) analysis to identify the crystal structure of the equilibrium phases. XRD patterns were generated by a D/max 2500 PC X-ray diffractometer (Rigaku, Japan) with Cu K α radiation. The data were collected in the range of 2θ from 10° to 90° at a step of 0.02°. Si powders were used as external calibrated standard. Jade 5.0 program was used to index and calculate the XRD patterns.

4. Experimentally determined phase relationship

4.1. Isothermal section at 700 °C

Table 2 gives the nominal compositions of the alloys, phases in each alloy, which were identified by a combination of XRD and SEM-EDS. All the phases can be easily differentiated based on their brightness on grayscale images and chemical composition.

Microstructures in back scattered electrons (BSE) of alloy A1 (60Fe-1Si-39Sn) is shown in Fig. 2(a). In this image, the dark phase is (α -Fe) and the other two phases are FeSn and Fe₃Sn₂, respectively. As the atomic number of Fe is less than that of Sn, the FeSn phase is much brighter than the Fe₃Sn₂ phase. Three-phase equilibrium between (α -Fe), Fe₃Sn₂ and FeSn in alloy A1 was further confirmed by XRD analysis shown in Fig. 2(b).

In alloy A2 (52Fe-5Si-43Sn), (Sn) coexisting with (α -Fe) and FeSn was identified by a combination of its BSE image (Fig. 3(a)) and XRD pattern (Fig. 3(b)). The gray phase is FeSn and the bright one is (Sn) based on their composition analysis. As the atomic number of Si is lower than that of Sn and Fe, the darkest phase is (α -Fe) (Fe_{77.1}Si_{22.9}). Seen from the XRD pattern exhibited in Fig. 3(b), characteristics peaks of the above three phases are

evidenced. The (Sn) phase is the solidified microstructure of the liquid phase above its melting point (M.P.).

The other three-phase equilibria: $\text{Liq.} + (\alpha\text{-Fe}) + \text{FeSi}$, $\text{Liq.} + \text{FeSi} + \text{FeSi}_2$ and $\text{Liq.} + \text{FeSi}_2 + (\text{Si})$, were determined from BSE images (Fig. 4) and XRD patterns (Fig. 5) of alloys A3 (55Fe–40Si–5Sn), A4 (40Fe–55Si–5Sn) and A5 (20Fe–75Si–5Sn), respectively. In Fig. 4, the white (Sn) phase is the solidified microstructure of liquid phase after water quenching, and all the Fe–Si compounds, $(\alpha\text{-Fe})$, FeSi and FeSi₂, can equilibrate with the liquid phase. XRD patterns shown in Fig. 5 evidenced that there was a one-to-one correspondence between the characteristic peaks of all phases in alloys and the standard peaks of each phase. Based on the composition listed in Table 2, no solubility of Sn in Fe–Si binary compounds was identified, this may be attributed to the obvious atomic radius difference between Sn (0.182nm) and Fe (0.124nm) or Si (0.117nm).

Based on information about the Fe–Si, Fe–Sn and Si–Sn binary systems [9, 17, 24] and the results of present experimental investigation, the 700 °C isothermal section of the Fe–Si–Sn system was constructed, as shown in Fig. 6. The following 5 three-phase regions were included: (1) $(\alpha\text{-Fe}) + \text{Fe}_3\text{Sn}_2 + \text{FeSn}$, (2) $\text{Liq.} + (\alpha\text{-Fe}) + \text{FeSn}$, (3) $\text{Liq.} + (\alpha\text{-Fe}) + \text{FeSi}$, (4) $\text{Liq.} + \text{FeSi} + \text{FeSi}_2$ and (5) $\text{Liq.} + \text{FeSi}_2 + (\text{Si})$. No ternary compound was found in the isothermal section of the Fe–Si–Sn system at 700 °C. Based on the phase compositions listed in Table 3, solubility of Sn in the Fe–Si compounds is limited.

4.2. Isothermal section at 890 °C

Based on the obtained experimental data listed in Table 3, isothermal section of the Fe–Si–Sn system at 890 °C is shown in Fig. 7. Compared with microstructure of the alloys annealed at 700 °C, two new phases, Fe₅Sn₃ and Fe₅Si₃, appeared in the alloys annealed at 890 °C. Fig. 8(a) shows three different phases (Fe₅Sn₃ + $(\alpha\text{-Fe})$ + (Sn)) in alloy B1 (50Fe–2Si–48Sn). The (Sn) phase is the solidified microstructure of the liquid phase. The gray Fe₅Sn₃ phase is precipitated and dispersively distributed around the black $(\alpha\text{-Fe})$ phase containing 92.1 at% Fe and 7.9 at% Si. Such morphology corresponds to the peritectic reaction, $\text{Liq.} + (\alpha\text{-Fe}) \leftrightarrow \text{Fe}_5\text{Sn}_3$. As shown in Fig. 8(b) and (c),

the Fe_5Si_3 phase was identified in the three-phase equilibria of $((\alpha\text{-Fe}) + \text{Liq.} + \text{Fe}_5\text{Si}_3)$ and $(\text{FeSi} + \text{Fe}_5\text{Si}_3 + \text{Liq.})$. The Fe_5Si_3 and $(\alpha\text{-Fe})$ can be easily distinguished from the shape. In the microstructure of alloy B3 (55Fe–40Si–5Sn) exhibited in Fig. 8(c), the white phase is the solidified microstructure (Sn), the gray phase is Fe_5Si_3 and the black one is FeSi. Three-phase equilibrium $(\text{FeSi} + \text{Liq.} + \text{FeSi}_2)$ and $((\text{Si}) + \text{Liq.} + \text{FeSi}_2)$ were identified in alloys B4 and B5 annealed at 890 °C, respectively.

Consequently, the isothermal section of the Fe–Si–Sn system at 890 °C contains 5 three-phase equilibrium regions: (1) $(\alpha\text{-Fe}) + \text{Liq.} + \text{Fe}_5\text{Si}_3$, (2) $(\alpha\text{-Fe}) + \text{Liq.} + \text{Fe}_5\text{Si}_3$, (3) $\text{FeSi} + \text{Fe}_5\text{Si}_3 + \text{Liq.}$, (4) $\text{FeSi} + \text{Liq.} + \text{FeSi}_2$, (5) $(\text{Si}) + \text{Liq.} + \text{FeSi}_2$. The liquid phase can be in equilibrium with all the Fe–Si and Fe–Sn binary phases, and no solubility of the ternary element was identified within these binary intermetallics.

5. Thermodynamic calculation and discussion

In the present modeling, the Gibbs energy functions for pure Fe, Si and Sn were taken from the SGTE compilation by Dinsdale [25]. The thermodynamic parameters in the Fe–Si, Fe–Sn, and Si–Sn systems were taken from Refs. [9, 17, 24], respectively. The calculated binary phase diagrams are presented in Fig. 1(a)–(c), respectively.

5.1 Substitutional solutions

The solution phases ϕ (Liquid, Fcc_A1, Bcc_A2 and Diamond_A4) in the Fe–Si–Sn system are described by the substitution solution model in the present work, for which the Gibbs energy is given by the following equation

$$G_m^\phi = x_{\text{Fe}} {}^0G_{\text{Fe}}^\phi + x_{\text{Si}} {}^0G_{\text{Si}}^\phi + x_{\text{Sn}} {}^0G_{\text{Sn}}^\phi + RT(x_{\text{Fe}} \ln x_{\text{Fe}} + x_{\text{Si}} \ln x_{\text{Si}} + x_{\text{Sn}} \ln x_{\text{Sn}}) + {}^E G_m^\phi \quad (1)$$

where ${}^0G_{\text{Fe}}^\phi$, ${}^0G_{\text{Si}}^\phi$ and ${}^0G_{\text{Sn}}^\phi$ are the molar Gibbs energies of pure Fe, Si and Sn in the solution phase. The term, x_{Fe} , x_{Si} and x_{Sn} denote mole fractions of Fe, Si and Sn, respectively. ${}^E G_m^\phi$ is the excess Gibbs energy, expressed in a Redlich–Kister polynomial as

$${}^E G_m^\phi = x_{\text{Fe}} x_{\text{Si}} \sum_i {}^i L_{\text{Fe, Si}}^\phi (x_{\text{Fe}} - x_{\text{Si}})^i + x_{\text{Fe}} x_{\text{Sn}} \sum_i {}^i L_{\text{Fe, Sn}}^\phi (x_{\text{Fe}} - x_{\text{Sn}})^i$$

$$+x_{Si}x_{Sn}\sum_i^iL_{Si,Sn}^\phi(x_{Si}-x_{Sn})^i+x_{Fe}x_{Si}x_{Sn}L_{Fe,Si,Sn}^\phi \quad (2)$$

where $L_{Fe,Si}^\phi$, $L_{Fe,Sn}^\phi$ and $L_{Si,Sn}^\phi$ are the interaction parameter between Fe and Si, Fe and Sn, and Si and Sn, respectively. The ternary interaction parameter $L_{Fe,Si,Sn}^\phi$ is usually expressed by an equation of the form:

$$L_{Fe,Si,Sn}^\phi = L_{Fe,Si,Sn}^0 + L_{Fe,Si,Sn}^1 x_{Fe} + L_{Fe,Si,Sn}^2 x_{Sn}^2 \quad (3)$$

The ordered Bcc_B2 phase is modeled as (Fe, Si, Sn, Va)_{0.5} (Fe, Si, Sn, Va)_{0.5}, where Va means vacancy. In order to represent the Gibbs energy of the order/disorder transition using a single function, the disordered Bcc_A2 phase is described by the model (Fe, Si, Sn, Va)₁. Ansara et al. [26, 27] have derived an equation, which allows the thermodynamic properties of the disordered phase to be evaluated independently. This is carried out by resolving the Gibbs energy into the following three terms:

$${}^0G_m^\theta = {}^0G_m^{A2}(x_{Fe}, x_{Si}, x_{Zn}) + {}^0G_m^{B2}(y_{Fe}', y_{Si}', y_{Zn}', y_{Fe}'', y_{Si}'', y_{Zn}'') - {}^0G_m^{B2}(x_{Fe}, x_{Si}, x_{Zn}) \quad (4)$$

in which the notation θ represents both Bcc_A2 and Bcc_B2 phases. y_{Fe}' , y_{Si}' and y_{Zn}' are the site fractions of Fe, Si and Zn in the first sublattice, while y_{Fe}'' , y_{Si}'' and y_{Zn}'' in the second one. ${}^0G_m^{A2}(x_{Fe}, x_{Si}, x_{Zn})$ is the Gibbs energy of the disordered Bcc_A2 phase. The second term ${}^0G_m^{B2}(y_{Fe}', y_{Si}', y_{Zn}', y_{Fe}'', y_{Si}'', y_{Zn}'')$ is described by the sublattice model and implicitly contains a contribution from the disordered state. The last term ${}^0G_m^{B2}(x_{Fe}, x_{Si}, x_{Zn})$ represents the contribution from the disordered state to the ordered one. When the site fractions are equal, i.e. $y_{Fe}' = y_{Fe}''$, $y_{Si}' = y_{Si}''$ and $y_{Zn}' = y_{Zn}''$ the last two terms cancel each other. In this case, Eq. (4) corresponds to the disordered state.

5.2 Binary compounds

Both of the solubilities of Si in Fe–Sn compounds and the solubilities of Sn in the Fe–Si binary compounds are low. Thus, in the present modeling, all of the Fe–Sn and Fe–Si binary phases are treated as pure binary ones. Their thermodynamic parameters were directly adopted from the binary systems.

5.3 Modeling procedure

The optimization was carried out by means of the optimization module PARROT of the thermodynamic

software Thermo-Calc [28], which works by minimizing the square sum of the differences between the experimental values and the computed ones. Firstly, the thermodynamic description of the liquid phase were obtained by a combination of the corresponding Gibbs energy functions from the assessments of binary systems using Muggianu interpolation of binary excess terms [29], ternary parameters were also introduced to improve the fit to the experimental data. Secondly, the parameters of the Fcc_A1 and bcc_A2 phases were optimized based on the related phase equilibria. Actually, no better agreement between the calculated results and the experimental data can be achieved with the introduction of ternary parameters. Thus, direct extrapolation of the Fcc_A1 and Bcc_A2 phase can be accepted in the present optimization. For the ordered Bcc_B2 phase no reliable parameter can be established due to the lack of experimental data. It was found that only one ternary parameter was needed to obtain a good fit to the experimental data associated with the disordered Bcc_A2 and the ordered Bcc_B2 phase. Thermodynamic parameters of the Fe–Si–Sn system are presented in Table 4. With these thermodynamic parameters, 700 °C and 890 °C isothermal sections were calculated. The results are presented in Fig. 9(a) and (b). The dash lines added in Fig. 9 represent the Bcc_A2/Bcc_B2 order-disorder transition lines. Compared to the experimental results in Figs. 6 and 7, phase relationships in the calculated isothermal sections agree well with experimental results, except the limited solubility range of the liquid phase. To have a much better thermodynamic description of this system, more experimental thermodynamic properties for the liquid phase are required. Figures 10 and 11 present the calculated liquidus projection and the Scheil reaction scheme, respectively, of the Fe–Si–Sn system, according to the present thermodynamic parameters. It should be noted that a stable liquid miscibility gap exists in the Fe–Si–Sn ternary system. In Fig. 10, 4 four-phase monotectic reactions occur in the Fe–Si–Sn system due to intersections of the L1 + L2 gap with the primary solidification fields of FeSi₂-H, FeSi, Fe₂Si, (Si), Fe₅Si₃ and Bcc_B2.

As an example of utilizing the present thermodynamic database to analyze microstructure of immiscible alloy, solidification process of a typical Fe–Si–Sn alloy was simulated utilizing the Scheil–Gulliver model [30, 31]

integrated in Pandat software. Fig. 12 shows a vertical section of the Fe–Si–Sn system, Fe₃₇Si₃₁Sn₃₂ alloy from liquid successively transforms to the FeSi, Fe₂Si, Fe₅Si₃, (α -Fe), FeSn and FeSn₂ phases, and solidifies into the (Sn) phase at the end. Mole fractions of solid phases are further calculated as illustrated in Fig. 13, two phases, FeSi and (Sn), are in fraction of 0.56 and 0.3 respectively. This is consistent with solidified products of ternary Fe₃₇Si₃₁Sn₃₂ reported by Wang et al. [6], where the major phases were FeSi and (Sn). However, the Fe₂Si phase, its mole fraction is 0.12 from this calculation, was not observed or detected in their study. It can be explained that the rapid cooling rate without keeping at 1138.5 °C for a period limited the formation of the Fe₂Si phase, as shown in Fig. 13.

6. Conclusions

The following conclusions can be drawn from this study:

- 1) Isothermal sections of the Fe–Si–Sn ternary system at 700 °C and 890 °C were experimentally established by using SEM–EDS and XRD technology. There is no existence of ternary compounds and Sn cannot dissolve into the Fe–Si binary phases.
- 2) The Fe–Si–Sn ternary system was thermodynamically calculated with extrapolation of three binary systems, calculated isothermal sections convince well with the experimental data determined in this study.
- 3) With the Scheil–Gulliver model, solidification path of Fe₃₇Si₃₁Sn₃₂ alloy was simulated. The calculated solidification path and mole fraction of the solid phases can reasonably explain experimental results from literature.

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Figure captions:

Fig.1 Binary phase diagrams constituting the Fe–Si–Sn ternary system. (a) Fe–Si system [9]; (b) Fe–Sn system [17]; (c) Si–Sn system [19]

Fig.2 Phase coexisting in alloy A1(60Fe–1Si–39Sn)(at%), (a) BSE image and (b) XRD pattern

Fig.3 Phase coexisting in alloy A2 (52Fe–5Si–43Sn)(at%), (a) BSE image and (b) XRD pattern

Fig.4 The BSE images of alloys, (a) A3 (55Fe–40Si–5Sn); (b) A4 (40Fe–55Si–5Sn); (c) A5 (20Fe–75Si–5Sn)(at%)

Fig.5 The XRD patterns of alloys: A3 (55Fe–40Si–5Sn), A4 (40Fe–55Si–5Sn) and A5 (20Fe–75Si–5Sn)(at%)

Fig.6 Phase relations in the ternary Fe–Si–Sn system, constructed from samples annealed at 700°C

Fig.7 Phase relations in the ternary Fe–Si–Sn system, constructed from samples annealed at 890°C

Fig.8 The BSE images of alloys. (a) B1 (50Fe–2Si–48Sn); (b) B2 (65Fe–30Si–5Sn); (c) B3 (55Fe–40Si–5Sn)(at%)

Fig.9 The (a) 700 °C and (b) 890 °C isothermal sections of the Fe–Si–Sn system calculated in this study

Fig.10 Calculated liquidus projection of Fe-Si-Sn system, according to the present work: (a) over entire composition range, (b) in Sn-rich corner

Fig.11 Reaction scheme of Fe-Si-Sn system, according to the present work

Fig.12 The vertical section of Fe–Si–Sn system

Fig.13 Mole fractions of solid phases of Fe₃₇Si₃₁Sn₃₂ alloy formed during solidification process

Table captions:

Table 1 Crystallographic data of the phases in the Fe–Si–Sn system

Table 2 Compositions of specimens and phases in the Fe–Si–Sn ternary system at 700 °C

Table 3 Compositions of specimens and phases in the Fe–Si–Sn ternary system at 890 °C

Table 4 Thermodynamic parameters of the Fe–Si–Sn system ^a

Table 1 Crystallographic data of the phases in the Fe–Si–Sn system

Phase	Pearson symbol	Prototype	Space group	Lattice parameter			Refs.
				a	b	c	
(α -Fe)	<i>cI2</i>	W	<i>Im-3m</i>	0.28665	0.28665	0.28665	[20, 21]
$\alpha_1(\text{Fe}_3\text{Si})$	<i>cF16</i>	BiF_3	<i>Fm-3m</i>	0.565	0.565	0.565	[20, 21]
$\eta(\text{Fe}_5\text{Si}_3)$	<i>hP16</i>	Mn_5Si_3	<i>P63/mcm</i>	0.6759	0.6759	0.50855	[20, 21]
$\varepsilon(\text{FeSi})$	<i>cP8</i>	FeSi	<i>P2_13</i>	0.2468	0.2468	0.3960	[20, 21]
$\zeta_\beta(\text{FeSi}_2)$	<i>oC48</i>	FeSi_2	<i>Cmca</i>	0.9863	0.7791	0.7833	[20, 21]
(Si)	<i>cF8</i>	C(diamond)	<i>Fd-3m</i>	0.5431	0.5431	0.5431	[20, 21]
Fe_5Sn_3	<i>hP6</i>	InNi_2	<i>P6_3/mmc</i>	0.422	0.422	0.523	[21, 22]
Fe_3Sn_2	<i>hR10</i>	...	<i>R-3m</i>	0.5344(5)	0.5344(5)	1.9845(5)	[21, 22]
FeSn	<i>hP6</i>	CoSn	<i>P6/mmm</i>	0.5300(1)	0.5300(1)	0.4449(1)	[21, 23]
(Sn)	<i>tI4</i>	βSn	<i>I4_1/amd</i>	0.58300	0.58300	0.31840	[21, 24]

Table 2 Compositions of specimens and phases in the Fe–Si–Sn ternary system at 700 °C

Alloy number	Nominal composition (at.%)	Phases	Composition (at.%) (700 °C)		
			Fe	Si	Sn
A1	Fe ₆₀ Si ₁ Sn ₃₉	Fe ₃ Sn ₂	60.4	–	39.6
		FeSn	50.9	–	49.1
		(α -Fe)	93.5	6.5	–
A2	Fe ₅₂ Si ₅ Sn ₄₃	FeSn	50.1	–	49.9
		(α -Fe)	77.1	22.9	–
		Liq.	0.5	–	99.5
A3	Fe ₅₅ Si ₄₀ Sn ₅	(α -Fe)	73.3	26.8	–
		FeSi	49.9	50.1	–
		Liq.	1.9	0.9	97.2
A4	Fe ₄₀ Si ₅₅ Sn ₅	Liq.	1.7	1.9	96.4
		FeSi	48.7	51.3	–
		FeSi ₂	32.9	67.1	–
A5	Fe ₂₀ Si ₇₅ Sn ₅	FeSi ₂	32.1	67.9	–
		(Si)	0.2	99.8	–
		Liq.	1.3	2.5	96.2

Table 3 Compositions of specimens and phases in the Fe–Si–Sn ternary system at 890 °C

Alloy number	Nominal composition (at.%)	Phases	Composition (at.%)		
			Fe	Si	Sn
B1	Fe ₅₀ Si ₂ Sn ₄₈	Fe ₅ Sn ₃	62.5	–	37.5
		Liq.	3.2	–	96.8
		(α -Fe)	92.1	7.9	–
B2	Fe ₆₅ Si ₃₀ Sn ₅	Fe ₅ Si ₃	62.3	37.7	–
		(α -Fe)	73.1	26.9	–
		Liq.	2.1	0.9	97.0
B3	Fe ₅₅ Si ₄₀ Sn ₅	Fe ₅ Si ₃	61.8	38.2	–
		FeSi	49.6	50.4	–
		Liq.	1.1	1.7	97.2
B4	Fe ₄₅ Si ₅₀ Sn ₅	Liq.	1.2	1.3	97.5
		FeSi	49.3	50.7	–
		FeSi ₂	33.2	66.8	–
B5	Fe ₂₀ Si ₇₅ Sn ₅	FeSi ₂	33.0	67.0	–
		(Si)	0.4	99.6	–
		Liq.	0.6	1.5	97.9

Table 4 Thermodynamic parameters of the Fe–Si–Sn system ^a

Phase	Thermodynamic parameters
Liquid: Model (Fe,Si,Sn) ₁	${}^0L_{\text{Fe,Si}}^{\text{Liq.}} = -164434.6 + 41.9773 \times T$; ${}^1L_{\text{Fe,Si}}^{\text{Liq.}} = -21.523 \times T$; ${}^2L_{\text{Fe,Si}}^{\text{Liq.}} = -18821.542 + 22.07 \times T$; ${}^3L_{\text{Fe,Si}}^{\text{Liq.}} = 9695.8$; ${}^0L_{\text{Fe,Sn}}^{\text{Liq.}} = 108744.390 - 441.227 \times T + 52.181 \times T \times \ln(T)$; ${}^1L_{\text{Fe,Sn}}^{\text{Liq.}} = -8992.657 + 2.027 \times T$; ${}^2L_{\text{Fe,Sn}}^{\text{Liq.}} = -9855.251 + 0.984 \times T$; ${}^3L_{\text{Fe,Sn}}^{\text{Liq.}} = 2552.588$; ${}^0L_{\text{Si,Sn}}^{\text{Liq.}} = 41080.4 - 9.8526 \times T$; ${}^1L_{\text{Si,Sn}}^{\text{Liq.}} = -32051.2 + 20.6468 \times T$; ${}^2L_{\text{Si,Sn}}^{\text{Liq.}} = 294.12$; ${}^0L_{\text{Fe,Si,Sn}}^{\text{Liq.}} = -50000 - 45 \times T$; ${}^0L_{\text{Fe,Si;Va}}^{\text{Bcc_A2}} = -153151.1 + 46.48 \times T$; ${}^1L_{\text{Fe,Si;Va}}^{\text{Bcc_A2}} = -92352$; ${}^2L_{\text{Fe,Si;Va}}^{\text{Bcc_A2}} = 62240$; ${}^0L_{\text{Fe,Sn;Va}}^{\text{Bcc_A2}} = +23984.142 + 8.722 \times T$; ${}^1L_{\text{Fe,Sn;Va}}^{\text{Bcc_A2}} = -22283.886$; Bcc_B2: Model (Fe,Si,Sn,Va) _{0.5} (Fe,Si,Sn,Va) _{0.5} (Va) ₃ ${}^0G_{\text{Fe;Si;Va}}^{\text{Bcc_B2}} = {}^0G_{\text{Si;Fe;Va}}^{\text{Bcc_B2}} = -20952.6$; Fcc_A1: Model (Fe,Si,Sn) ₁ (Va) ₁ ${}^0L_{\text{Fe,Si;Va}}^{\text{Fcc_A1}} = -125247.7 + 41.116 \times T$; ${}^1L_{\text{Fe,Si;Va}}^{\text{Fcc_A1}} = -142707.6$; ${}^2L_{\text{Fe,Si;Va}}^{\text{Fcc_A1}} = 89907.3$; ${}^0L_{\text{Fe,Sn;Va}}^{\text{Fcc_A1}} = 24140.28$; (Si): Model (Si,Sn) ${}^0L_{\text{Si,Sn}}^{(\text{Si})} = 25265.7 + 23.84 \times T$; FeSi: Model (Fe) ₁ (Si) ₁ ${}^0G_{\text{Fe;Si}}^{\text{FeSi}} = -72761.2 + 4.44 \times T + G_{\text{Fe}}^{\text{Bcc}} + G_{\text{Si}}^{\text{Dia}}$; Fe ₂ Si: Model (Fe) ₂ (Si) ₁ ${}^0G_{\text{Fe,Si}}^{\text{Fe}_2\text{Si}} = -71256.6 - 10.62 \times T + 2 \times G_{\text{Fe}}^{\text{Bcc}} + G_{\text{Si}}^{\text{Dia}}$; FeSi ₂ _H: Model (Fe) ₃ (Si) ₇ ${}^0G_{\text{Fe,Si}}^{\text{FeSi}_2\text{-H}} = -196490 - 9.2 \times T + 3 \times G_{\text{Fe}}^{\text{Bcc}} + 7 \times G_{\text{Si}}^{\text{Dia}}$; FeSi ₂ _L: Model (Fe) ₁ (Si) ₂ ${}^0G_{\text{Fe,Si}}^{\text{FeSi}_2\text{-L}} = -82149 + 10.44 \times T + G_{\text{Fe}}^{\text{Bcc}} + 2 \times G_{\text{Si}}^{\text{Dia}}$; Fe ₅ Si ₃ : Model (Fe) ₅ (Si) ₃ ${}^0G_{\text{Fe,Si}}^{\text{Fe}_5\text{Si}_3} = -241144 + 2.16 \times T + 5 \times G_{\text{Fe}}^{\text{Bcc}} + 3 \times G_{\text{Si}}^{\text{Dia}}$; Fe ₅ Sn ₃ : Model (Fe) ₅ (Sn) ₃ ${}^0G_{\text{Fe,Sn}}^{\text{Fe}_5\text{Sn}_3} = -96838.075 + 50.094 \times T + 5 \times G_{\text{Fe}}^{\text{Bcc}} + 3 \times G_{\text{Sn}}^{\text{Bct}}$

Fe ₃ Sn ₂ : Model (Fe) ₃ (Sn) ₂	${}^0G_{\text{Fe:Sn}}^{\text{Fe}_3\text{Sn}_2} = -92422.023 + 60.951 \times T + 3 \times G_{\text{Fe}}^{\text{Bcc}} + 2 \times G_{\text{Sn}}^{\text{Bct}};$
FeSn: Model (Fe) ₁ (Sn) ₁	${}^0G_{\text{Fe:Sn}}^{\text{FeSn}} = -55594.349 + 42.111 \times T + G_{\text{Fe}}^{\text{Bcc}} + G_{\text{Sn}}^{\text{Bct}};$
FeSn ₂ : Model (Fe) ₁ (Sn) ₂	${}^0G_{\text{Fe:Sn}}^{\text{FeSn}_2} = -68923.848 + 54.473 \times T + G_{\text{Fe}}^{\text{Bcc}} + 2 \times G_{\text{Sn}}^{\text{Bct}};$

^a In J/(mol of atom); temperature (T) in Kelvin. The Gibbs energies for the pure elements are from the SGTE compilation [25]. The thermodynamic parameters in the Fe–Si, Fe–Sn and Si–Sn systems are taken from [9,17,19], respectively. Ternary interaction parameters for the liquid were estimated based on results from this work and literature information.

(a)

(b)

(b)

(Sn)

FeSi₂

FeSi

20μm

(a)

(b)

Fe-Si

Fe-Si-Sn

Fe-Sn

1478.34	e2
L1=FeSi ₂ _H+(Si)	
1477.19	e3
L1=FeSi ₂ _H+FeSi	
1475.78	e4
L1=FeSi+Fe ₂ Si	
1470.36	e5
L1=Fe ₂ Si+B2	
1364.43	p1
Fe ₂ Si+FeSi=Fe ₅ Si ₃	

1275.68	p2
FeSi+FeSi ₂ _H=FeSi ₂ _L	

1097.85	p4
Fe ₅ Si ₃ =B2+FeSi	

Si-Sn

505.08	e8
L=(Sn)+(Si)

1174.17	p3
L1+B2=Fe ₅ Sn ₃	

1074.98	p5
L1+Fe ₅ Sn ₃ =Fe ₃ Sn ₂	

1046.55	p6
Fe ₅ Sn ₃ =B2 + Fe ₃ Sn ₂	

1024.82	p7
L1+Fe ₃ Sn ₂ =FeSn	

875.08	p8
Fe ₃ Sn ₂ =FeSn + B2	

775.52	p9
L1+FeSn=FeSn ₂	

505.09	e7
L=FeSn ₂ +(Sn)	