

Fe-Si-Ti (Iron-Silicon-Titanium)

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The previous review of this ternary system by [1987Rag] presented a liquidus surface for Fe-rich alloys from the studies of [1938Vog] and an isothermal section at 800 °C from [1966Mar]. Recently, [2008Wei] reinvestigated the solidification characteristics over the entire composition range and presented a liquidus projection, a corresponding reaction sequence and a tentative isothermal section at 900 °C. Earlier, [2002Lof] investigated the Si-lean region and presented three partial isothermal sections at 1150, 1000, and 800 °C. This unpublished thesis result was quoted by [2005Ste], who presented the isothermal sections at 1150 and 800 °C. The isothermal section at 800 °C of [2002Lof] was also reproduced by [2004Lof], who studied the mechanical properties of Si-lean alloys.

Binary Systems

The Fe-Si phase diagram [Massalski2] is characterized by a gamma loop enclosing (γ Fe) (fcc). The bcc α phase is present in the disordered α (A2) form and the ordered α_1 ($D0_3$, BiF_3 -type cubic) and α_2 ($B2$, $CsCl$ -type cubic) forms. The intermediate phases are: Fe_2Si (hexagonal), Fe_5Si_3 ($D8_8$, Mn_5Si_3 -type hexagonal), $FeSi$ ($B20$ -type cubic), $\alpha FeSi_2$ (orthorhombic), and $\beta FeSi_2$ (tetragonal). The Fe-Ti phase diagram [1998Dum] depicts the following intermediate phases: Fe_2Ti ($C14$, $MgZn_2$ -type hexagonal) and $FeTi$ ($B2$, $CsCl$ -type cubic). The Si-Ti phase diagram [Massalski2, 2008Wei] depicts the following intermediate phases:

Table 1 Fe-Si-Ti crystal structure and lattice parameter data [2008Wei]

Phase	Composition, at.%	Space group	Prototype	Lattice parameter, nm
$FeSi_2Ti$ (τ_1)	24-25 Fe 49-50 Si 25-26 Ti	$Pbam$	$MnSi_2Ti$	$a = 0.86115$ $b = 0.95427$ $c = 0.76313$
$FeSiTi$ (τ_2)	31-33 Fe 33-35 Si 33-35 Ti	$Ima2$	$FeSiTi$	$a = 0.69869$ $b = 1.0827$ $c = 0.62991$
Fe_4Si_3Ti (τ_3)	49 Fe 35.5 Si 15.5 Ti	$P6/mmm$	$Pd_{40}Sn_{31}Y_{13}$	$a = 1.72073$ $c = 0.79819$
τ_4	28 Fe 45.6 Si 26.3 Ti
τ_5	7.4 Fe 64.3 Si 28.3 Ti
τ_6	~12.5 Fe ~49 Si ~38.5 Ti
τ_7	10 Fe 40 Si 50 Ti
τ_8	20 Fe 40 Si 40 Ti
τ_9	17 Fe 43 Si 40 Ti
Fe_7Si_2Ti	69 Fe 20 Si 11 Ti	$\bar{I}\bar{4}3m$	$Fe_5Si_2V_3$	$a = 0.8837$
Fe_2SiTi (metastable)	50 Fe 25 Si 25 Ti	$Fm\bar{3}m$	$MnCu_2Al$	$a = 0.5709$

Section II: Phase Diagram Evaluations

Ti_3Si (Ti_3P -type tetragonal), Ti_5Si_3 (D_{8g} , Mn_5Si_3 -type hexagonal), $\text{Ti}_5\text{Si}_4(\text{o})$ (Sm_5Ge_4 -type orthorhombic; low-temperature modification), $\text{Ti}_5\text{Si}_4(\text{t})$ (Zr_5Si_4 -type tetragonal; high-temperature modification), TiSi ($B27$, FeB -type orthorhombic), and TiSi_2 ($C54$ -type orthorhombic).

Ternary Phases

[1987Rag] summarized the then-available structural details of the ternary phases of this system: FeSi_2Ti (τ_1) (MnSi_2Ti -type orthorhombic), FeSiTi (τ_2) (FeSiTi -type orthorhombic), $\text{Fe}_4\text{Si}_3\text{Ti}$ (τ_3) ($\text{Pd}_{40}\text{Sn}_{31}\text{Y}_{13}$ -type hexagonal), $\text{Fe}_{10}\text{Si}_{44}\text{Ti}_{46}$ (X') (unknown structure), and $\text{Fe}_{15}\text{Si}_{40}\text{Ti}_{45}$ (X'') (unknown structure). In the ordered phase Fe_3Si (α_1), Ti dissolves up to $x = 0.7$ in $\text{Fe}_{3-x}\text{SiTi}_x$. The $L2_1$ -type Fe_2SiTi is a metastable superstructure based on Fe_3Si . [2008Wei] reported a number of additional ternary phases τ_4 , τ_5 , τ_6 , τ_7 , τ_8 , and τ_9 . The compositions of these phases were determined, but the crystal structures were not. The compositions of the ternary phases X' and X'' reported by [1966Mar] were found by [2008Wei] to be two-phase mixtures of $\tau_9 + \text{Ti}_5\text{Si}_4(\text{o})$ and $\tau_7 + \tau_8$, respectively. In addition to the above, [2002Lof] reported a ternary phase at the composition $\text{Fe}_7\text{Si}_2\text{Ti}$. The composition region within which this phase occurs was not investigated by [2008Wei]. The above phases are listed in Table 1 with updated structural data.

Liquidus Projection

With starting metals of 99.98% Fe, 99.99% Si, and 99.98% Ti, [2008Wei] arc-melted in Ar atm more than 80 ternary alloys. The alloys were annealed at 1000, 950, and 900 °C for 2 weeks (or more) and quenched in water. Differential thermal analysis was carried out at a heating/cooling rate of 5 °C per min. The arrests were read from the heating curves. X-ray powder diffraction and energy dispersive x-ray analysis on a scanning electron microscope were employed for structure identification and for determination of local composition.

To identify the invariant reactions, [2008Wei] assigned the first strong peak during the heating cycle in thermal analysis with “the formation of liquid phase from three solid phases.” The three co-existing solid phases were identified from the annealing experiments in the solid state. All three solid phases melt to form the liquid in a ternary eutectic reaction. One out of the three solid phases melts during a ternary peritectic reaction. The transition reactions, on the other hand, are characterized by the interchange of the tie-lines with no fresh melting at the invariant temperature. Using the reaction sequence derived from the invariant temperatures, the liquidus projection was constructed by [2008Wei], as shown in Fig. 1. The fields of primary crystallization are marked. For clarity, the U-type transition reactions are not numbered. The ternary eutectic reactions E_1 , E_2 , E_3 , and E_4 occur at 1254, 1175, 1151, and 1034 °C,

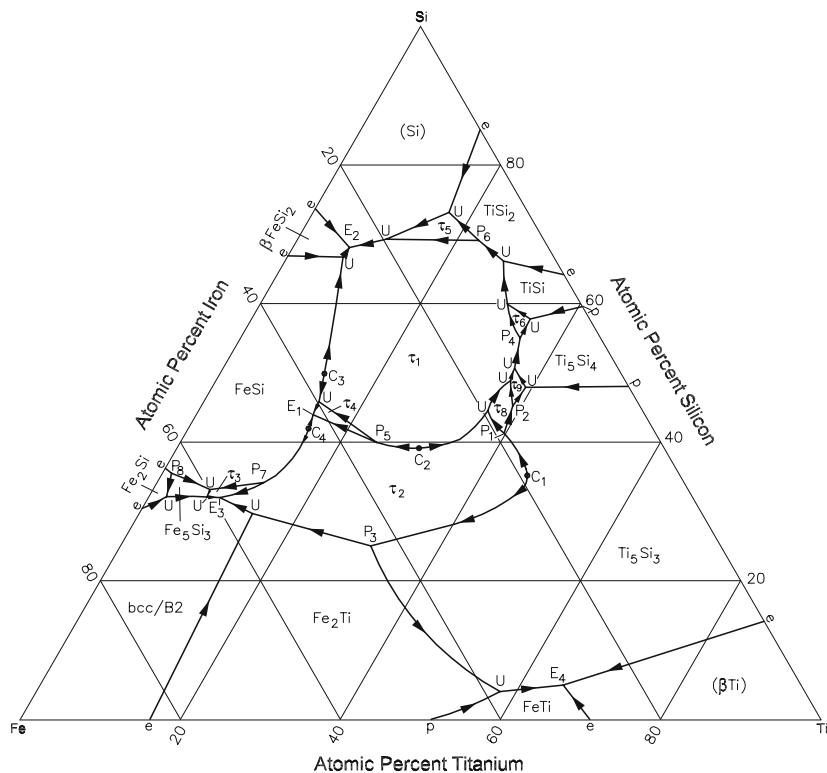


Fig. 1 Fe-Si-Ti liquidus projection [2008Wei]

respectively. The ternary phases τ_3 , τ_4 , τ_5 , τ_6 , τ_8 , and τ_9 form through ternary peritectic reactions P_7 ($1241\text{ }^\circ\text{C}$), P_5 ($1414\text{ }^\circ\text{C}$), P_6 ($1263\text{ }^\circ\text{C}$), P_4 ($1450 < T < 1480\text{ }^\circ\text{C}$), P_1 ($1640\text{ }^\circ\text{C}$), and P_2 ($1597\text{ }^\circ\text{C}$), respectively. The ternary phases τ_1 and τ_2 form at temperature maxima of C_3 ($1328\text{ }^\circ\text{C}$) and C_1 ($>1662\text{ }^\circ\text{C}$), respectively. The binary phases Fe_2Ti and Fe_5Si_3 nucleate in the ternary region through peritectic reactions P_3 and P_8 at 1591 and $1201\text{ }^\circ\text{C}$,

respectively. The ternary phase τ_7 does not take part in the liquid-solid equilibria. Among the ternary phases, τ_1 and τ_2 have large areas of primary crystallization.

The tentative isothermal section constructed by [2008Wei] at $900\text{ }^\circ\text{C}$ is shown in Fig. 2. The ternary phases τ_1 , τ_2 , τ_3 , τ_5 , τ_7 , τ_8 , and τ_9 are present. The phases τ_4 and τ_6 decompose above $1000\text{ }^\circ\text{C}$ [2008Wei]. The phase τ_7 forms in the solid state and is found to be stable at $900\text{ }^\circ\text{C}$. The

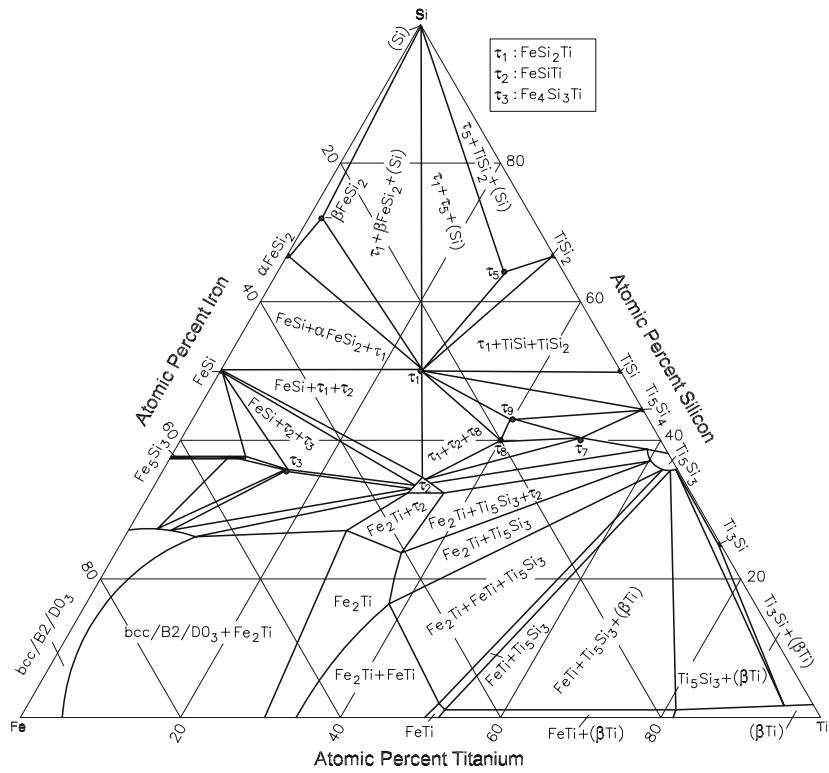


Fig. 2 Fe-Si-Ti tentative isothermal section at $900\text{ }^\circ\text{C}$ [2008Wei]. Narrow two-phase regions are omitted

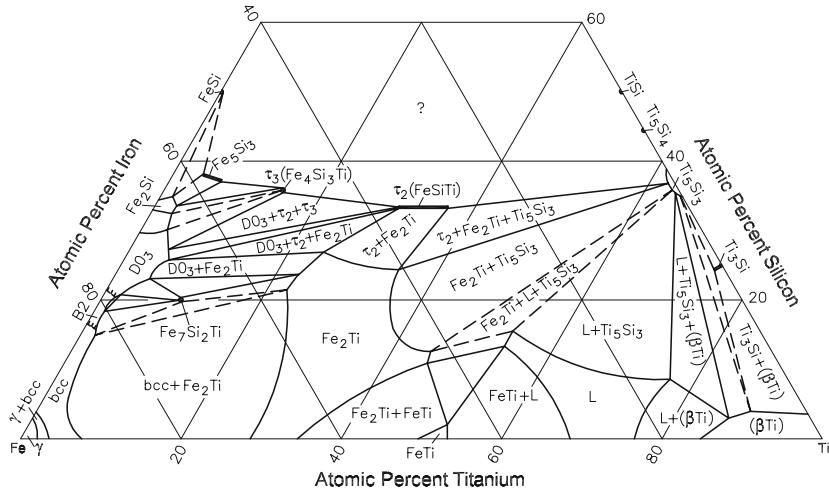


Fig. 3 Fe-Si-Ti isothermal section at $1150\text{ }^\circ\text{C}$ [2002Lof, 2005Ste]

Section II: Phase Diagram Evaluations

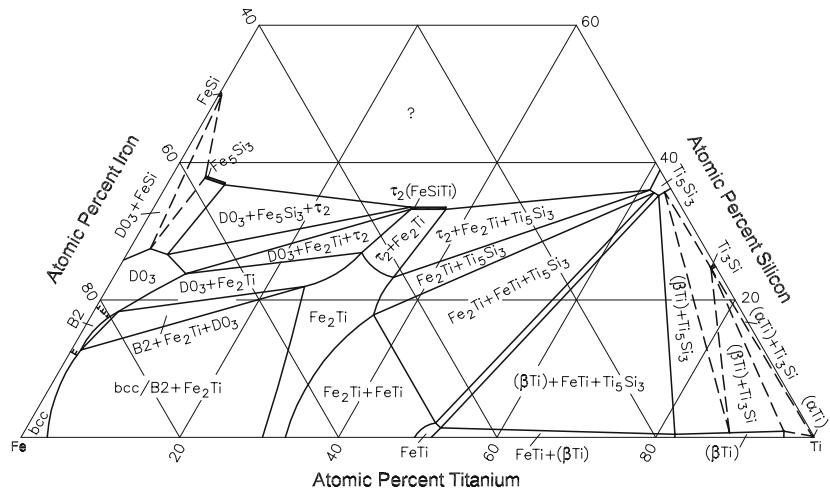


Fig. 4 Fe-Si-Ti isothermal section at 800 °C [2002Lof, 2005Ste]

isothermal sections at 1150 and 800 °C in the Si-lean region determined by [2002Lof] are redrawn in Fig. 3 and 4 from [2005Ste]. At 1150 °C (Fig. 3), the ternary phases FeSiTi (τ_2), $\text{Fe}_4\text{Si}_3\text{Ti}$ (τ_3) and $\text{Fe}_7\text{Si}_2\text{Ti}$ are present. At 800 °C (Fig. 4), only FeSiTi (τ_2) is present. The binary phase Fe_5Si_3 is stable between 1050 and 825 °C. The presence of Ti increases the temperature range of stability of this phase. It is seen within the ternary region at 1150 and 800 °C in Fig. 3 and 4. At all three temperatures (Fig. 2-4), Fe_2Ti dissolves large amounts of Si.

The work of [2008Wei] marks a step forward in characterizing the phase equilibria in this complex system. More detailed studies, especially on the crystal structures of ternary compounds, are needed to establish a complete picture.

References

1938Vog: R. Vogel and W. Schluter, The Iron Corner of the Iron-Silicon-Titanium System, *Arch. Eisenhüttenwes.*, 1938, **12**(4), p 207-212, in German

1966Mar: V.Ya. Markiv, L.A. Lysenko, and E.I. Gladyshevskii, The Titanium-Iron-Silicon System, *Neorg. Mater.* 1966, **2**(11), p 1980-1984, in Russian

1987Rag: V. Raghavan, The Fe-Si-Ti (Iron-Silicon-Titanium) System, *Phase Diagrams of Ternary Iron Alloys, Part I*, ASM International, Materials Park, OH, 1987, p 65-72

1998Dum: L.F.S. Dumitrescu, M. Hillert, and N. Saunders, Comparison of Fe-Ti Assessments, *J. Phase Equilib.*, 1998, **19**(5), p 441-448

2002Lof: F. Löffler, "Investigation of the Ternary Systems Fe-Si-Mg and Fe-Si-Ti: Phase Equilibrium and Mechanical Behavior of Selected Alloys," Thesis, Fortschritt-Berichte VDI, Series 5, No. 676, Düsseldorf, Germany, 2002, in German (as quoted by [2004Lof])

2004Lof: F. Löffler, M. Palm, and G. Sauthoff, Iron-Rich Iron-Titanium-Silicon Alloys with Strengthening Intermetallic Laves Phase Precipitates, *Steel Res. Int.*, 2004, **75**(11), p 766-772

2005Ste: F. Stein, M. Palm, and G. Sauthoff, Structure and Stability of Laves Phases: Part II-Structure Type Variations in Binary and Ternary Systems, *Intermetallics*, 2005, **13**, p 1056-1074

2008Wei: F. Weitzer, J.C. Schuster, M. Naka, F. Stein, and M. Palm, On the Reaction Scheme and Liquidus Surface in the Ternary System Fe-Si-Ti, *Intermetallics*, 2008, **16**, p 273-282