



DISSERTATION

Titel der Dissertation

„PHASE-EQUILIBRIA, STRUCTURAL AND PHYSICAL
CHARACTERIZATION IN
THE TERNARY SYSTEM Al–Fe–Si
AND THE QUATERNARY SYSTEM Al–Fe–Si–Ti“

Verfasser

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THE AIM IS ONLY AS WORTH AS ITS CIRCUMSTANCE

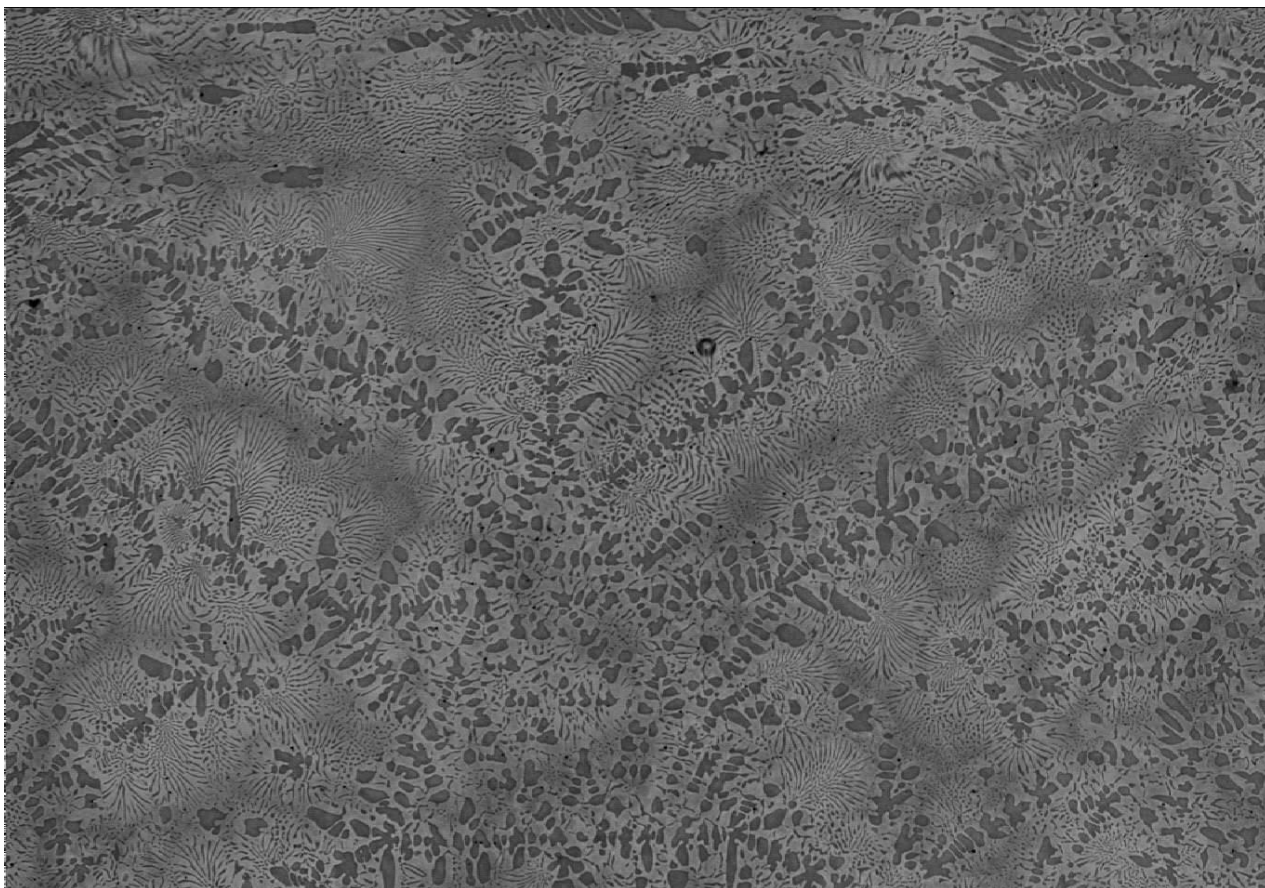
To my beloved mother who brought three wonderful children into the world ...

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ART OF CRYSTALLIZATION

1. Introduction

Intermetallic alloys

Since the Middle Bronze Age iron has become one of the most important materials in human history. In nature pure iron is not stable and is mostly found in form of iron ore, rarely as iron meteorites (Fe-Ni alloy). Around 1500 BC lumpy sponge iron was produced by using a *bloomery furnace* and since the 13th century AD cast iron could be produced in smelting furnaces and used for wrought iron. Because of high strength and low cost it is indispensable for technical applications e.g. steel industry. The disadvantage of pure iron is the high susceptibility to corrosion in humid air. Within the past decades numerous research papers have reported on various properties of Fe-based alloys, many of them focussed on mechanical and physical properties (e.g. magnetic properties) as well as ordering phenomena. (See, for example [1-20]). Mechanical as well as other physical or chemical properties can be positively influenced and optimized by alloying elements.

On alloying with other elements, iron forms frequently among others three different structure types: a disordered A2 type phase (αFe) phase and two ordered phases of B2-type (α_2) and D0₃-type (α_1), as observed in the Al-Fe system in [1]. A general proposal for ordering processes regarding changes or reduction of symmetry, respectively, was given by Landau [2, 3]. These symmetry changes cause a change of properties such as e.g. magnetic or dielectric susceptibility. According to Landau's interpretation the transition from a ferromagnetic to a paramagnetic state at the Curie temperature is one example of a second-order phase transitions ("A system has higher symmetry above a transition point than below it [2, 3]"). Whereas the melting and solidification respectively, represents a first-order phase transition.

Concerning the defect structure of the B2-phase (*cP2*, CsCl-structure type) two types of defect mechanisms are established: substitution, i.e. antistructure atoms on both sublattices [4], and triple defects [5]. By these mechanisms variable extension of the homogeneity ranges can be explained. A detailed investigation of ordering and disordering in the B2-phase of the Al-Fe system was done by Haberkern [6].

Al-Fe-based alloys are highly interesting for the development of new light-weight structural materials due to excellent corrosion resistance, high-temperature oxidation resistance and their low cost but they also suffer from lack of strength at high temperatures [7]. Al-Fe alloys, mainly those of B2 and D0₃-structure intermetallics were intensively studied [8-12]. For technical applications it is also important that the temperature of transition from D0₃→B2 occurring at 550 °C in the binary AlFe₃ increases by about 50 °C per at.% Ti due to alloying with Ti and 60 °C per at.% Si due to alloying Si [13-15]. A review of iron-aluminides is given by Sauthoff [16].

Al-Si alloys show low density and good tensile strength and are therefore used as structural materials [17]. Alloying with silicon, in general, improves the materials' properties such as corrosion resistance, ductility, thermal and electrical conductivity. Further advantages are low shrinkage which improves weldability and castability. A low thermal expansion coefficient [18, 19] is also beneficial for e.g. fabrication of pistons. A disadvantage, on the other hand, is low fracture toughness. Due to the economic and environmental requirements it is becoming increasingly important to reduce vehicle weight and still retain a high strength over weight ratio; thus Al-Si based alloys, e.g., are commercially used to produce engine blocks [20].

AlTi-based alloys and composites [21] are among of the most advanced materials for high-temperature structural applications and are considered for applications in aero-engine and automotive industry because of their combination of high strength and light weight [22, 23]. The disadvantages of TiAl-alloys are poor ductility and fracture toughness at low temperature.

Ti-Si alloys exhibit excellent chemical, physical and mechanical properties e.g. oxidation and creep resistance, low density, bending stiffness or yield strength. In addition Ti-silicides exhibit good electrical and thermal conductivity. In particular TiSi₂ are used in microelectronic devices (ultra-large- scale integration) due to the low electrical resistivity and chemical stability. [24-29].

FeTi-alloys based on the B2 structure are highly interesting for hydrogen storage materials [30-38].

Motivation

Ternary intermetallic compounds of transition metals with Al and Si are of potential interest for alloy development. Some phases existing in these systems are highly important for industrial application because of their advantageous properties. It is necessary to understand the change of equilibrium under the influence of temperature, mechanical stress and composition. Therefore phase diagram studies are essential in order to develop and optimize new alloys.

The ternary system Al–Fe–Si is of high interest because iron and silicon are two of the most common impurities in aluminium alloys; it was therefore well investigated in the context of alloy development, e.g. [39-44]. In combination with aluminium, these elements form hard and brittle ternary phases which exert an influence on the chemical and mechanical properties, like corrosion resistance and the surfaces properties. At the same time, a large variety of aluminium materials are known in which iron is a basic and necessary component. Among such materials are alloys produced by rapid solidification and by mechanical alloying; composite materials, and some wrought and heat-resistant conducting and corrosion-resistant cast alloys. Fe-based alloys with aluminium, titanium and silicon may also be important and therefore the intermetallic system Al–Fe–Si–Ti can be of potential interest for the development of new structural alloys based on Fe- and Ti-aluminides and composites with Ti-silicides for high temperature applications.

The present work represents a study in the ternary system Al–Fe–Si and the quaternary system Al–Fe–Si–Ti. This investigation was part of a research project with the aim to systematically investigate phase equilibria in Al–TM–Si systems (TM = Co, Cu, Fe, Mo, Ti, V). The aim of the investigations was to determine the phase equilibria and to characterize selected physical properties in the ternary system Al–Fe–Si and quaternary system Al–Fe–Si–Ti.

The Al–Fe–Si system was studied for an isothermal section at 800 °C in the Al-rich part and at 900 °C in the Fe-rich part and with particular emphasis on the description of half a dozen vertical sections at 27, 35, 40, 50 and 60 at.% Fe and 5 at.% Al in order to compare these with predictions based on the existing reaction scheme and liquidus surfaces [45, 46].

Furthermore detailed crystallographic information on trigonal τ_1 is presented, and a new high temperature phase τ_{12} is introduced.

Phase equilibria of Al–Fe–Si–Ti have been studied in the Fe-rich corner for sections at 50, 60 and 70 at.% Fe at 900 °C. Isothermal phase equilibria were investigated and phase boundaries of the phases, in particular of the Laves phase (Fe_2Ti) and of the extended phase field of A2/B2/D0₃, were investigated. Selected samples containing the Laves phase and the B2 phase were characterized by microhardness measurements at different compositions throughout the quaternary homogeneity range of the phases.

Furthermore, thermal reactions in the Fe-rich part were studied by differential thermal analysis (DTA). As cast alloys were investigated in order to gain additional information about primary crystallization fields. Three sections through the liquidus projection were constructed at 50, 60 and 70 at.% Fe considering the experimental data and those from literature. In addition, five selected vertical sections are presented. The microstructure of selected as-cast alloys in the primary crystallization fields of the Laves phase Fe_2Ti , the A2/B2 phase, FeSi and τ_2 (FeSiTi) are discussed.

The results of the present thesis were published in the three research papers [47-49] . Use of full article [47, 48] with permission from the publisher *Elsevier* (Elsevier Ltd, PO Box 800, Oxford OX5 1DX, UK) under license numbers: 3158210832280; 3158210600114.

2. Literature review

For the investigation of higher order systems the information of the limiting systems is essential and helpful to understand e.g. thermal reactions or to estimate phase boundaries. Therefore the information on the respective subsystems is of utmost importance.

2.1. The binary systems Al–Fe, Al–Si, Fe–Si and Fe–Ti

The binary limiting systems Al–Fe, Al–Si, Fe–Si and Fe–Ti are given in Massalski's Handbook of Binary Alloy Phase Diagrams [50, 51]. Phase equilibria of the binary systems are generally well known.

Al–Fe

The binary Al–Fe system [51, 52] given in Figure 1 was investigated and assessed repeatedly and most recently re-investigated by Stein and Palm [53] using DTA. The following phases have been found to exist: Al_2Fe [54], Al_5Fe_2 [55] and $\text{Al}_{13}\text{Fe}_4$ [56], (labeled as Al_3Fe from some authors) and. The iron rich part is dominated by the extended solid solutions of Al in (αFe) (A2), and the ordered phases AlFe (B2) and AlFe_3 (D0_3) [57, 58]. The D0_3 phase is only stable at temperatures below 600 °C. At 900 °C the phase boundary between (αFe) (A2) to AlFe (B2) is reported to be around 73 at.% Fe [53]. The fcc solid solution $\gamma(\text{Fe})$ (Strukturbericht designation A1, $cF4$, $Fm\bar{3}m$, Cu-type) solves up to 1.3 at.% Al and shows the so-called γ -loop between 912 °C and 1394 °C. Between 1401 °C and 1538 °C paramagnetic bcc (δFe) is the stable modification.

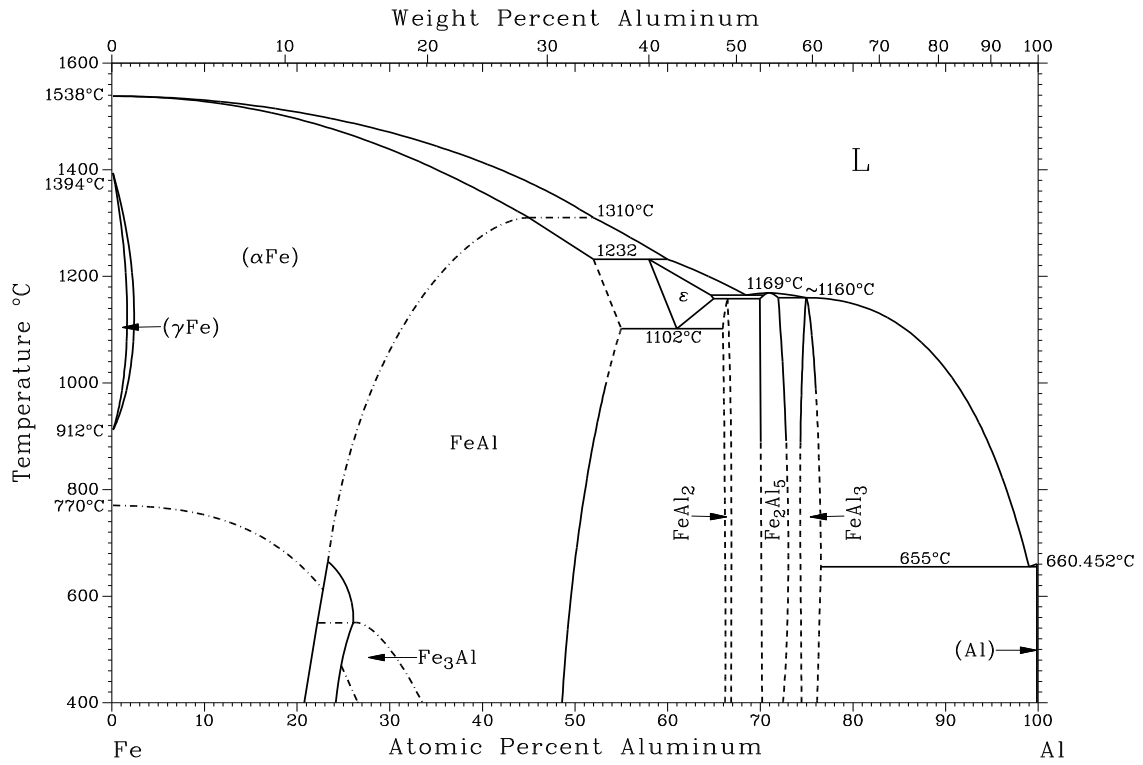


Figure 1. The binary phase diagrams Al-Fe [51].

Table 1. Stable crystal structure data of the Al–Fe system.

Phase	Composition (at.% Al)	Pearson symbol	Space group	Strukturbericht designation	Structure-type	Reference
(α Fe)	0 – $\approx$ 45	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	[59-61]
(γ Fe)	0 – 1.3	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	[62]
AlFe	23.3 – $\approx$ 55	<i>cP8</i>	<i>Pm</i> $\bar{3}m$	B2	CsCl	[57, 63-65]
AlFe ₃	$\approx$ 23 – $\approx$ 34	<i>cF16</i>	<i>Fm</i> $\bar{3}m$	D0 ₃	BiF ₃	[66, 67]
Al ₈ Fe ₅ (ϵ)	$\approx$ 58 – $\approx$ 65	<i>cI52</i>	<i>I</i> $\bar{4}3m$	D8 ₂	Cu ₅ Zn ₈	[53]
Al ₂ Fe	66 – 66.9	<i>aP18</i>	<i>P1</i>	–	Al ₂ Fe	[54]
Al ₅ Fe ₂	70 – 73	<i>oC*</i>	<i>Cmcm</i>	–	–	[55]
Al ₃ Fe Al ₁₃ Fe ₄	74.5 – 76.6	<i>mC102</i>	<i>C2/m</i>	–	–	[68, 69] [56]
(Al)	$\approx$ 100	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	[70, 71]

Al-Si

The binary Al-Si system [50] shown in Figure 2 is a simple eutectic system with a eutectic reaction of the fcc (Al) ($cF4$, $Fm\bar{3}m$, Cu-type) and the cubic (Si) ($cF8$, $Fd\bar{3}m$, C_{diamond} -type) at 577 °C at the composition $\text{Al}_{87.8}\text{Si}_{12.2}$.

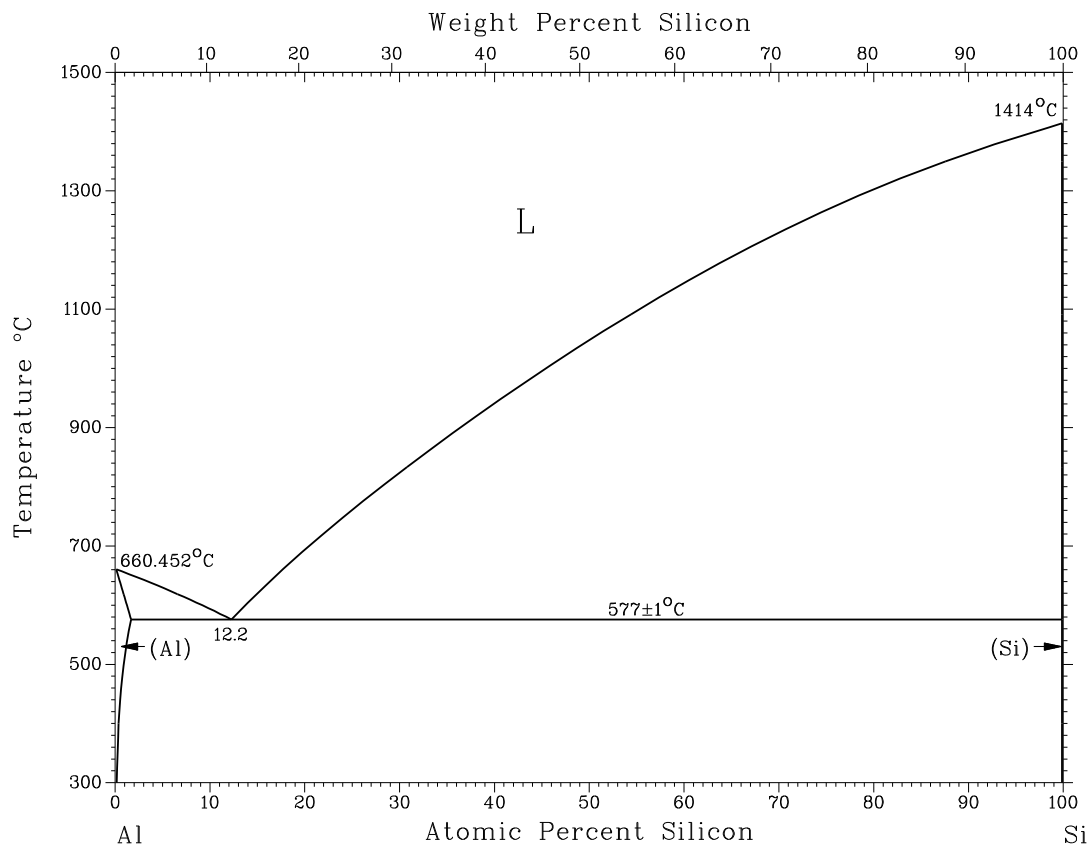


Figure 2. The binary phase diagrams Al-Si [51].

Table 2. Stable crystal structure data of the Al–Si system.

Phase	Composition (at.% Si)	Pearson symbol	Space group	Strukturbericht designation	Structure-type	Reference
(Al)	0 – 1.5	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	[51, 70, 71]
(Si)	99.984 – 100	<i>cF8</i>	<i>Fd</i> $\bar{3}m$	A4	C _(diamond)	[51, 72, 73]

Fe–Si

In the binary Fe–Si system [51, 74], given in Figure 3, similar as in the Al–Fe system the iron-rich alloys exist in both ordered, B2 and D0₃, and in disordered A2 modification. At 900 °C the solubility of Si in the D0₃ phase is about 27 at.%. Additional compounds established in the Fe-rich part of the system are Fe₂Si (β) [75], Fe₅Si₃ [76], FeSi [77] and FeSi₂ in a high- and low-temperature modification, ζ_β [78] and ζ_α [79], respectively. Selected crystal structure data are given in Table 3.

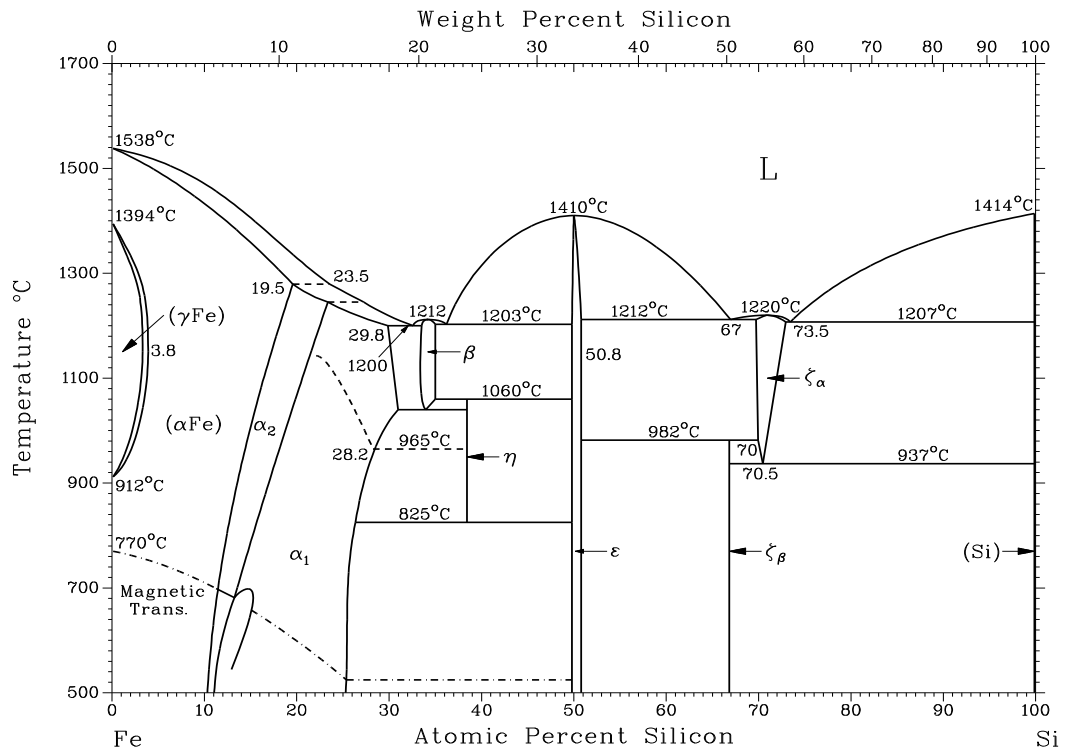


Figure 3. The binary phase diagrams Fe–Si [51].

Table 3. Stable crystal structure data of the Fe–Si system.

Phase	Composition (at.% Si)	Pearson symbol	Space group	Strukturbericht designation	Structure-type	Reference
(α Fe)	0 – 3.19	<i>cI2</i>	$Im\bar{3}m$	A2	W	[59-61]
(γ Fe)	0 – 19.5	<i>cF4</i>	$Fm\bar{3}m$	A1	Cu	[62]
α_2	$\approx 10 - 22$	<i>cP2</i>	$Pm\bar{3}m$	B2	CsCl	[57, 63-65]
α_1	$\approx 10 - \approx 30$	<i>cF16</i>	$Fm\bar{3}m$	D0 ₃	BiF ₃	[66, 67]
Fe ₂ Si	≈ 33.3	<i>hP6</i>	$P\bar{3}m1$	–	–	[75]
Fe ₅ Si ₃	37.5	<i>hP16</i>	$P6_3/mmc$	D8 ₈	Mn ₅ Si ₃	[76, 80]
FeSi	≈ 50	<i>cP2</i>	$P2_13$	B20	FeSi	[77]
α FeSi ₂ ¹⁾	66.7	<i>oC48</i>	<i>Cmca</i>	–	–	[79]
β FeSi ₂ ²⁾	69.5 – 73.5	<i>tP3</i>	$P4/mmm$	–	–	[78]
(Si)	100	<i>cF8</i>	$Fd\bar{3}m$	A4	C _(diamond)	[51, 72, 73, 81]

¹⁾ α FeSi₂ = LT-modification

²⁾ β FeSi₂ = HT-modification

Fe–Ti

In the binary Fe–Ti system the Fe-rich region is much less complicated (Figure 4) [81-84]. At 900 °C, the solubility of Ti in (α Fe) (A2) is about 4 at.%. The hexagonal Laves-phase Fe_2Ti (C14) [85, 86] shows a homogeneity range from around 66 to 72 at.% Fe and melts congruently at 1427 °C. Cubic FeTi (B2 structure) [87] shows a homogeneity range of about 2 at.% and melts in a peritectic reaction at 1317 °C. Selected crystal structure data are given in Table 4.

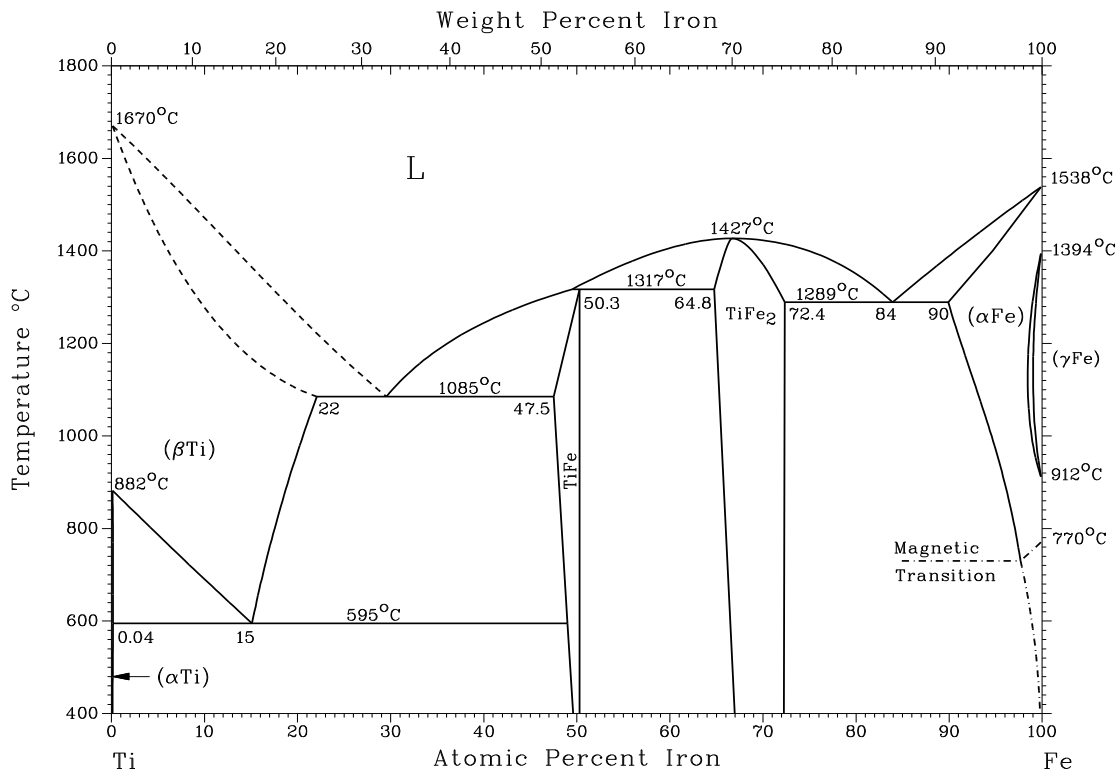


Figure 4. The binary phase diagrams Fe–Ti [51].

Table 4. Stable crystal structure data of the Fe–Ti system.

Phase	Composition (at.% Fe)	Pearson symbol	Space group	Strukturbericht designation	Structure-type	Reference
(α Ti)	0 – 0.04	<i>hP2</i>	<i>P6₃/mmc</i>	A3	Mg	[88, 89]
(β Ti)	0 – 22	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W	[90]
FeTi	48 – 50.2	<i>cP2</i>	<i>Pm$\bar{3}m$</i>	B2	CsCl	[91-93]
Fe ₂ Ti	64.5 – 72.4	<i>hP12</i>	<i>P6₃/mmc</i>	C14	MgZn ₂	[94]
(α Fe)	90 – 100	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W	[59-61]
(γ Fe)	99.4 – 100	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	A1	Cu	[62]

2.2. The ternary systems Al–Fe–Si, Al–Fe–Ti and Fe–Si–Ti

Al–Fe–Si

The ternary system Al–Fe–Si is characterized by a large number of ternary phases, both stable and metastable. 19 invariant reactions and 10 ternary phases were listed in [95, 96]. A number of detailed investigations were performed especially in the aluminium-rich corner. But only the Al-rich corner of the phase diagram was well understood and some of the phases were not sufficiently characterized in terms of their crystal structures and composition ranges. A critical review of the ternary Al–Fe–Si system was given by Ghosh [95, 97]. The author assessed the work of more than 150 research papers up to the year 1989. A comprehensive compilation of evaluated constitutional data and phase diagrams including recent updates is given in [98-100]. Krendelsberger et al. [46] reinvestigated the complete ternary system Al–Fe–Si within several isothermal sections and by thermal analysis. These authors constructed a complete liquidus surface projection and a consistent reaction scheme (Scheil diagram). Du et al. [45] subsequently published a thermodynamic assessment of the ternary system which basically relies on the data of Krendelsberger et al. [46], but differences are found in the liquidus projection as well as in parts of the reaction scheme. Maitra and Gupta [101] investigated the Al–Fe–Si system in the temperature range between 600 and 900 °C concerning the microstructure of binary and ternary phases using ternary diffusion couples. The drawn isothermal sections are inconsistent in some details with literature given by [98]. The 10 stable ternary phases are listed together with the respective references in Appendix-Table 1. Note that τ_9 is missing in this Table, as it was found to be identical with τ_1 by [46].

The Fe-rich corner is dominated by an extended A2/B2/D0₃ phase field. At temperatures below 600 °C it was found that phase separation between B2/D0₃ and A2/D0₃ occurs in the ternary system [8, 102]. At 700°C, however, no phase separation was observed [29]. At 900 °C the A2 modification ranges from approximately 26 at. % Al [81, 103] in Fe–Al to 13.5 at.% Si in Fe–Si. With regard to a comparison of isothermal sections from literature and found in this work it should be emphasized that orientation of the components in the Gibbs triangle is different. Note also that phase boundaries from literature (given in Figures 5 and 6) of several phases are drawn as circles only.

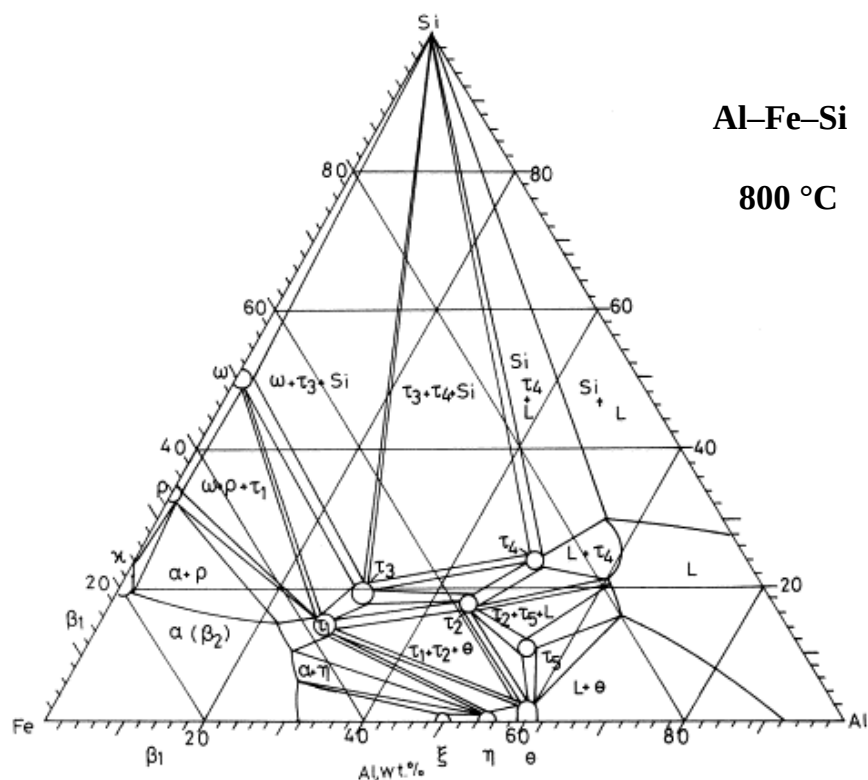


Figure 5. Isothermal section at 800 °C of the ternary system Al-Fe-Si from Gupta et. al [104].

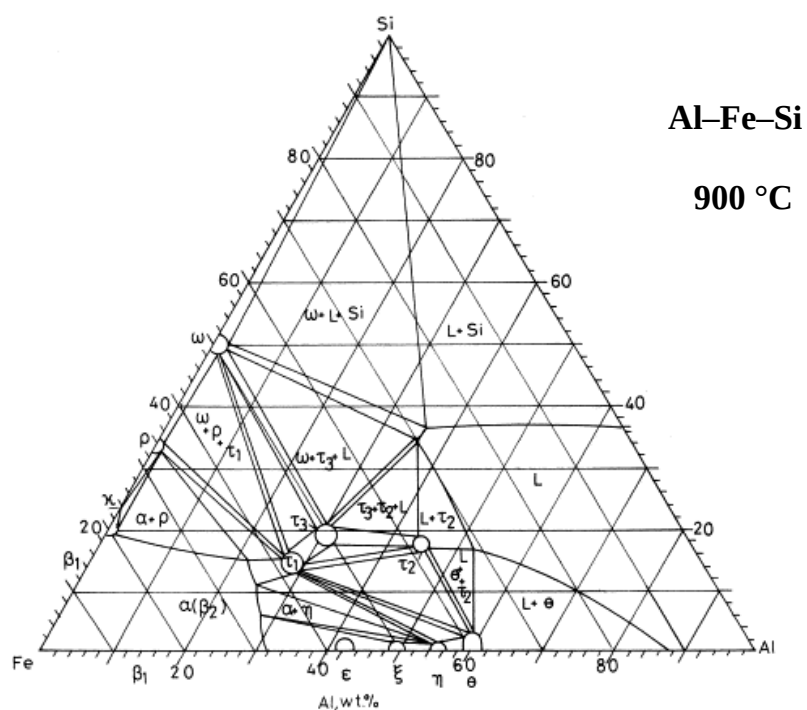


Figure 6. Isothermal section at 900 °C of the ternary system Al-Fe-Si from Gupta et. al [104].

Liquidus surface

In the liquidus projection of the Al–Fe–Si system (Figure 7) the thermal reaction scheme possesses a large number of invariant reactions mainly in the Al-rich corner [46, 98].

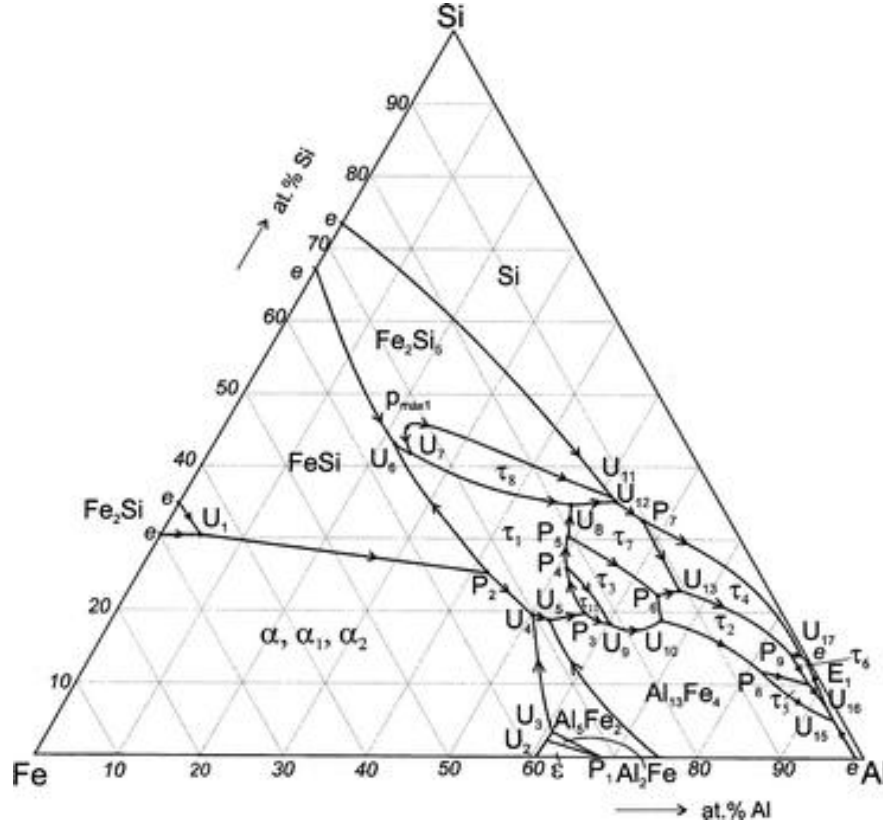
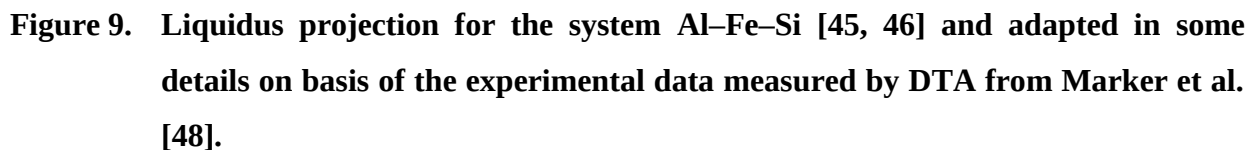


Figure 7. Liquidus projection for the system Al–Fe–Si [46].

The isotherms shown in the liquidus projection of the ternary system Al–Fe–Si shown in Figure 8 have been adopted from the calculation by Du et al. [45] and were adapted in some details on basis of the experimental data measured by DTA from Marker et al. [48] given in Figure 9. It should be mentioned that the primary crystallization of disordered A2 and ordered B2 from the melt has not been studied experimentally. Therefore no details are given in Figure 1 and the primary crystallization field is designated as bcc/B2. For the Fe-rich part (≥ 50 at.% Fe) only the transition-reaction U1: $L + \text{Fe}_2\text{Si} \rightleftharpoons (\text{A2/B2}) + \text{FeSi}$ is of importance.



Al–Fe–Ti

Detailed compilations of the ternary system Al–Fe–Ti are given by Raghavan [105] and Ghosh [106]. For this work the assessment of the ternary system given by Palm and Lacaze [107] was taken. Three ternary phases are reported in the system, but only two of them were confirmed [106, 107]: Al_2FeTi (τ_2) with primitive tetragonal crystal structure which shows a wide homogeneity range, and cubic Al_8FeTi_3 (τ_3 , L_{12} structure, $cP4$, $Pm\bar{3}m$, AuCu_3 -type). In the Fe-rich part a two-phase field between B2 and L_{21} exists. Phase fields of A2/B2 and B2/ L_{21} are separated by second order transition lines. The Laves phase (Fe_2Ti) and FeTi show extended solubilities for Al [94]. The solid solubility of Ti in (αFe) (A2) and AlFe (B2) increases with increasing temperature and reaches approximately 10 at.% at 900 °C.

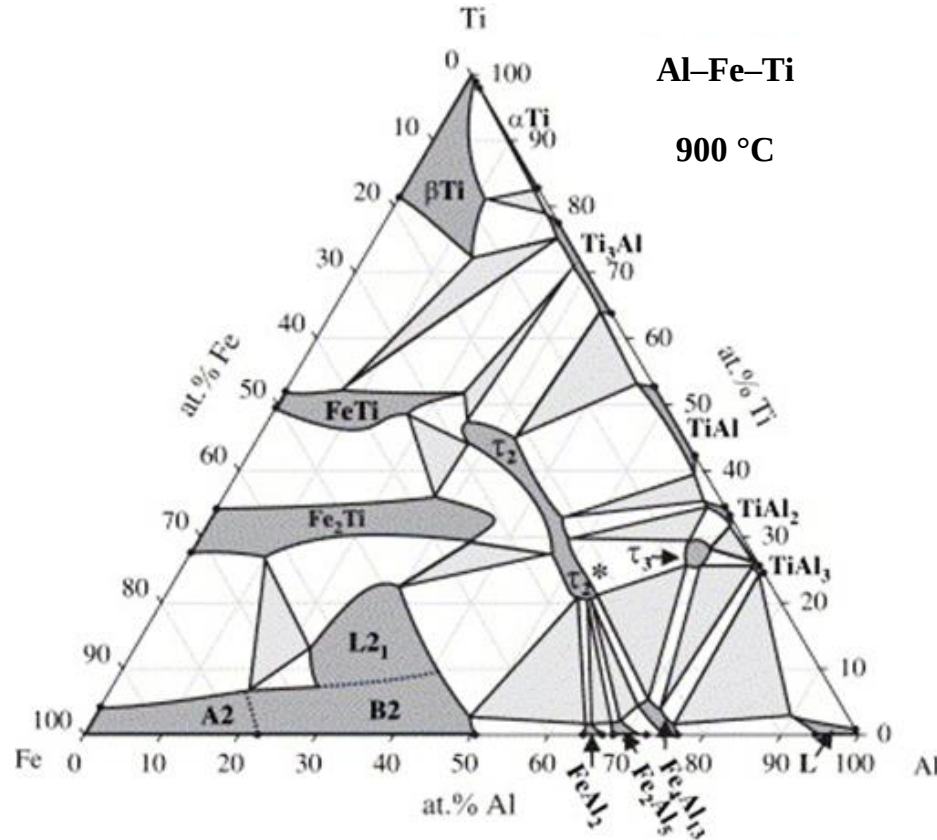


Figure 10. Isothermal section at 900 °C of the system Al–Fe–Ti from Palm and Lacaze [107].

The D0_3 ordered phase is only present in the ternary and shows a solubility of up to approximately 25 at.% Ti at 900°C [108],[107]. This means a significant stabilization of D0_3 by the

addition of Ti, as the D0₃/B2 transition temperature increases from 574 °C in the binary to 1212 °C in the ternary system. Note that this phase field is denoted L2₁ (corresponding to the ternary ordered variant) in Figure 10, but will be designated as D0₃ throughout the current work for the sake of consistency.

Liquidus surface

For the Al–Fe–Ti [107, 109, 110] system, the Al-rich corner shows a couple of invariant reactions which are well established. The two fields of primary crystallization of the Laves phase and A2/B2 dominate the Fe-rich area. The existence of a L2₁ primary crystallization field reported earlier, could not be confirmed later [109].

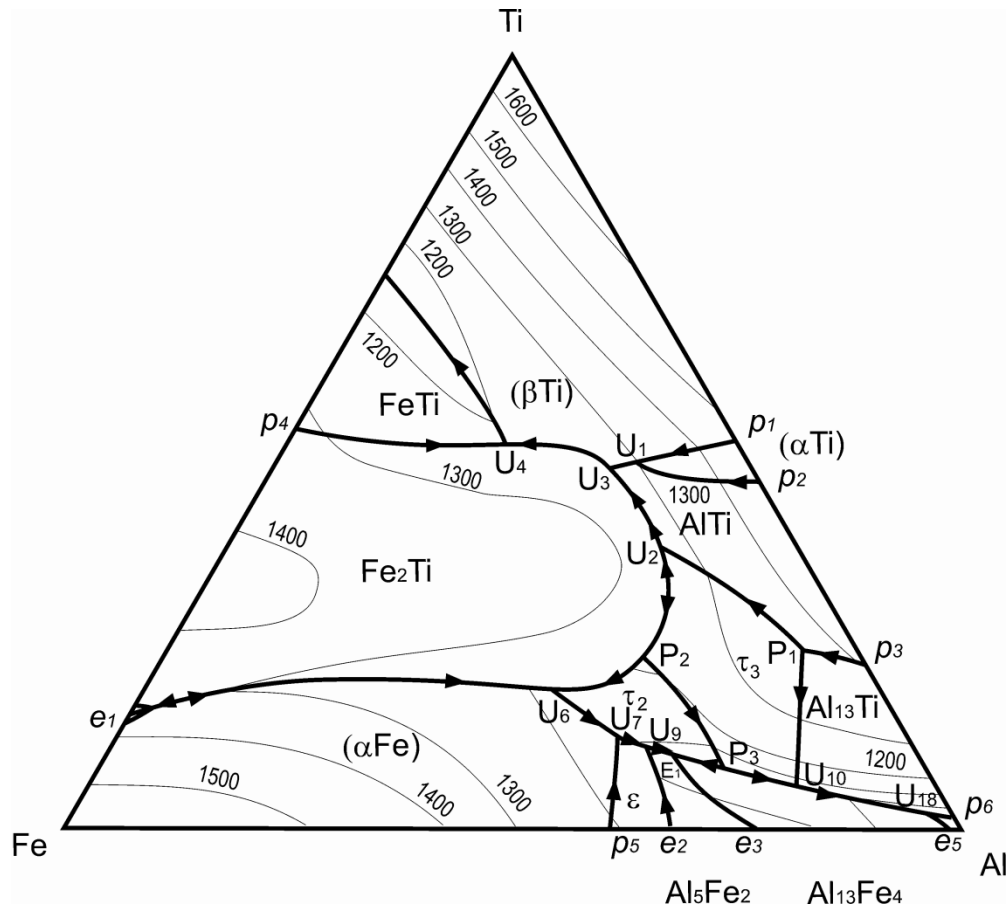


Figure 11. Liquidus projection for the system Al–Fe–Ti [109].

Fe–Si–Ti

The ternary system Fe–Si–Ti (Figure 12) is reviewed by Raghavan [111]. Similar to Al–Fe–Si it is a rather complex system with many ternary compounds. For the current investigation only two ternary phases are of interest; orthorhombic FeSiTi (τ_2) and Fe₄Si₃Ti (τ_3) with hexagonal Pd₄₀Sn₃₁Y₁₃-structure type. Schuster et al. [112] report a large solubility of more than 25 at.% Si in the Laves-phase Fe₂Ti. At 900 °C, the composition of FeSiTi is varying between 31.7 - 37.0 at.% Fe, 30.5 - 33.5 at.% Si and 31.0 - 37.5 at.% Ti. A solubility of 9.5 at.% Ti was found for Fe₅Si₃ [112]. For the binary Fe₃Si phase (D0₃-structure) a solubility of about 2 at.% Fe from 68.2-70 at.%, 1 at.% Si ranging from 26.3-27.2 at.% and 2 at.% Ti in the range of 3.3-5.5 at.% at 900 °C was found [112]. The solubility of Ti in FeSi is limited to 1 at.%. The maximum solubility of Ti in the A2/B2/D0₃ phase field was found to be around 9 at.% [112].

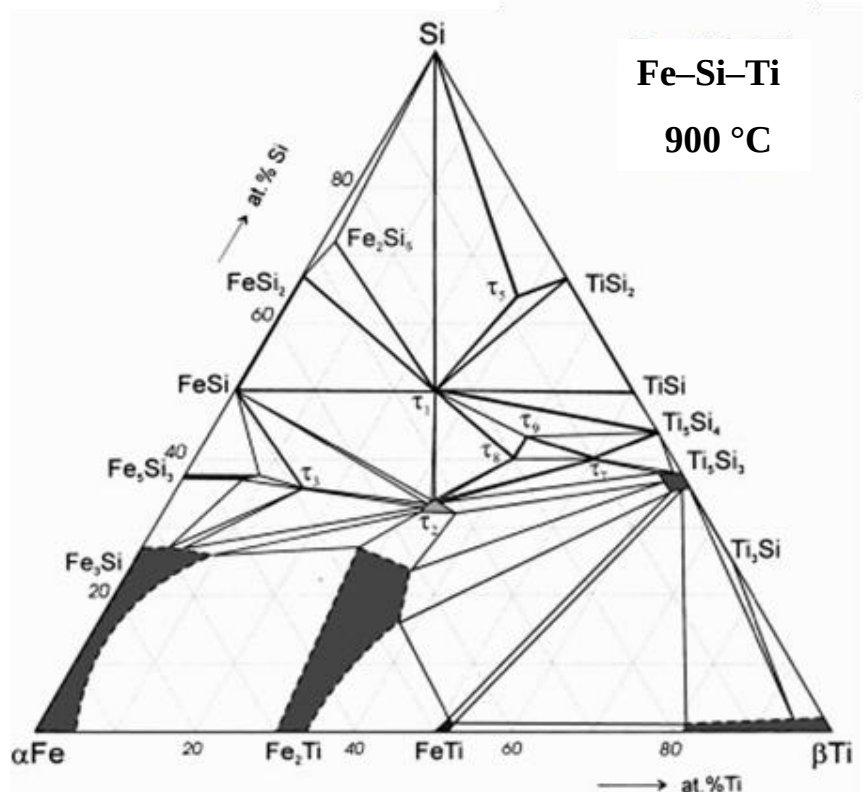


Figure 12. Isothermal section at 900 °C of the ternary system Fe–Si–Ti from Schuster et al. for Fe–Si–Ti [112].

Liquidus surface

The reaction scheme of Fe–Si–Ti is well-known and was investigated thoroughly by Schuster et al. [112]. With increasing silicon content the melting point of the Laves phase is shifted to higher temperature. An incongruent melting of the ternary Laves phase $(\text{Fe}_{1-x}\text{Si}_x)_2\text{Ti}$ at 1591 °C was observed [112] which is in agreement with Böhm et al. [113]. In contrast the binary Laves phase Fe_2Ti melts congruently at 1427 °C [51]. Furthermore, the monovariant eutectic reaction $L \rightleftharpoons \text{A2/B2} + \text{Fe}_2\text{Ti}$ was found at higher temperature between 1311 - 1317 °C in the ternary alloys [112], whereas the binary eutectic formation takes place at 1293 °C. They also could confirm the ternary eutectic reaction $E_3: L \rightleftharpoons \tau_3 + \text{B2} + \text{Fe}_5\text{Si}_3$ at 1151 °C mentioned before in [114]. For the ternary compound FeSiTi (τ_2) a congruent melting reaction was determined at 1760 ± 20 °C by [115]. Also, the peritectic formation of the ternary phase $\text{Fe}_4\text{Si}_3\text{Ti}$ (τ_3), $P_7: L + \text{FeSi} + \tau_2 \rightleftharpoons \tau_3$ at 1241 °C was determined [112]. Isotherms were given in a partial liquidus projection of Fe–Si–Ti only for the Fe-rich corner (> 75 at.% Fe) [116, 117].

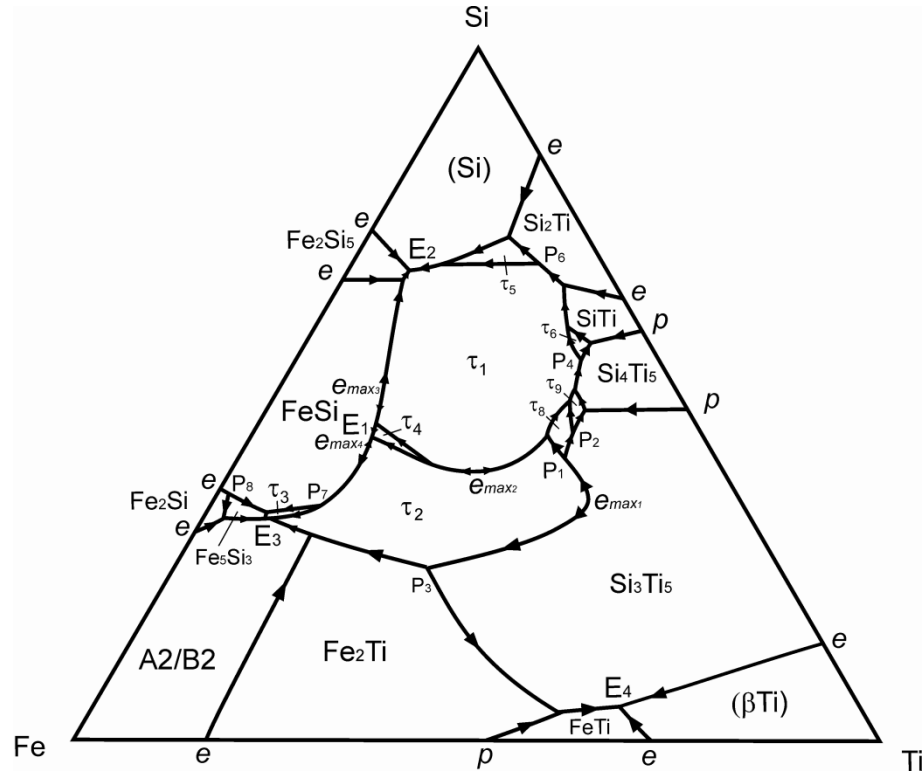


Figure 13. Liquidus projection for the system Fe–Si–Ti. The phase fields of A2 and B2 are not separated [112].

Al-Fe-Si-Ti

For the quaternary system Al-Fe-Si-Ti, literature data are only available in the aluminium corner. The system was studied by DTA at 550-850 °C in the concentration range of 10-14 at.% Si, 0-3 at.% Fe and 0-0.6 at.% Ti) at and was reviewed by Zakharov et al.[118].

3. Experimental and methods

3.1. Sample preparation

All samples were prepared from pure elements using aluminium slug (3.175 mm, 99.999 % Alfa Aesar, Karlsruhe, Germany), an iron foil/sheet (99.95%, melted and cast in vacuum), silicon lump (0.1 – 2.5 cm, 99.9999 % Alfa Aesar, Karlsruhe, Germany) and titanium rod (6.4 and 3.175 mm dia., 99.99 % Alfa Aesar, Karlsruhe, Germany). Calculated amounts of the elements were weighed to an accuracy of better than 0.06 % and then arc melted on a water-cooled copper plate under an argon atmosphere of 0.5 bar, using zirconium as a getter material (Figure 14). More than 100 samples were prepared for the investigation in the ternary system Al–Fe–Si and were re-melted 2 – 4 times for homogenization. For the investigation in the quaternary system Al–Fe–Si–Ti a total number of more than 70 samples were prepared. After the first melting, each ingot was pulverized, pressed to a pellet and re-melted for homogenization.



Figure 14. Water-cooled copper plate, serves as anode. Under an argon atmosphere of 0.5 bar, using zirconium (in the centered position) as a getter material, the alloy is melted.

After this procedure the samples were weighed back in order to check the mass losses. The mass loss was between 0.2 – 0.8 %. For equilibration the ternary ingots were annealed in alumina crucibles at 800 °C and 900 °C for 336 – 870 hours in sealed and evacuated quartz glass tubes. A part of the samples prepared for investigation in the quaternary system Al–Fe–Si–Ti was used as-cast for primary crystallization studies, while the rest of the alloys was wrapped in Mo-foil, sealed in evacuated quartz glass tubes and annealed at 900 °C for 360 – 1030 hours in a muffle-furnace. All handling of the samples was done with due care to minimize any potential reaction with oxygen. The variation of annealing time for different sample series did not have significant effects on the observed phase compositions. Although it cannot be ruled out that some of the samples were not fully equilibrated after annealing, it was concluded that the annealing time was generally sufficient to reach equilibrium at 800 and 900°C respectively. After quenching in water, the samples were separated into several pieces that were used for subsequent characterization.



Figure 15. Sealed and evacuated quartz glass tubes with (quaternary) ingots wrapped in Mo-foil and embedded samples.

3.2. Characterization methods

In each system series of samples were prepared with varying nominal compositions. For investigation of phase equilibria alloys were heat-treated, then separated and investigated with different methods: (I) For metallographic investigations, pieces of the as-cast and quenched samples were incorporated into a mixture of resin and carbon powder. The embedded samples were ground and polished in order to perform optical microscopy (LOM). Electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) were used to determine the exact phase compositions. (II) Powdered alloys were used for structure identification with X-ray diffraction (XRD). (III) Thermal reactions of equilibrated alloys were studied by differential thermal analysis (DTA). Mechanical properties of embedded samples were characterized by microhardness measurements (MH).

3.2.1. Optical microscopy (LOM)

The reflected light microscope or metallurgical microscope is a convenient method to get a first impression of the quality of the samples such as number, size and dispersion of phases, kind of reactions (eutectic, peritectic texture) and homogeneity of microstructure. The optical imaging is done by using embedded alloys with flat polished surface. Using the bright field mode phases can be identified due to their different reflectance or roughness. Dark field mode can be used to detect small edges related to the presence of scratches, cracks, grain boundaries or holes. Therefore an estimation of the quality of the polished surface and surface structure is possible. For identification of number and orientation of phases the polarization mode is used. Due to the optical properties of each phase and the use of polarized light different phases appear in varying colours. Different behavior of the polarizing surfaces can be identified by rotating the embedded sample.

For the investigation by optical microscopy a Zeiss Axiotech 100 microscope equipped for operation under darkfield, brightfield as well as polarized light and a Zeiss STEMI 2000 microscope for single crystals selection respectively, were used.

3.2.2. Electron probe microanalysis (EPMA) and Scanning electron microscopy (SEM)

Electron microscopy is a powerful technique to get information about microstructure and quantitative information of composition. Therefore it is used in a broad range of applications in the fields of research and industry. Due to the varying electron density of atoms reflected by the respective atomic numbers, each element has a higher or lower backscatter coefficient. A higher atomic number is related to a brighter contrast and vice versa. Backscattered electrons (BSE) produced by the primary electron beam represent high energy electrons. Using this method the contrast is obtained due to the difference of the average atomic number. Using secondary electrons for imaging the contrast is obtained by the topology of the surface. Hence for optical imaging of the surface of specimens to obtain grains boundaries and analyse phase composition BSE and SE imaging are used.

By excitation with high-energy electrons each element emits its own characteristic X-ray spectrum. The spectra of the specific atoms provide the concentration and consequently the composition of the specimen. For the quantitative analysis two different analytical techniques can be used: wavelength dispersive spectroscopy (WDS) and energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) uses EDS. Electron probe micro analysis (EPMA) uses WDS and is used predominantly for a quantitative analysis of the composition of equilibrium phases.

Selected samples were analyzed by EPMA in order to determine reliable compositions of the various phases. Measurements were carried out on a Cameca SX 100 electron probe, a JEOL JXA8800 micro-analyzer and a Zeiss Supra 55 VP scanning electron microscope, using wavelength dispersive X-ray spectroscopy (WDS) for quantitative analysis. Conventional ZAF matrix correction was used to calculate the final composition from the measured X-ray intensities; i.e. matrix effects of atomic number Z, X-ray absorption A and X-ray fluorescence F have been calculated separately for Al, Fe, Si and Ti.

Pure element standards (aluminium, iron, silicon and titanium) were used for calibration before the measurement with a relative accuracy of about $\pm 1\%$. The measurements were carried out at 15–20 kV and 20–30 nA.

3.2.3. X-ray diffraction measurements (XRD)

X-ray powder diffraction is the most important method for phase identification and partially quantitative information of phase composition and is deployed for manifold applications. Therefore it is used for the qualitative identification of crystalline phases or compounds (e.g. quality control in industry), phase identification and determination of cell parameters, structural model refinement, and solubility of texture analysis or investigation of domain size. Based on the *Laue equation* $a \cdot \sin \Phi = n \cdot \lambda$ [119, 120] and the subsequent approach of *Bragg's law* $2 \cdot d \cdot \sin \vartheta = n \cdot \lambda$ [121] it is possible to get information on the cell metric. Hence the Bragg approach is to consider crystals as built up of layers or planes such that they act as semi-transparent mirrors. The respective planes correspond to the crystallographic planes which are described by the Miller Indices (h k l). Each crystalline solid has its own characteristic powder pattern.

In general terms, peak positions give the information of the unit cell parameters a , b , c , α , β and γ , intensity of peaks about crystal structure details such as electron density hence atom position (x , y , z), site occupation and thermal displacement parameters.

With the structure information from literature e.g. Pearson's handbook of crystallographic data [122] or from the ICSD (Inorganic Crystal Structure Database from FIZ/NIST¹), it is possible to refine parameters of the measured diffractogram. The principle is based on the comparison of the measured diffractogram with the calculated pattern based on a literature structural model. Positions and intensities of peaks can be shifted in the refined pattern due to the characteristics of respective measured component or compound. Hence the information about substitution or preferred occupation of respective atom positions is possible. In this context the refinement of atom positions can be done, information on substitution and hence partially quantitative information on phase composition is possible.

The X-ray powder diffractograms were refined by the Rietveld method [123-125] using a least square approach. The Rietveld method used in this work was done with the *fundamental parameter approach* [126-128].

¹ Fachinformationszentrum Karlsruhe / The National Institute of Standards and Technology
http://www.fiz-karlsruhe.de/crystal_structure_dep.html

It is a mathematical description using structure-, profile- and instrument-related parameters, i.e. profiles are calculated from instrumental setup and no empirical profile parameters are refined. For the refinement of the measured data based on this method the software program TOPAS[®] 3 [129] was used. The process of refinement of parameters has to be done step by step. After each step the refined parameters have to be controlled in order to obtain physically reasonable results. Refinement of cell parameters and atom positions should be carried out in any case whenever no more details of structure information are required. In case of substitution or of elements with similar scattering factor and minority phases the refinement of further parameters e.g. site occupation or displacement factor needs experience and has to be done therefore with care.

X-ray powder diffraction was performed with Cu K α -radiation, using a Bruker D8 Advance diffractometer with Bragg–Brentano pseudo-focusing geometry and the ratio of sample/detector moving was $\theta/2\theta$. For detection a one-dimensional silicon-strip detector (Lynxeye) was used. The principle is based on the fact that a certain angular range is detected simultaneously and added to form the overall signal at the respective angle. The Lynxeye detector was used in most cases. However, for high contents of Fe in the specimens, an energy-dispersive detector (Sol-X, Lithium drifted Silicon detector) was used in order to avoid background/peak ratio problems related to the X-ray fluorescence of Fe caused by Cu K α -radiation.

Single crystal X-ray diffraction (XRD) was used for crystal structure determination. Single crystals for the structure determination were separated from the bulk sample under an optical microscope. Diffraction data were collected on a NONIUS four-circle diffractometer equipped with a CCD detector and a 300 μm capillary-optics collimator (Mo tube, graphite monochromator). Unit-cell parameters were obtained by least-squares refinements of 2θ values. Corrections for Lorentz polarization and absorption effects were done by application of the multi-scan method, complex scattering functions [130]. The structure solution by direct methods and subsequent structure refinement was performed using SHELXL-97 [131, 132].

3.2.1. Differential thermal analysis (DTA)

Thermal analysis represents the characterization and measurement of physical and chemical properties/transformations of materials as a function of temperature. Uses of thermal analysis in solid state chemistry include the study of solid state reactions, thermal decompositions and phase transitions. This information is used supplementary and combined with additional methods for phase diagram determination.

The principle of DTA is the measurement of difference of the temperature ΔT between the sample and a reference, which is an inert material, as a function of temperature. The signal therefore is due to changes in heat content during a programmed change of temperature. In principle, the temperature of the sample and the reference should be the same during heating until a thermal reaction such as a solid state reaction, a phase transition, decomposition or melting takes place. Depending on the nature of effect the temperature of the sample drops behind the reference material in case of an endothermic reaction (e.g. melting), or leads the temperature, in case of an exothermic reaction (e.g. solidifying). Interpretation of observed effects (invariant and non-invariant reactions) should be done in combination with additional information of the phase reactions/equilibria in the system of interest. The determination of values of reaction temperatures is done by the analysis of the onset, the peak maximum or the step (end of the reaction) for non-invariant reactions and by the extrapolated onset for invariant reactions. An example of a DTA-curve and interpretation of observed effects is given in Figure 16. Usually two heating- and cooling-cycles are carried out in order to get representative values for repeatable reaction temperatures. Equilibrium effects of the measured alloy can usually only be observed in the first heating curve. During the solidification process sometimes the phenomenon of supercooling can be observed, i.e. the crystallization temperature is lower than the melting temperature. This effect can be affected by e.g. the sample volume, crystal structure of the solid or cooling rate.

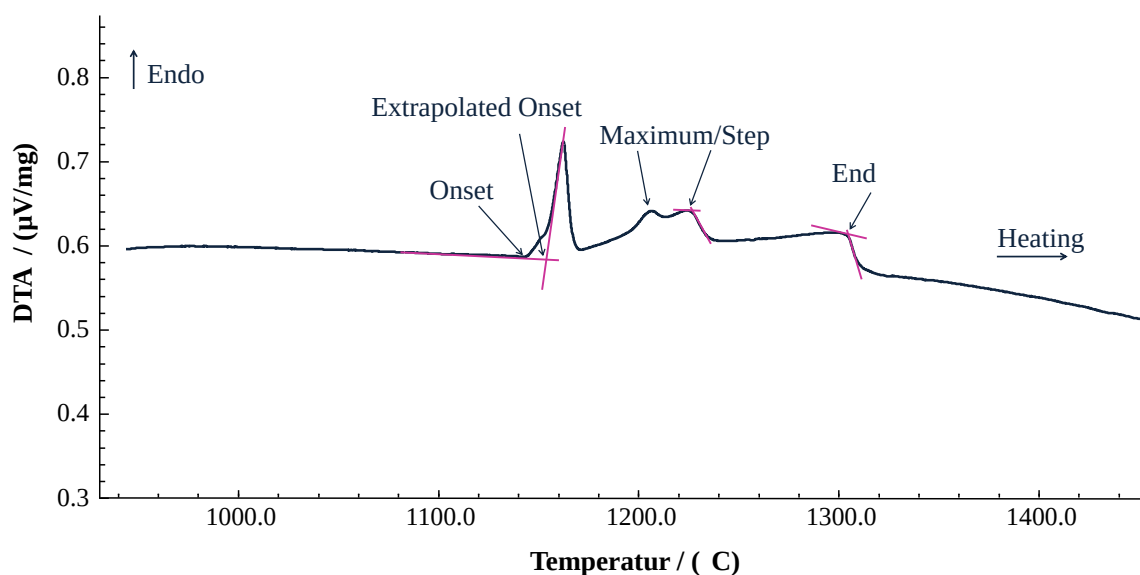


Figure 16. Experimental DTA curve and significant points.

The equilibrated samples were used for DTA measurements which were performed on a DTA 404 S and 404 PC (NETZSCH, Germany) using alumina crucibles with cover and employing a slow permanent argon flow of $50 \text{ ml} \cdot \text{min}^{-1}$. A sample mass between 25 and 60 mg was used for the experiments and the samples were checked routinely for possible mass changes during the DTA investigations. No relevant mass changes were observed. Two heating- and cooling-curves were recorded for each sample starting at the temperature of equilibration at 800 and 900 °C in the ternary system and 900 °C in the quaternary system respectively, using a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$. The maximum temperature was 1490 °C. The Pt/Pt10%Rh thermocouples of the DTA instrument were calibrated using the melting points of pure Al, Au and Ni.

3.2.2. Microhardness measurements (MH)

Microhardness measurement is a powerful method for measuring hardness and elastic modulus. The advantage of this method in the micro/nanometer scales is the determination of mechanical properties such as creep properties of the material of e.g. intermetallic alloys

directly from the indentation load and unload respectively. From the shape of the measured curve, mechanical parameters can be calculated. A detailed explanation of this method is given in [133-137]. In Figure 17 the schematic representation of the experimental arrangement and the measurement principle is shown.

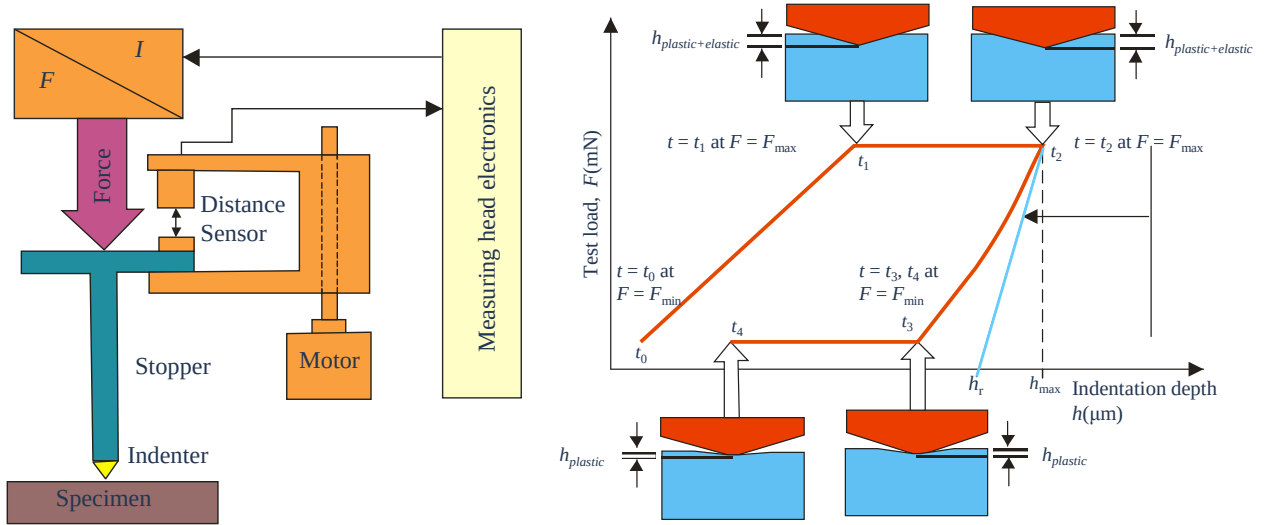


Figure 17. Calculating the “modulus of indentation” E_{IT} on the basis of the slope of the tangent on the unloading curve with $F = F_{\max}$. The plastic hardness or the indentation hardness is calculated as per h_r [138].

The plastic and elastic deformation is obtained by the hardness indentation obtained from the application of the test load minimum at time t_0 and maximum at t_1 . Within this period the hardness will be calculated as a function of indentation depth. Information about creep properties of the material can be obtained by the change in indentation depth during $t_1 - t_2$ (compare also Figure 17). In this step the maximum test load is kept constant. The "modulus of indentation" is calculated from unload of the test load during $t_2 - t_3$ and is given by slope of the curve at $F_{\max}$. While the test load is kept at a constant minimum in $t_3 - t_4$, the relaxation can be analyzed. From the form of damage conclusions can be drawn about the constitution of the surface layer of the specimen. The measuring head contains the indenter, the test load generating unit and the position measurement unit for determining the indentation depth.

The indenter is generally a square-based diamond pyramid as per Vickers with 136° plane angle (compare Figure 18). The value of HV is determined by:

$$HV = \frac{2F \cdot \sin \frac{136^\circ}{2}}{d^2} = 1.8544 \cdot 0.1020 \cdot \frac{F}{d^2} = 0.1891 \frac{F}{d^2} . \quad \text{Eq. (1)}$$

F applied test load (N) instead of kilopond (1 N = 0.1020 kp)

d diagonal length of the indentation

Microhardness measurements were performed using a Microhardness tester FISCHER-SCOPE® HM2000 Analyzer on the embedded samples previously analysed with EPMA. All measurements were performed under the following condition: $F = 50.000 \text{ mN}$ for 20s.

From the recorded measurement plot, the Vickers hardness HV was used for characterization. Evaluation of data was done with the WIN-HCU® software [139], which is a computer-controlled measuring system for microhardness testing and determination of material parameters according to ISO 14577-1.

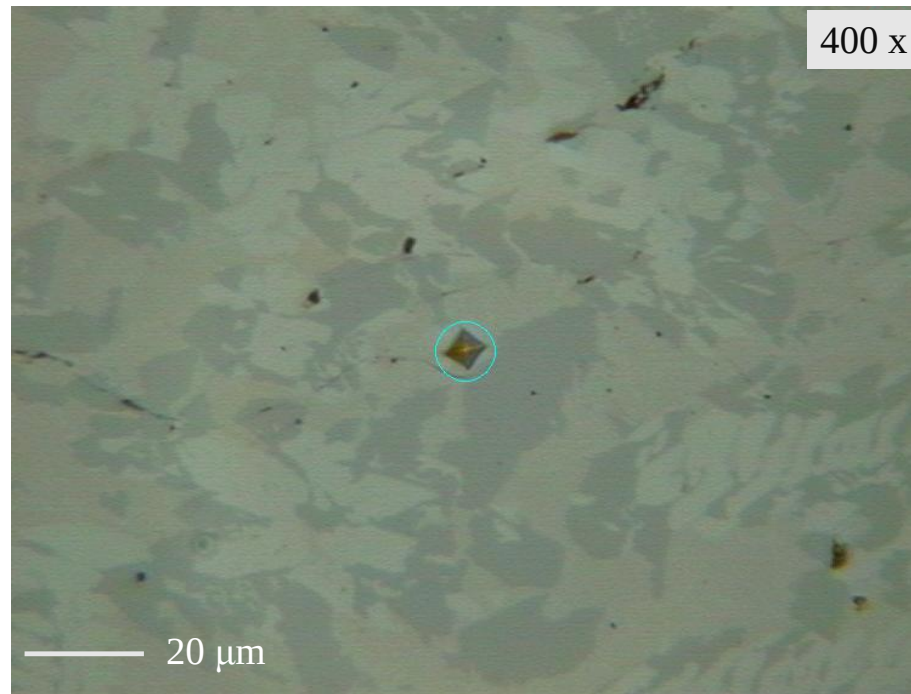


Figure 18. Typical indentation of penetration of a Vickers diamond on the specimen surface. (Quaternary alloy No. 07 with the nominal composition $\text{Al}_5\text{Fe}_{50}\text{Si}_{35}\text{Ti}_{10}$).

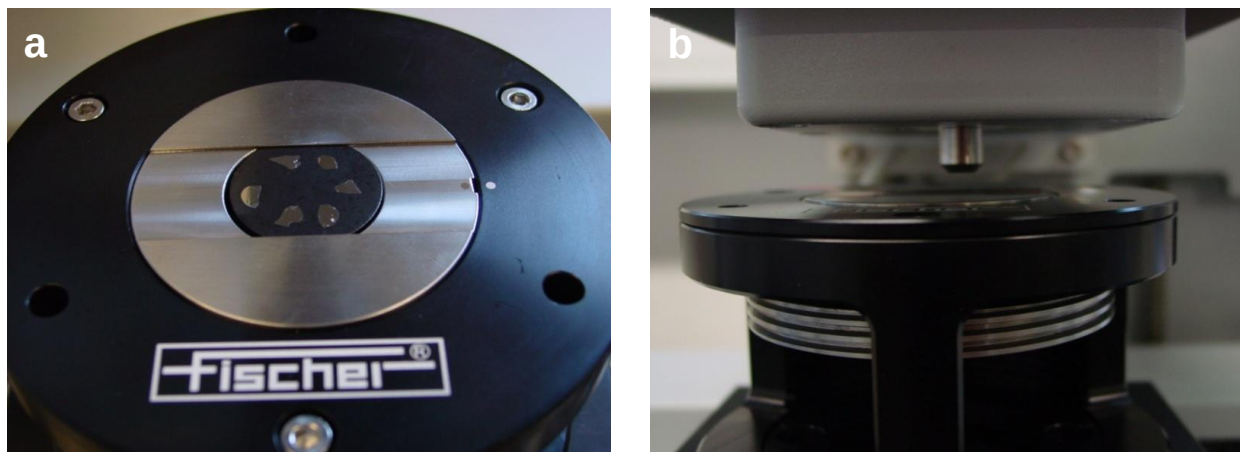


Figure 19. Sample stage (a) and measuring head (b) of the Microhardness tester FISCHERSCOPE® HM2000 Analyzer.

3.3. Method of presentation

Phase diagrams

Knowledge of phase diagrams is taken for granted, but with respect to the presented quaternary system discussed later in text and a better readability of the quaternary phase relationships, selected basics and definitions are given below.

In general, a phase diagram describes the state of a materials system in thermodynamic equilibrium as a function of temperature, pressure and composition. According to the *Gibbs phase rule* for condensed systems ($p = \text{constant}$; variation of pressure has for conventional experiment conditions insignificant effect on the equilibrium [140]):

$$P + F = C + 1 \quad \text{Eq. (2)}$$

F ...degrees of freedom respectively the variance of the system

C ...numbers of independent components

P ...phases

According to Eq. 2 in general, following reaction-types are possible (compare Table 5):

Table 5. General reaction-types for binary, ternary and quaternary systems.

		Binary system		Ternary system		Quaternary system	
degrees of freedom	reaction-type	components	phases	components	phases	components	phases
$F = 0$	invariant	$C = 2$	$P = 3$	$C = 3$	$P = 4$	$C = 4$	$P = 5$
$F = 1$	monovariant	$C = 2$	$P = 2$	$C = 3$	$P = 3$	$C = 4$	$P = 4$
$F = 2$	bivariant	$C = 2$	$P = 1$	$C = 3$	$P = 2$	$C = 4$	$P = 3$
$F = 3$	tervariant	–	–	$C = 3$	$P = 1$	$C = 4$	$P = 2$
$F = 4$	quadrivariant	–	–	–	–	$C = 4$	$P = 1$
<i>and so on</i>							

So the theoretical study of phase diagrams begins with the thermodynamics of first-order phase transition. For two phases the condition for thermodynamic equilibrium is the equality of temperature, pressure, and chemical potential of all components [141]. With this information the “reading” of phase diagrams is possible. The complexity of construction of phase diagrams increases with the number of components and therefore a short introduction is given in this context.

Three component system A–B–C

An example of a ternary phase diagram is given in Figure 20. It is a three dimensional representation of the content of the three components A, B, C given in triangular coordinates as a function of temperature. For the construction of phase equilibria at a given temperature T_1 the isothermal section is presented by a plane in form of a triangle (pink triangles) given in Figure 20.

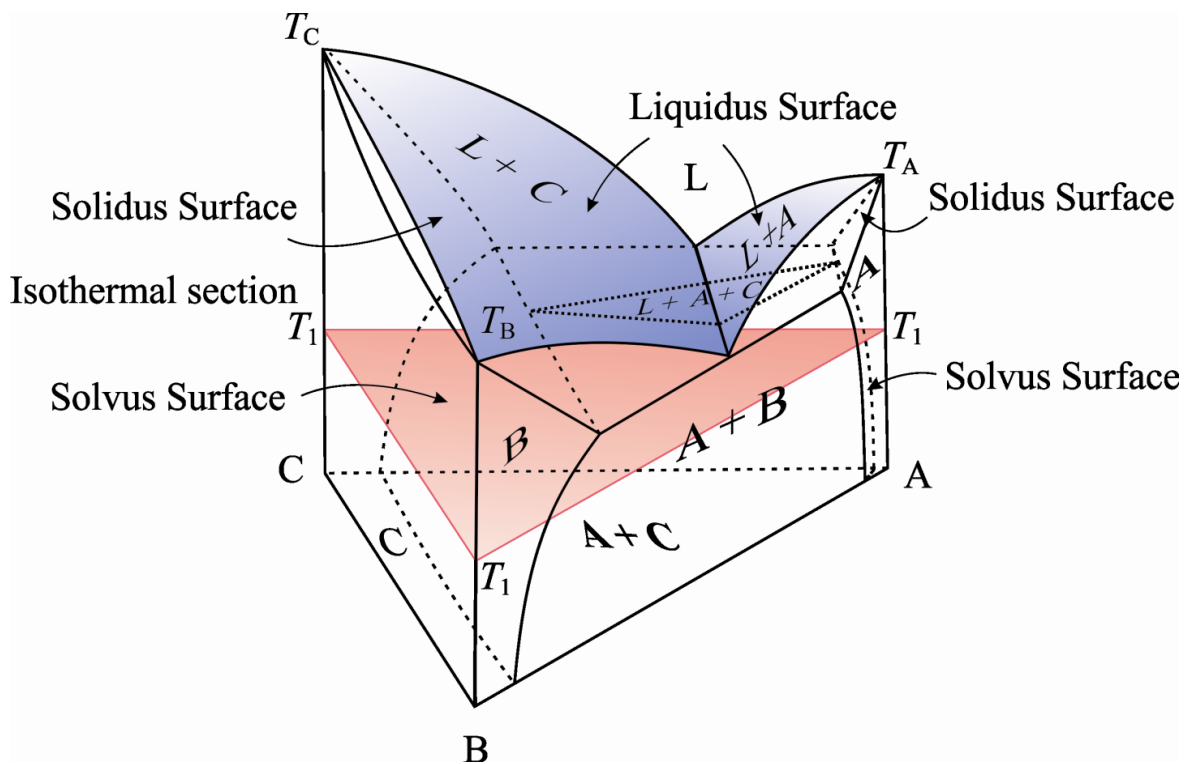


Figure 20. Three-component phase diagram of A, B and C.

A different way for representation of phase reactions is a two-dimensional construction in form of a vertical section (isopleth). It is a section along a constant content of one component or constant concentration ratio of two components as a function of temperature (compare also Figure 21). To see the position of the vertical section (given as blue square), the context to the three-dimensional phase diagram is presented in Figure 21. An example of a ternary isopleth is given in Figure 22.

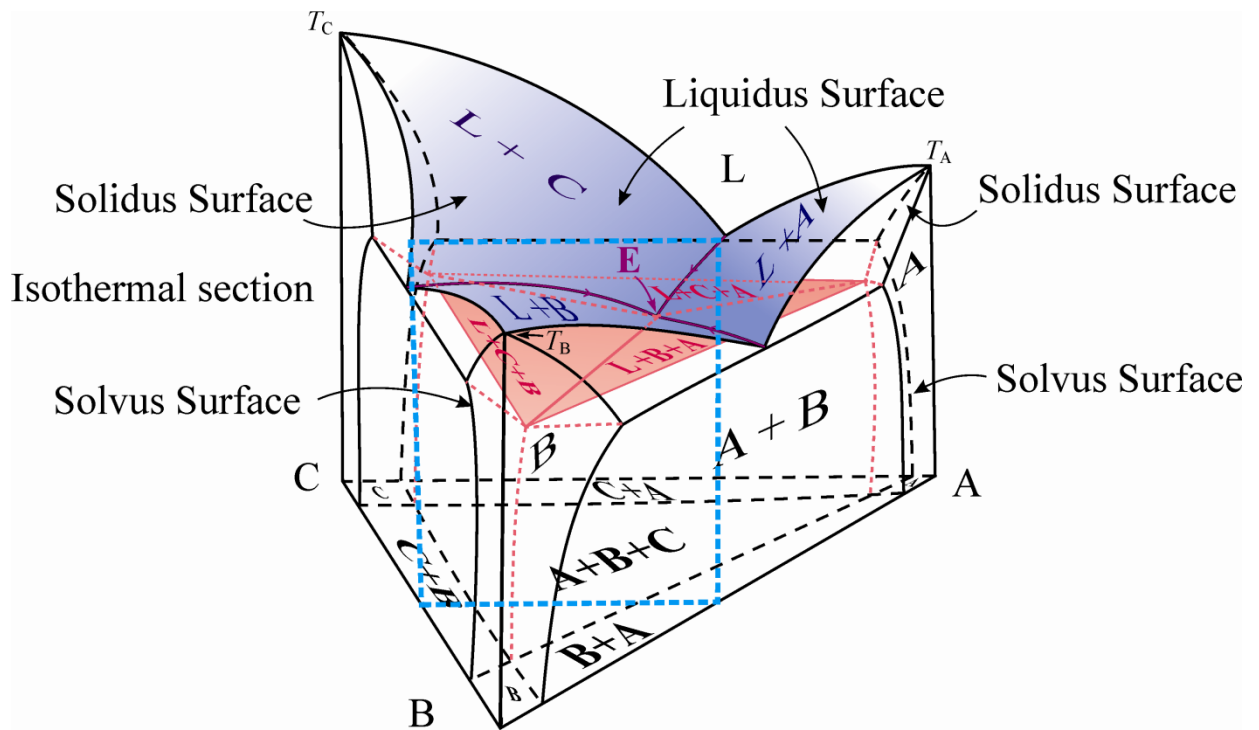


Figure 21. Eutectic reaction in the ternary system A-B-C.

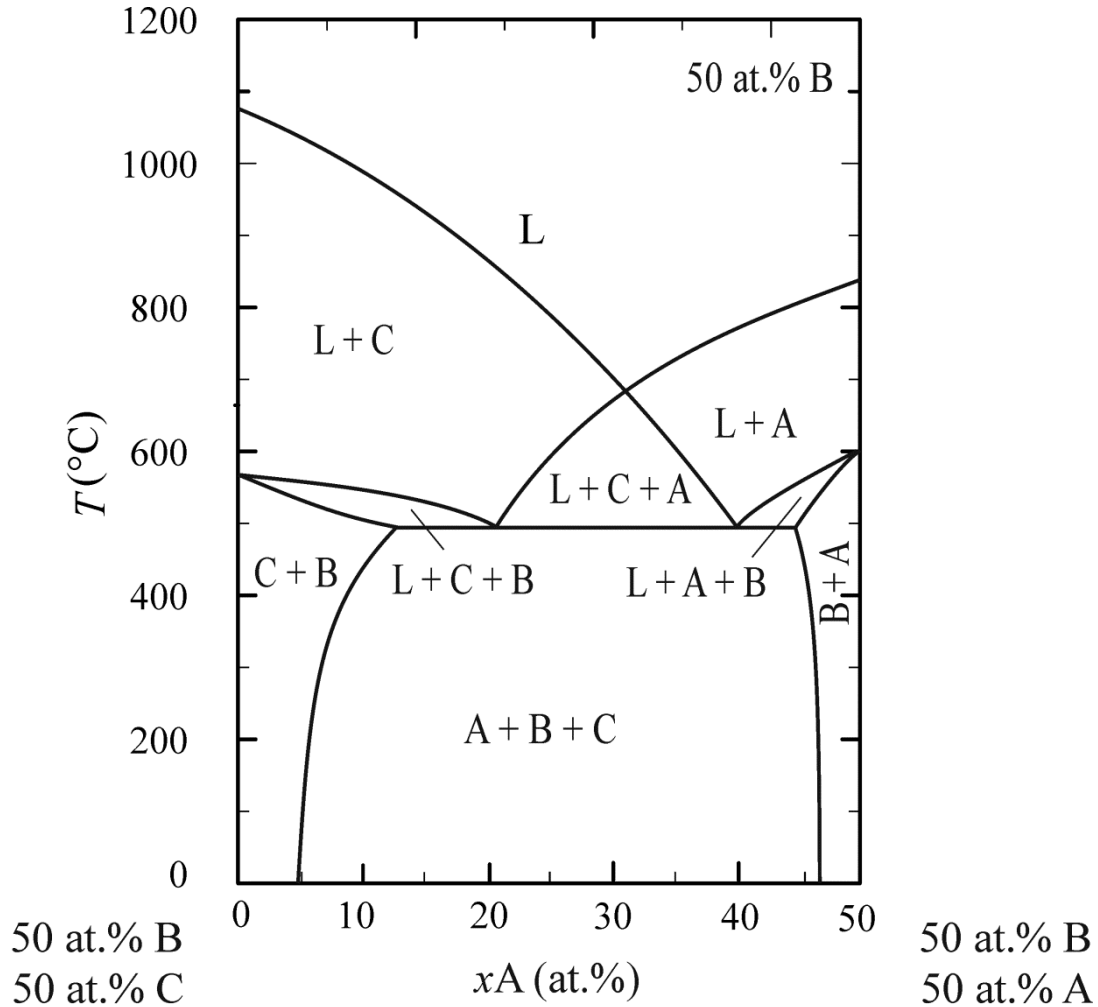


Figure 22. Vertical section (isopleth) at 50 at.% B in the ternary system A-B-C.

In addition, equilibrium data can be represented as liquid projection in the form of the composition triangle and the various reaction paths, in this case represented by the monovariant lines (liquidus troughs) which separate the primary crystallization fields. This form can be used to study sequences of solidification and primary crystallization, respectively. It is a top view on the liquidus surface. An example of a ternary eutectic phase reaction including the trenches separating the primary crystallization fields is given in Figure 23 in form of a liquidus projection.

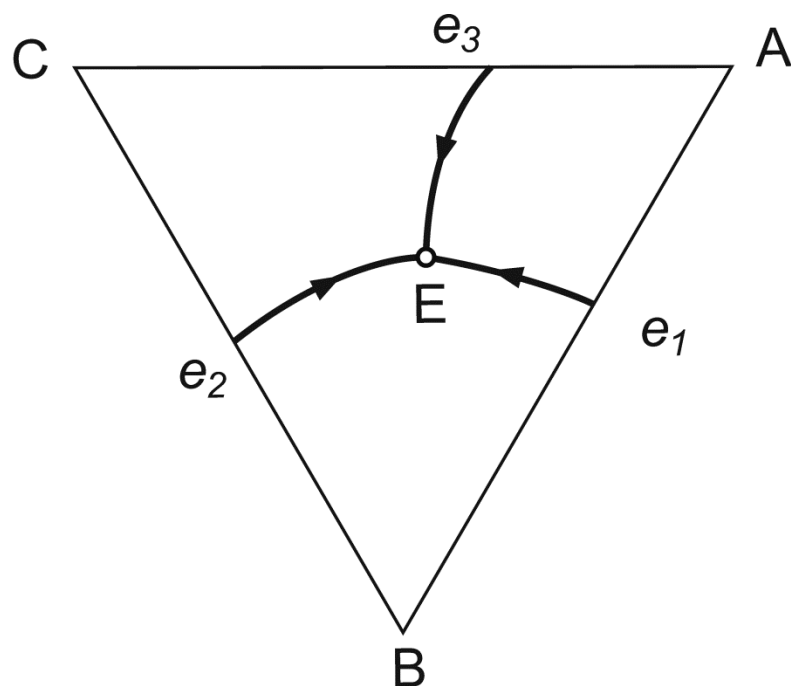


Figure 23. Schematic liquidus projection of a ternary eutectic phase reaction.

With regard to the different phase reactions which can be drawn in the diagram it is clear that due to the presence of additional reactions (e.g. invariant reactions) such phase diagram constructions will appear far more complex and confusing. There are different options for drawing multi-component phase diagrams, depending on the number of variables, and additionally by the possibility of 2- and 3-dimensional phase diagram representations, respectively.

A detailed explanation of construction of ternary phase equilibria is given in [142].

Four component system A–B–C–D

A quaternary system contains four components: A, B, C and D. It is represented by the four variables compositions X_A , X_B , X_C and temperature T ($X_D = 1 - (X_A + X_B + X_C)$). For the graphical presentation of phase equilibria the temperature must be kept constant. A full isothermal section of a quaternary system can only be represented in three dimensions

(in the form of a composition tetrahedron) which is, however, not very practical for use. The depiction of composition in the form of tetrahedron coordinates is shown in Figure 24.

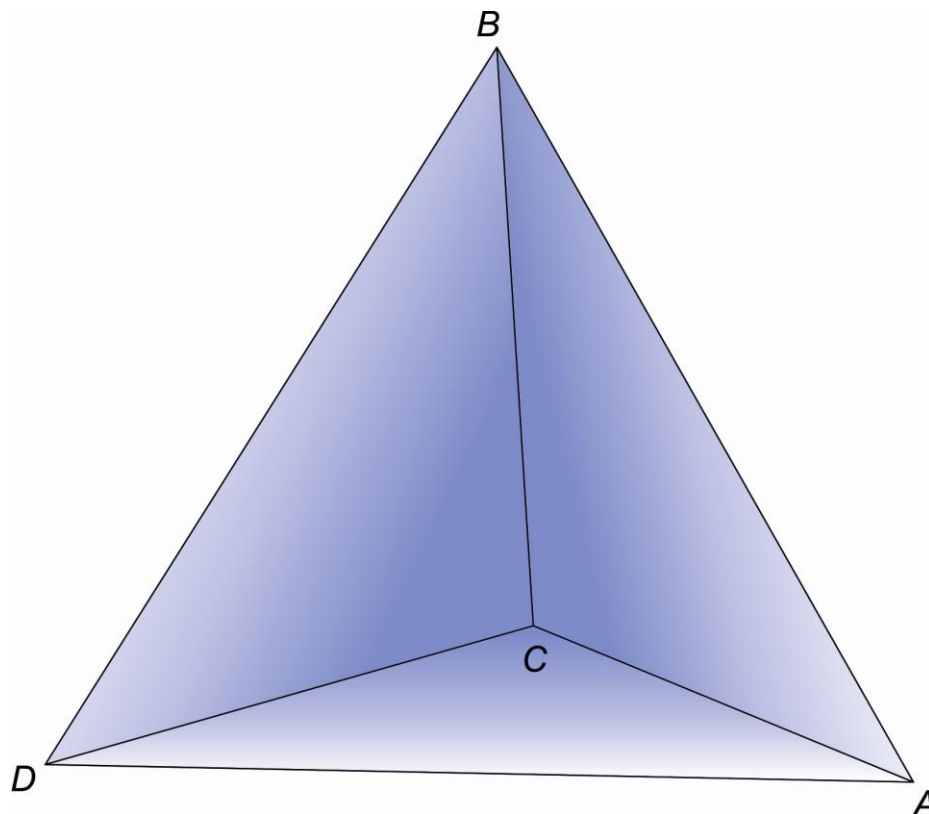


Figure 24. Graphical representation of a quaternary system A–B–C–D. The tetrahedron shows isobaric and isothermal conditions with the variables X_A , X_B , X_C .

To draw a two-dimensional section, some options are possible. In Figure 25 two examples for an isobaric-isothermal intersection through a quaternary system are shown. An alloy at *c* has the binary composition 50 at.% D and 50 at.% B. Alloys along the line *a-b*, *b-c* and *c-a* are binary and within the section *a-b-c* have a composition of 50 at.% B. Alloys along *d-f* show always the same concentration ratio of $X_A : X_C$. All alloys prepared in the section *d-e-f* possess the same and constant ratio of $(X_A + X_D) : X_C$. A more detailed explanation of drawing phase equilibria, and also with regard to the correlation to the ternary systems will be discussed in 4.2.

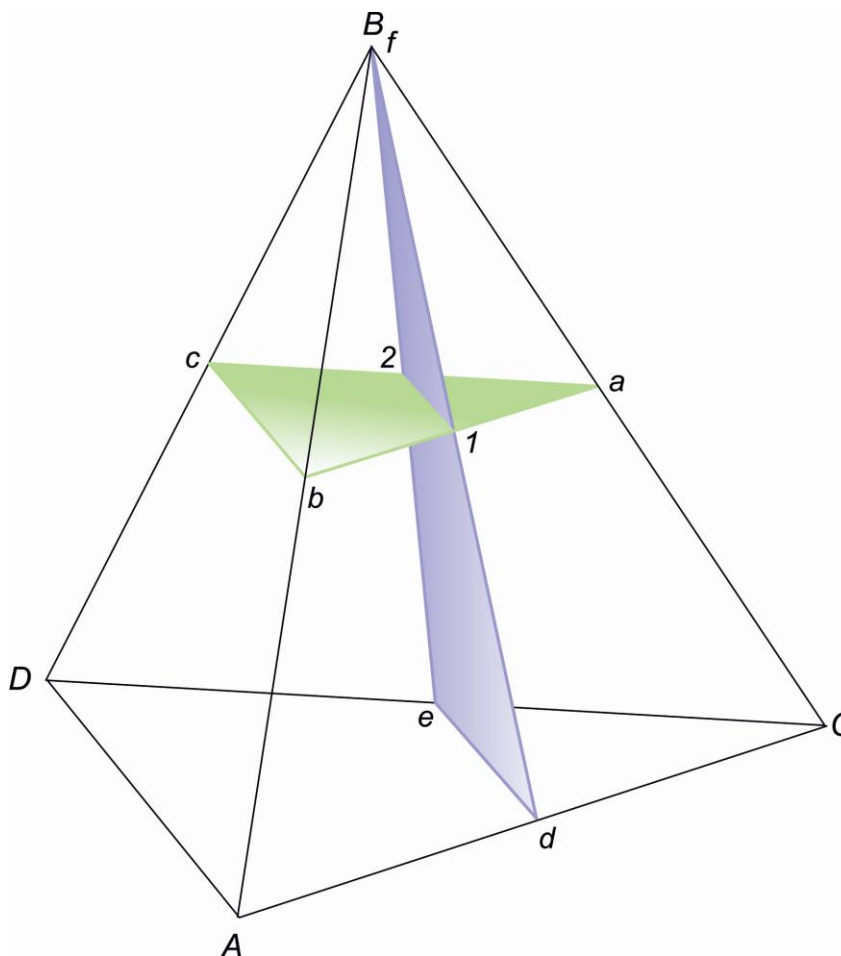


Figure 25. Graphical representation of two intersections in a quaternary isothermal tetrahedron.

To keep the overview of phase reactions in a diagram a concise representation is helpful. In higher order systems the form of presentation is crucial for the conveyance of the information. For presentation of the thermal phase reactions (vertical section) in a four-component system the composition of two components or any relations among them has to be fixed and the composition of the residual components (difference to 100 at.%) is given as a function of temperature.

Last, but not least, for the graphical construction of phase diagrams certain rules have to be taken into account: Gibbs phase rule, Schreinemakers rule [143] or Palatnik-Landau's contact rule [144].

4. Results and discussion

4.1. Results in the ternary system Al–Fe–Si

Text and figures of this chapter are taken from the publication: *M.C.J. Marker, B. Skolyszewska-Kühberger, H.S. Effenberg, C. Schmetterer, K.W. Richter, Phase equilibria and structural investigations in the system Al-Fe-Si, Intermetallics, 19 (2011) 1919-1929.* A few additional remarks and comments have been added.

A total number of 73 samples were studied for isothermal phase equilibria and for thermal reactions. These samples were situated in 6 different sections at 27, 35, 40, 50 and 60 at.% Fe and at 5 at.% Al, respectively. The sample compositions are shown in Figure 26 with different symbols indicating annealing at 800 and 900 °C, respectively.

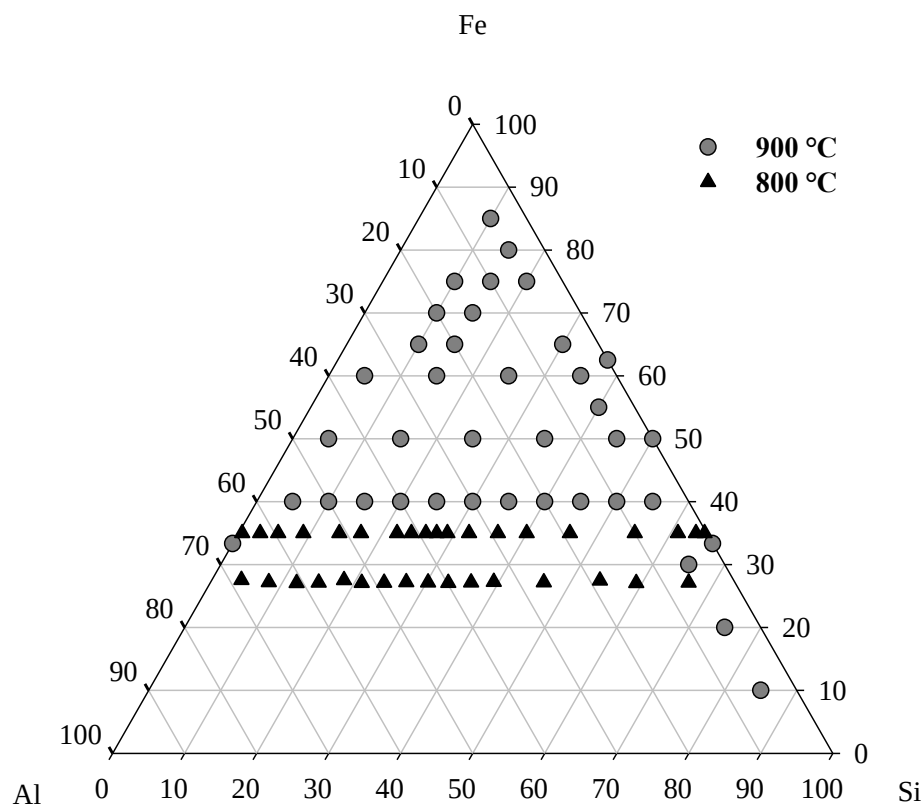


Figure 26. Sample composition of binary and ternary samples investigated in the system Al–Fe–Si annealed at 800 °C (black triangles) and 900 °C (grey circles).

Additional samples were prepared in different areas of the system for primary crystallization tests (as cast), and for various annealing experiments to clarify details of solid state equilibria at different temperatures.

4.1.1. Isothermal sections at 800 and 900 °C

The isothermal sections as proposed from the experimental investigations are shown in Figures 27 and 28. These figures combine the results from XRD with exact phase compositions measured by EPMA, shown as open circles. The iron-poor part of the system, i.e. the equilibria with the liquid and τ_4 were not directly measured by EPMA. Instead the phase fields were extrapolated on basis of the work from Krendelsberger et al. [46]. Experimental data for selected samples situated in relevant three-phase fields are listed in Appendix-Table 2.

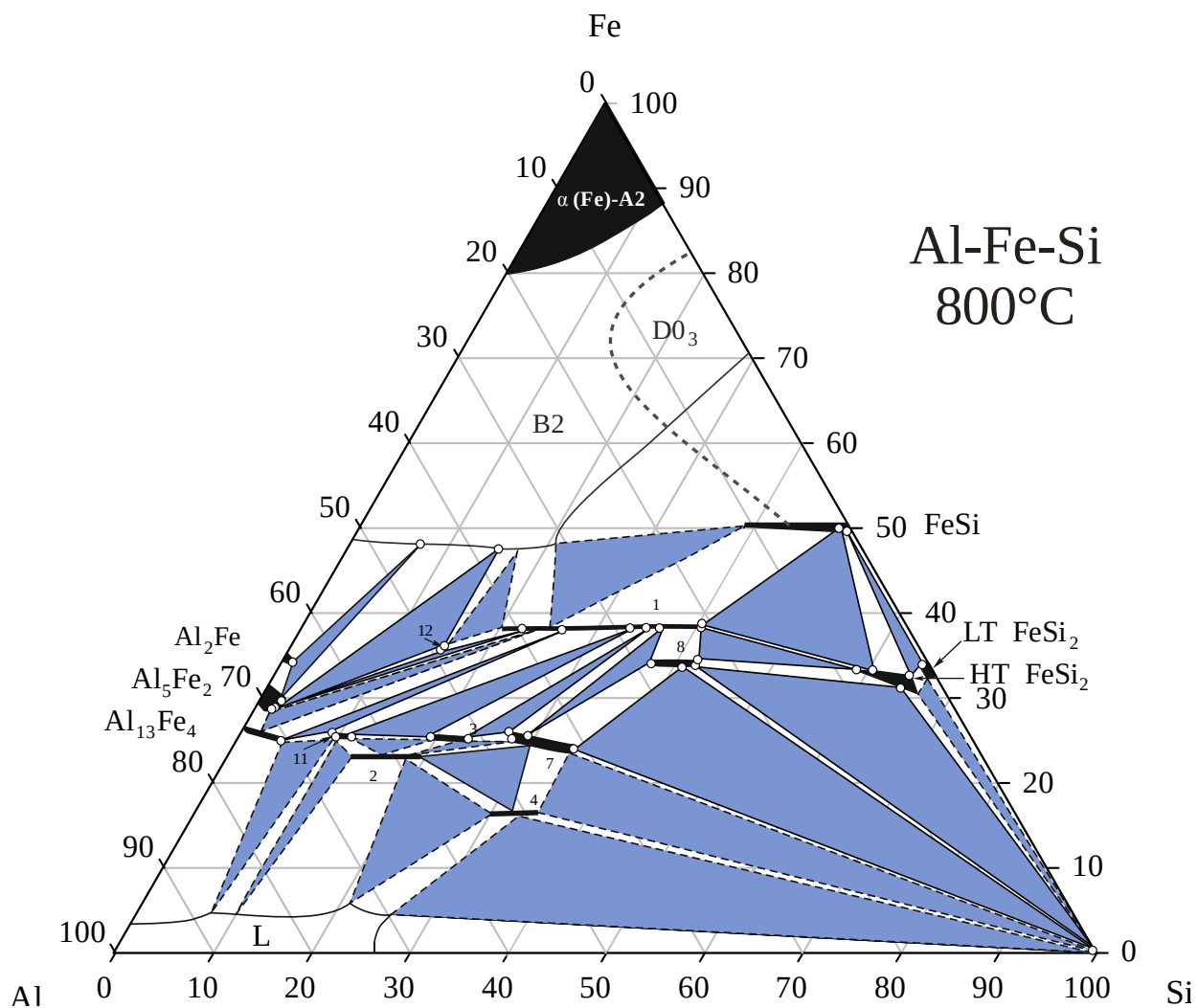


Figure 27. Isothermal section of Al-Fe-Si at 800 °C. Phase equilibria are drawn according to experimental results listed in Appendix-Table 2. The composition of the phase boundaries measured with EPMA, are plotted with white circles.

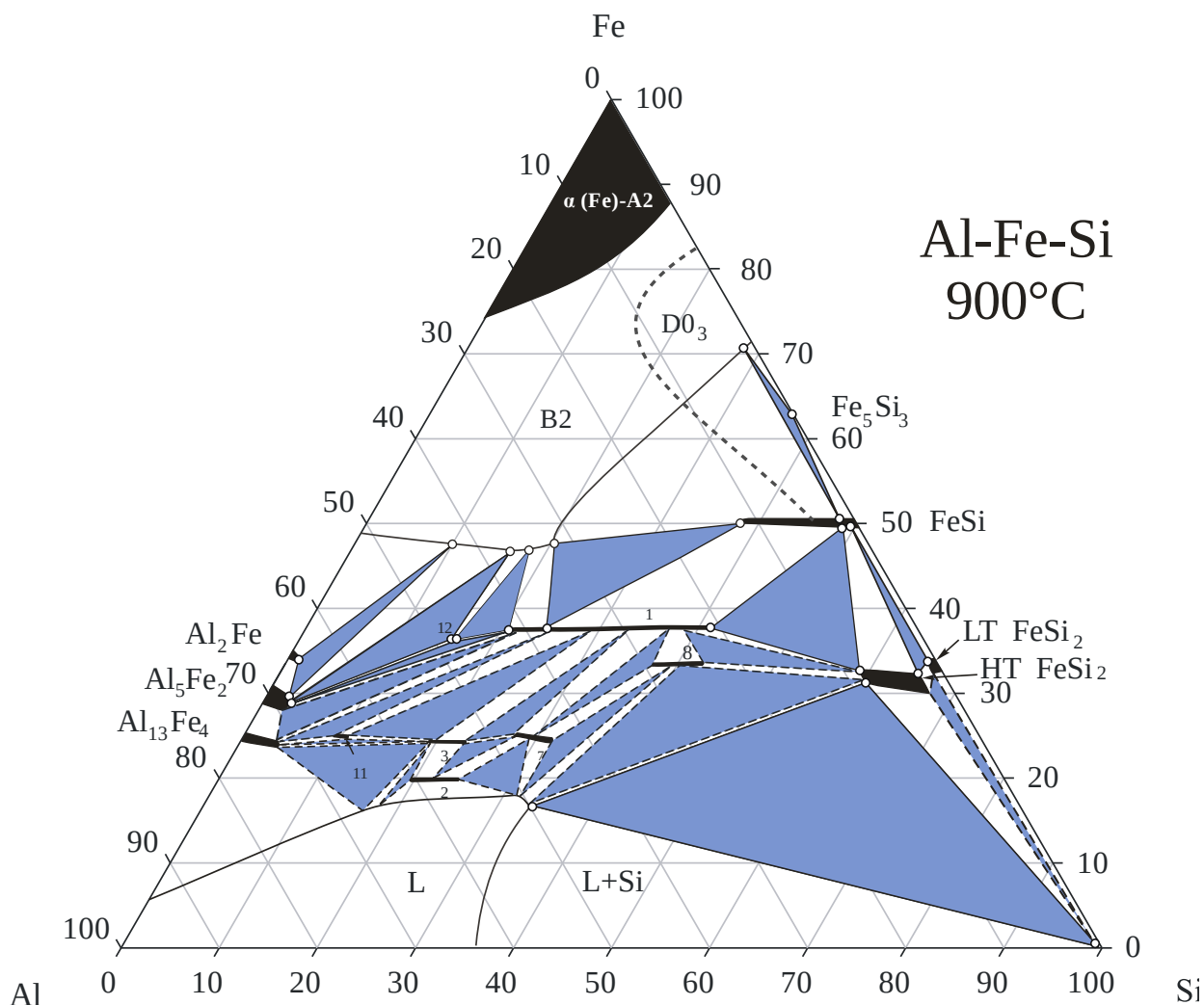


Figure 28. Isothermal section of Al–Fe–Si at 900 °C. Phase equilibria are drawn according to experimental results listed in Appendix-Table 2. The composition of the phase boundaries measured with EPMA, are plotted with white circles.

The isothermal sections at 800 °C and 900 °C in their basic outline are consistent with the section at 550 °C given by Krendelsberger et al. [46]. They contain, however, two additional features. The first point concerns the observation of a new ternary phase τ_{12} with the measured composition $\text{Al}_{48}\text{Fe}_{36}\text{Si}_{16}$ occurring in both sections. Details on this new compound are given in section 4.1.4.

The second point concerns the binary phase FeSi_2 . In both sections, the high temperature phase as well as the low temperature phase was found to be present, although the high temperature form is not stable at temperatures below 937°C in the binary. While the low-temperature modification does not dissolve significant amounts of Al, the high temperature form is only present as ternary phase field and was found to dissolve up to 8.5 at.% Al. Details on the ternary stabilization and decomposition of the high temperature phase are discussed in section 4.1.3.

The two points mentioned above are not in contradiction to the work of Krendelsberger et al. [46], as they concern phase equilibria at higher temperatures and are not found at 550°C . In fact, it was already suggested in [46], that the high temperature form of FeSi_2 is stabilized by Al additions down to temperatures of approx. 700°C . However, isothermal sections at 800°C and 900°C given in [45, 96, 101] do not show these features and are therefore partly incorrect.

The solubility ranges of τ_1 , τ_3 , τ_7 , τ_8 and τ_{11} were re-determined in the present study and noticeable differences to the values given by other authors were observed. Appendix-Table 2 contains full information on lattice parameters and phase compositions in various three-phase fields. The corresponding homogeneity ranges observed at 800°C are listed in Table 6. The details for the extended homogeneity range of the triclinic phase τ_1 are discussed in section 4.1.2.

Table 6. Homogeneity ranges of various ternary phases in the Al–Fe–Si system at 800°C determined by EPMA.

Phase	Homogeneity range / at. %
τ_1	$\text{Al}_{21.0-41.5}\text{Fe}_{37.5-38.5}\text{Si}_{41.5-21.0}$
τ_3	$\text{Al}_{52.0-54.5}\text{Fe}_{25.0-26.5}\text{Si}_{23.0-19.0}$
τ_7	$\text{Al}_{41.5-46.5}\text{Fe}_{24.0-26.0}\text{Si}_{35.0-27.5}$
τ_8	$\text{Al}_{23.0-28.5}\text{Fe}_{33.5-34.5}\text{Si}_{42.5-37.5}$
τ_{11}	$\text{Al}_{62.5-65.0}\text{Fe}_{26.0}\text{Si}_{11.5-9.0}$

4.1.2. The homogeneity range of $\text{Al}_2\text{Fe}_3\text{Si}_3$ (τ_1)

In 2001 Krendelsberger [145] established that the previously reported phases τ_1 ($\text{Al}_{21.5-45}\text{Fe}_{36.5-37.5}\text{Si}_{8.5-41.5}$) and τ_9 ($\text{Al}_{36}\text{Fe}_{36}\text{Si}_{28}$) are actually the same phase and she also confirmed a triclinic structure for τ_1 / τ_9 ($aP16$, $P\bar{1}$, $\text{Al}_2\text{Fe}_3\text{Si}_3$ -type). Bosselet et al. [146] came to the same conclusion. The identification of τ_1 by X-ray powder diffraction is especially demanding, because this phase combines a large homogeneity range with a low symmetry structure (space group $P\bar{1}$), so the XRD powder pattern changes drastically over the composition range. In fact, the initial attempts to index the observed patterns based on existing literature structure data [46, 99, 145] failed. Therefore a detailed study of lattice-parameter variation with the composition was performed. More than 15 samples prepared within the entire composition range of the phase were characterized by Rietveld-refinement and combined with data from single crystal lattice-parameter determination at a composition at 33 at.% Al and literature data from [145]. The single crystal data for τ_1 determined in this study agree well with structural data published earlier [22], and selected data collection and structure refinement are given in Tables 7 and 8. Further details of the crystal structure investigation were deposited in the Inorganic Crystal database of the *FIZ Karlsruhe*² under the depository number CSD 422342.

In this way it was possible to accurately determine the course of lattice parameters with the composition for τ_1 . A graphical representation of the lattice parameters of the triclinic unit cell a , b , c , α , β and γ as a function of composition is shown in Figure 29. The parameters a and γ decrease with increasing Si-content while b , c , α and β increase.

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Table 7. Single crystal data collection and structure refinements of τ_1 .

Empirical formula	$\text{Al}_2\text{Fe}_2\text{Si}_3$
Z	2
Crystal system, Space group	$P\bar{1}$
Structure type	$\text{Al}_2\text{Fe}_3\text{Si}_3$
Cell parameters ($\text{\AA}$)	$a = 4.684(1)$
	$b = 6.325(1)$
	$c = 7.498(2)$
	$\alpha = 100.99(1)$
	$\beta = 105.60(1)$
	$\gamma = 101.62(1)$
Cell volume ($\text{\AA}^3$)	202.4
Crystal dimensions (μm)	11×17×29
2 θ range for data collection	3 – 75
Reflections collected / unique	2150 / 2046
Extinction coefficient	0.0510(2)
$R1 = \Sigma(F_o - F_c) / \Sigma F_o$ (164 merged reflections)	0.027 / 0.026
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$	1.050
Final difference Fourier map / $\text{e}\text{\AA}^{-3}$	-1.37 to +0.92

Table 8. Fractional atomic coordinates and displacement parameters of Al₃Fe₂Si (τ_1).

Position	Wyckoff symbol	Fractional coordination			Displacement parameters						
		<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	$U_{equiv.}$
Fe1	2(i)	0.03698(5)	0.30012(4)	0.40831(3)	0.0141(2)	0.00915(10)	0.0098(1)	0.00163(7)	0.00582(8)	0.00261(7)	0.01076(7)
Fe2	2(i)	0.13163(5)	0.31991(4)	0.05574(3)	0.0097(1)	0.0072(1)	0.0083(1)	0.00232(7)	0.00330(7)	0.00223(7)	0.00826(6)
Fe3	2(i)	0.36206(5)	0.02398(4)	0.22443(3)	0.0120(1)	0.0092(2)	0.0099(1)	0.00186(7)	0.00310(7)	0.00340(7)	0.01047(7)
Al1	2(i)	0.06814(12)	0.65441(9)	0.27676(7)	0.0123(2)	0.0092(2)	0.0090(2)	0.0021(2)	0.0042(2)	0.0028(2)	0.0101(1)
Al2	2(i)	0.40363(12)	0.67391(9)	0.03217(8)	0.0087(2)	0.0072(2)	0.0173(2)	0.0011(2)	0.0060(2)	0.0017(2)	0.0111(1)
Si1	2(i)	0.28252(11)	0.05495(9)	0.54012(8)	0.0106(2)	0.0178(2)	0.0145(2)	0.0073(2)	0.0047(2)	0.0055(2)	0.0135(1)
Si2	2(i)	0.54301(11)	0.41573(8)	0.34732(7)	0.0113(2)	0.0110(2)	0.0096(2)	0.0018(2)	0.0031(2)	0.0027(2)	0.0109(1)
Si3	2(i)	0.82738(11)	0.01759(8)	0.12078(7)	0.0120(2)	0.0079(2)	0.0096(2)	0.0015(2)	0.0045(2)	0.0012(2)	0.0099(1)

The anisotropic displacement parameters are defined as: $\exp [-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$ [147].

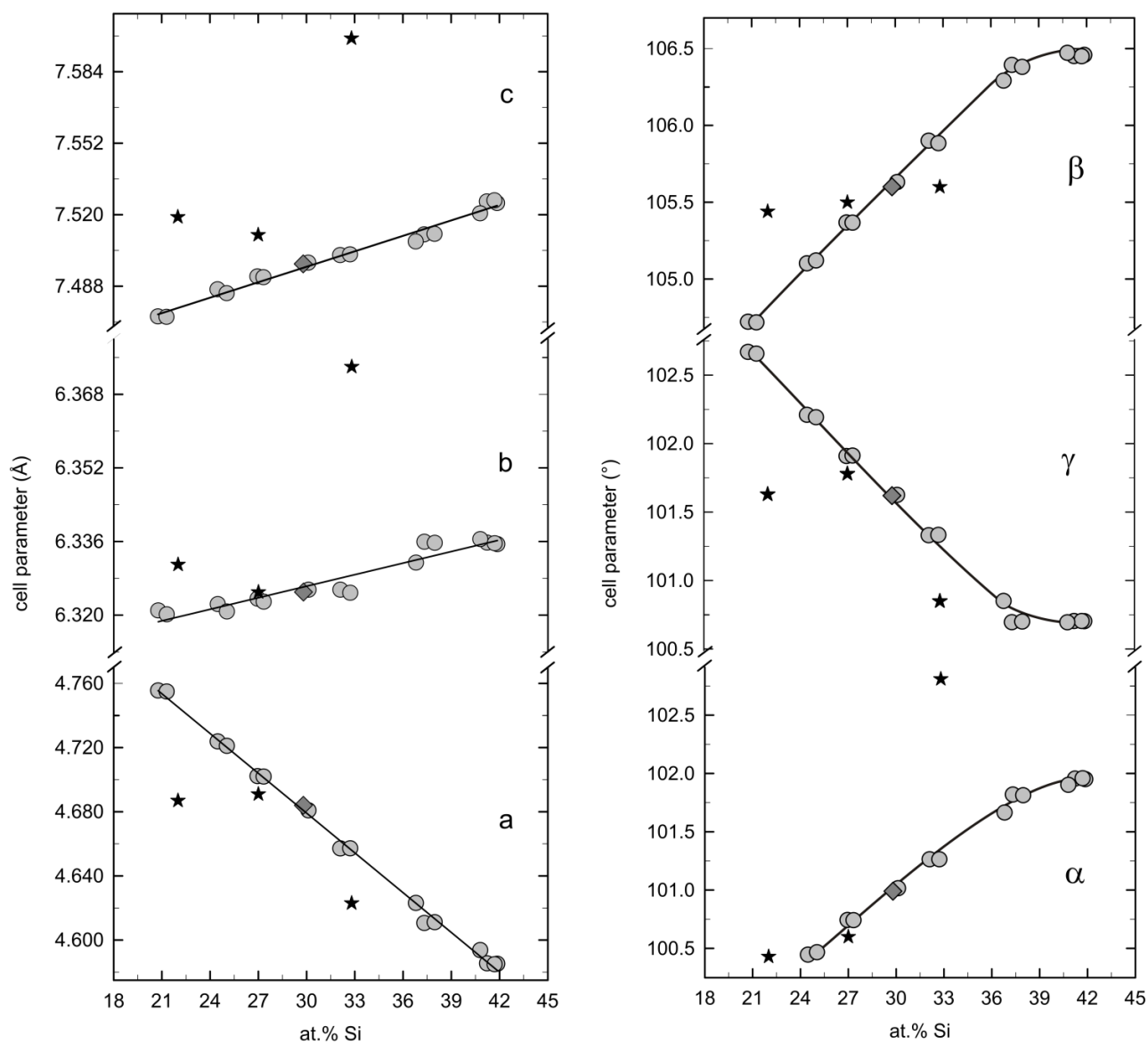


Figure 29. Unit-cell parameters of τ_1 phase ($\text{Al}_{1+x}\text{Fe}_3\text{Si}_{4-x}$, $aP16$, $P\bar{1}$) shown as a function of the composition. Grey circles show results from powder XRD; dark grey diamond show data from single crystal XRD; black stars representing literature data from Krendelsberger given in [145].

Figure 30 shows the variation of the cell volume with the composition which is practically linear. The cell volume decreases with increasing Si-content, which is consistent with the substitution of the larger Al- by smaller Si-atoms. The respective covalent radii are 125 pm for Al and 117 pm for Si [148].

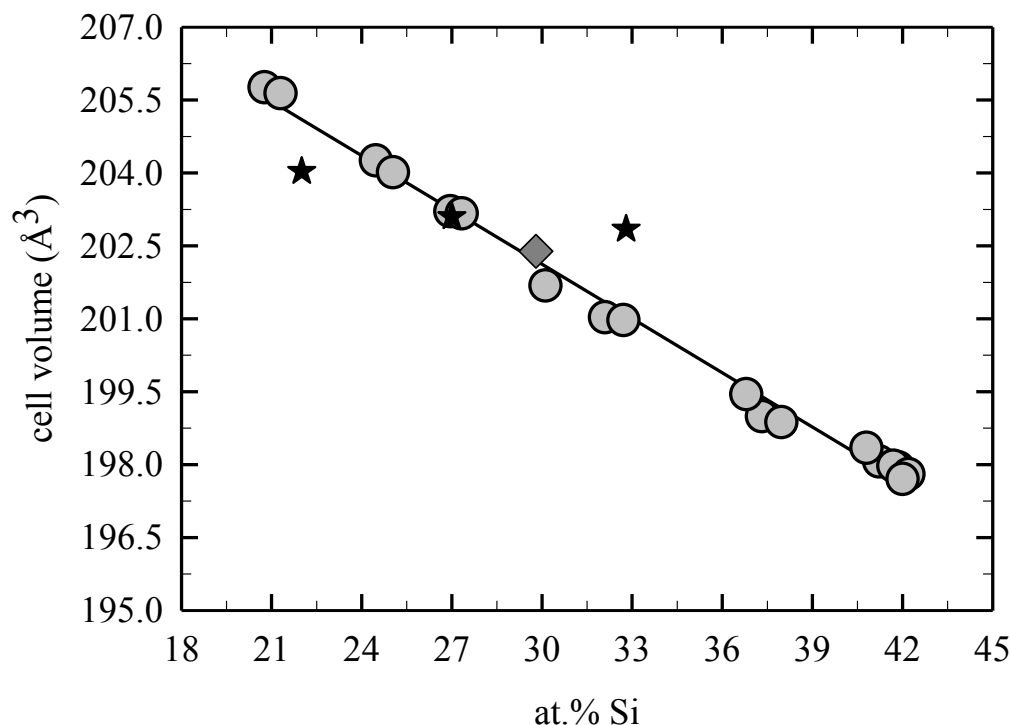


Figure 30. Cell volume of τ_1 phase ($\text{Al}_{1+x}\text{Fe}_3\text{Si}_{4-x}$, $aP16$, $P\bar{1}$) shown as a function of the composition. Grey circles show results from powder XRD; dark grey diamond show data from single crystal XRD; black stars representing literature data from Krendelsberger given in [145].

The phase τ_1 represents an unusual combination of broad homogeneity range with a very low symmetry crystal structure. The original structure determination describes the phase as $\text{Al}_2\text{Fe}_3\text{Si}_3$ [149] with two positions occupied by Al and three by Si atoms, respectively. Given our homogeneity range from $\text{Al}_{21.0}\text{Fe}_{37.5}\text{Si}_{41.5}$ to $\text{Al}_{41.5}\text{Fe}_{37.5}\text{Si}_{21.0}$ the phase has to be described as $\text{Al}_{2+x}\text{Fe}_3\text{Si}_{3-x}$ with $-0.3 < x < 1.3$. It is clear, that Al and Si are sharing at least some of the

positions by mixed occupation, but these mixed occupations cannot be determined directly by XRD due to the very similar scattering factors of Al and Si. In order to address this problem, the site volumes (volumes of the Wigner-Seitz cell) were calculated from our structural data as function of the composition using the program DIDO95 [39].

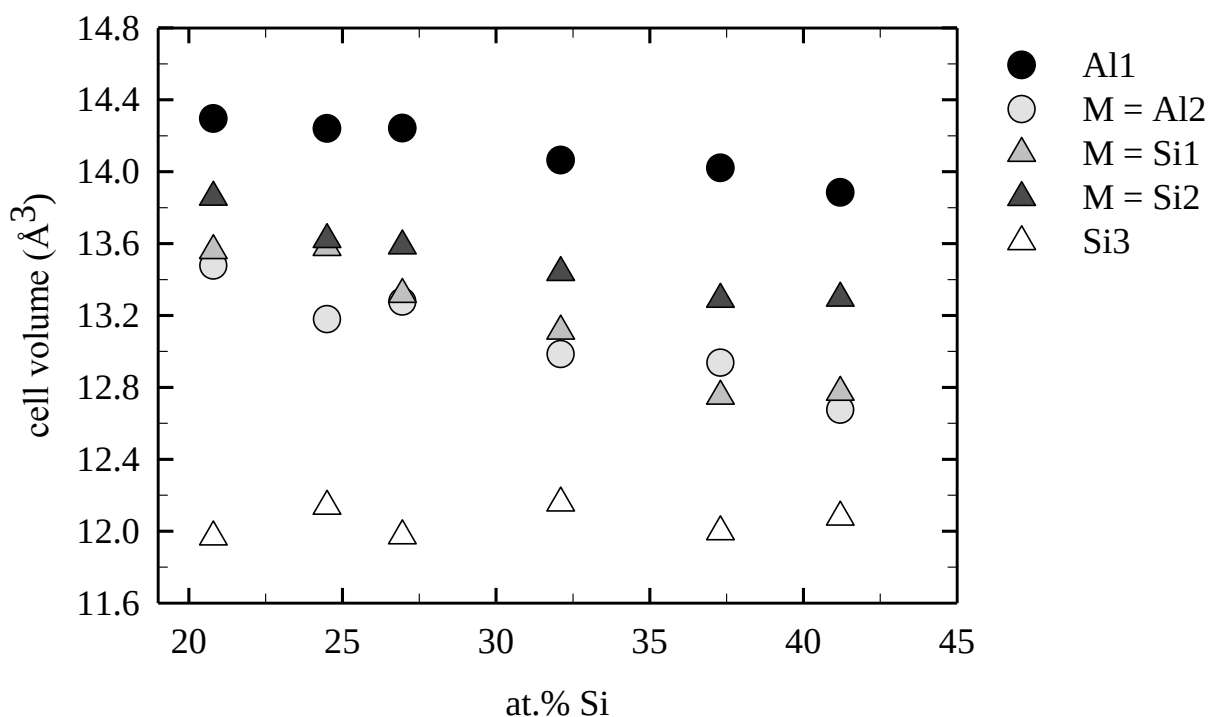


Figure 31. Cell volume of the Wigner-Seitz cell for the five Al/Si positions of the τ_1 phase ($\text{Al}_{1+x}\text{Fe}_3\text{Si}_{4-x}$, $aP16$, $P\bar{1}$) shown as a function of the composition.

The graphical representation of the site volume change shown in Figure 31 may be interpreted as follows: Position Al 1 (the largest) and Si 3 (the smallest) do not significantly change their size with composition, and are therefore regarded to be fully occupied by Al and Si. The other three positions (Al2, Si1, Si2) have intermediate site volume which changes with the composition. Therefore it can be concluded that mixing at Al and Si takes place mainly at these 3 positions and that the Al / Si ratio at these positions is varying with the composition. The coordination-polyhedrons of Al2 (a), Si1 (b), Si2 (c) are given in Figure 32.

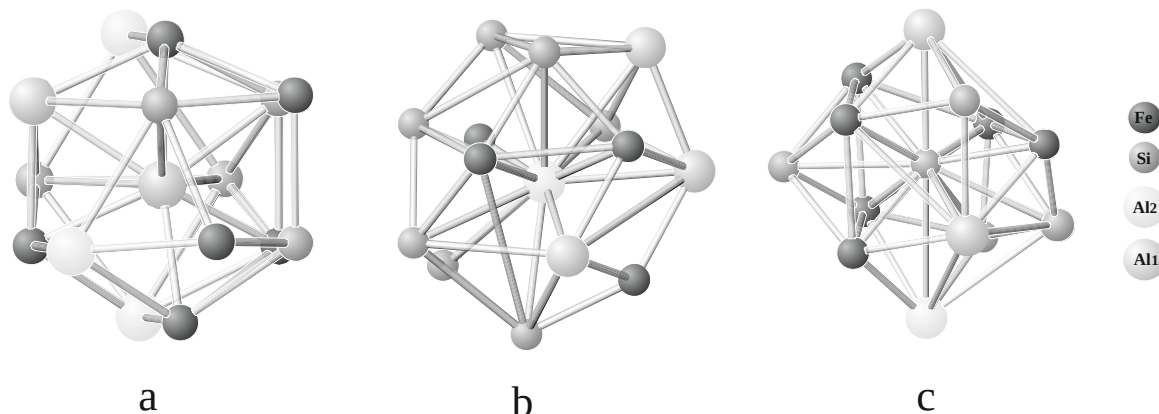


Figure 32. Coordination-polyhedrons of the three atom positions of (a) Al2, (b) Si1 and (c) Si2 of the τ_1 phase ($\text{Al}_{1+x}\text{Fe}_3\text{Si}_{4-x}$, $aP16$, $P1̄$).

4.1.3. Solid state reactions involving HT-FeSi₂ (ζ_α , Fe₂Si₅) and LT-FeSi₂ (ζ_β)

In the binary Fe–Si system, two modifications of FeSi₂ are established. In the literature the terms α -FeSi₂, β -FeSi₂, ζ_α and ζ_β are not used systematically for these compounds, yielding some confusion. So HT and LT were used to designate the high- and low-temperature form in this work. The binary high temperature phase is stable between 1220 °C (congruent melting) and 937 °C (eutectoid decomposition). The low-temperature form is stable up to 982 °C and decomposes in a peritectoid reaction. The high-temperature phase deviates from the stoichiometric composition, and has a tetragonal structure ($tP3$, $P4 / mmm$) with about 13% Fe vacancies. The low-temperature phase has a stoichiometric composition with orthorhombic structure ($oC48$, $Cmca$). In their thermodynamic assessment of Al–Fe–Si, Angl  zio et al. [150] allowed Al/Si substitution in HT-FeSi₂ and found this phase to be stable down to room temperature with a maximum solubility of about 6 at.% Al. According to the assessment of Gu  neau et al. [151] the compound (Al,Si)_{2.4}Fe dissolves up to 10 at.% Al at room temperature. On the other hand, Krendelsberger et al. [46] did not find the high-temperature modification in the sample with composition Al₁₀Fe₄₀Si₅₀ at 550, 700 as well as at 800 °C. In contrast they found the three-phase field [(Si) + Fe₂Si₅ + τ_7] in a sample with the composition Al₂₀Fe₂₀Si₆₀ at 700 °C. At 800 °C they found the three-phase field [(Si) + Fe₂Si₅ + τ_8] at the composition Al₁₂Fe₂₃Si₆₅. Their conclusion is that the HT-modification is stabilized by Al in the ternary down to 700 °C.

In the present work a small solubility of 0.7 at.% Al (800 °C) to 0.6 at.% Al (900 °C) in the orthorhombic LT-modification could be observed, whereas a solubility of 8.5 at.% Al for the tetragonal HT-modification was found. Both modifications are found in equilibrium with each other in the ternary isothermal sections at 800 °C (Figure 27) and 900 °C (Figure 28).

Thus, the tetragonal high-temperature form of FeSi₂ is definitely stabilized to lower temperatures by the addition of Al. By systematic annealing experiments the stability of ternary HT-FeSi₂ was confirmed down to a temperature of 750 °C where the phase field [LT-FeSi₂+HT-FeSi₂+τ₈] was observed. Samples annealed below this (i.e. at 720°C and 700°C) did not show HT-FeSi₂ anymore. At 720°C the three-phase fields [LT-FeSi₂ + τ₁ + FeSi], [LT-FeSi₂ + τ₈ + τ₇] and [LT-FeSi₂ + τ₇ + (Si)] were found; at 700°C [LT-FeSi₂ + τ₈ + τ₇] and [LT-FeSi₂ + τ₈ + FeSi] were found.

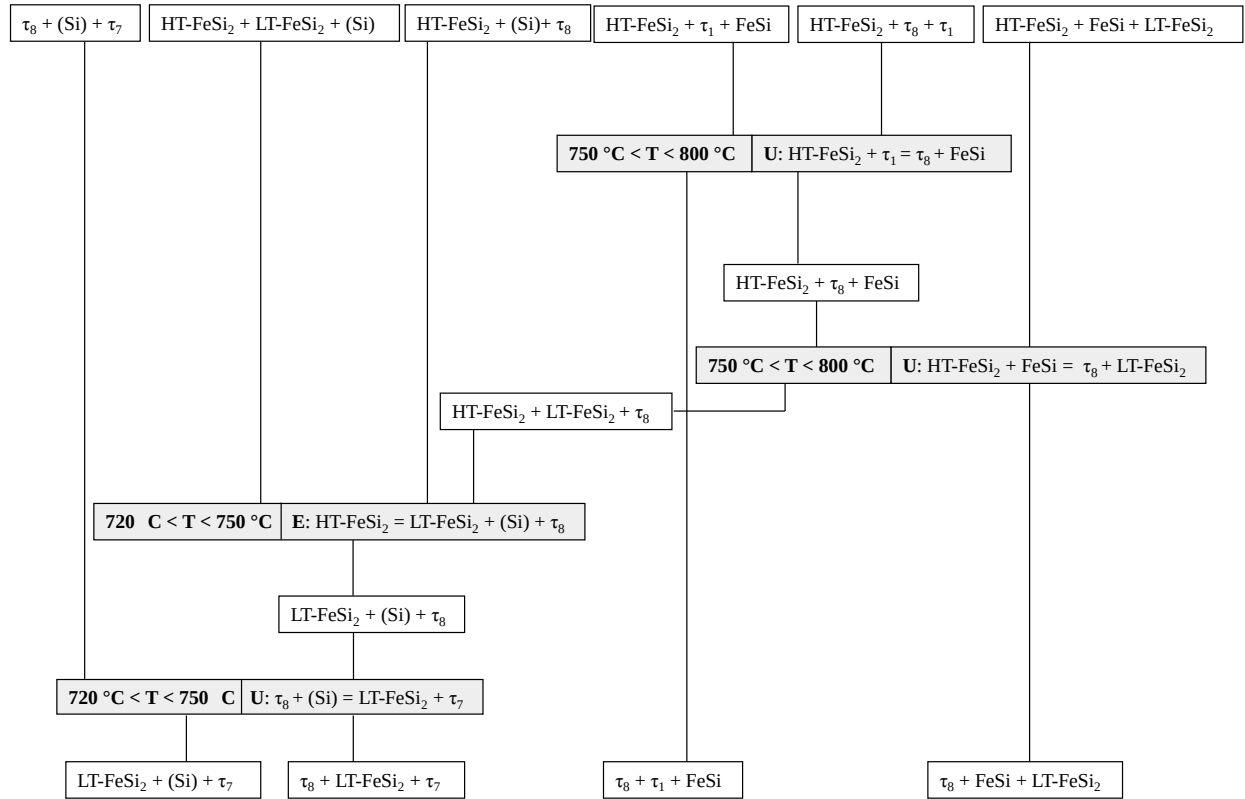


Figure 33. Reaction scheme of solid state reactions including the ternary solid solution of HT-FeSi₂.

These findings are not in agreement with the isothermal section at 727°C given by Bosselet et al. [146], who proposed different phase equilibria at this temperature, but also confirmed that the high-temperature form is not any longer present at this temperature. Based on the current experimental results, a eutectoidic decomposition reaction E: $\text{HT-FeSi}_2 \rightleftharpoons \text{LT-FeSi}_2 + (\text{Si}) + \tau_8$ at $720^\circ\text{C} < T < 750^\circ\text{C}$ is proposed. This reaction and the reaction temperature are different to the eutectoid of $\text{HT-FeSi}_2 \rightleftharpoons \text{LT-FeSi}_2 + (\text{Si}) + \tau_7$ between 600°C and 700°C which is suggested in [46]. A hypothetical but conclusive schematically representation of the reaction path based on the results is given in Figure 33.

4.1.4. Crystal structure of $\text{Al}_3\text{Fe}_2\text{Si}$ (τ_{12})

During the investigations of the exact homogeneity range and the lattice parameters of τ_1 , a new, previously unknown powder pattern was observed at the Al-rich side of τ_1 . In order to determine the exact composition of this phase a couple of samples were prepared in the corresponding composition area. EPMA measurements and the X-ray powder diffraction refinement are consistent, as results of selected samples given in Appendix-Table 2 show.

The diffractogram of sample No. 12 ($\text{Al}_{48}\text{Fe}_{37}\text{Si}_{15}$) annealed at 900°C showing the three-phase field of $[\text{AlFe} + \text{Al}_5\text{Fe}_2 + \tau_{12}]$ and with τ_{12} as the main phase is given in Figure 34. The percentage of phases given in Figure 34, correspond to the refined area of the powder pattern and are in good agreement with expectations from the lever rule.

The microstructure of the sample No. 13 ($\text{Al}_{45}\text{Fe}_{40}\text{Si}_{15}$) representing the same phase field is given in a BSE image in Figure 35. According to EPMA measurements, the phase τ_{12} does not show a significant homogeneity range and the composition is approximately given by $\text{Al}_{48}\text{Fe}_{36}\text{Si}_{16}$.

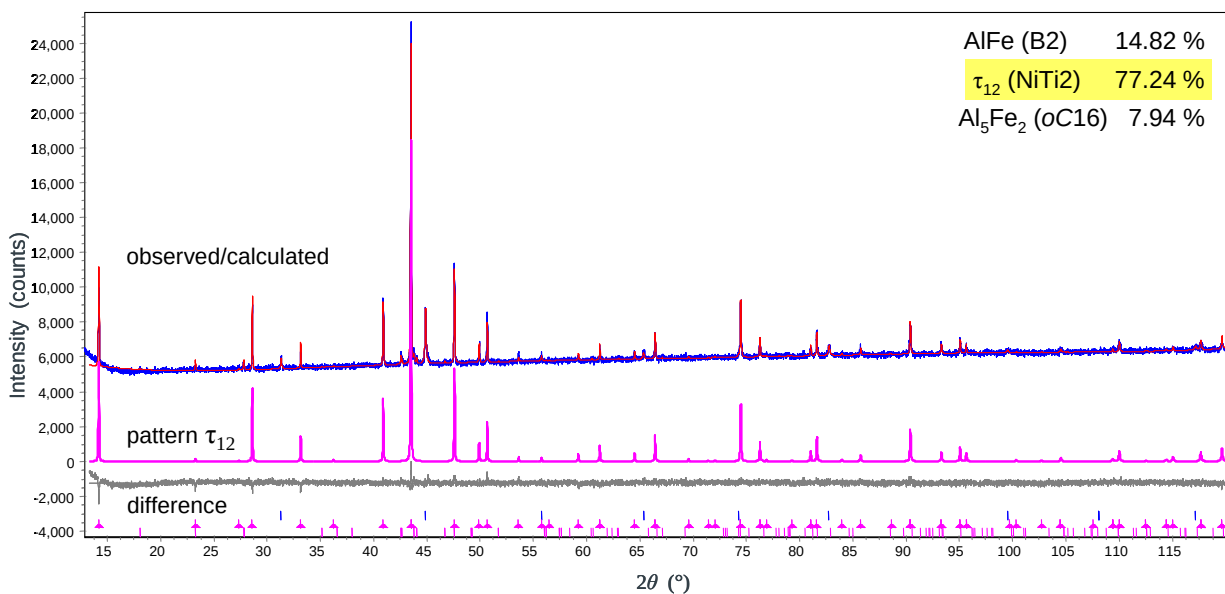


Figure 34. X-ray diffractogram of sample No. 12 with the nominal composition $\text{Al}_{48}\text{Fe}_{37}\text{Si}_{15}$, showing the three phases AlFe, τ_{12} and Al_5Fe_2 . The calculated pattern of τ_{12} and the difference curve are shown in the bottom of the graph.

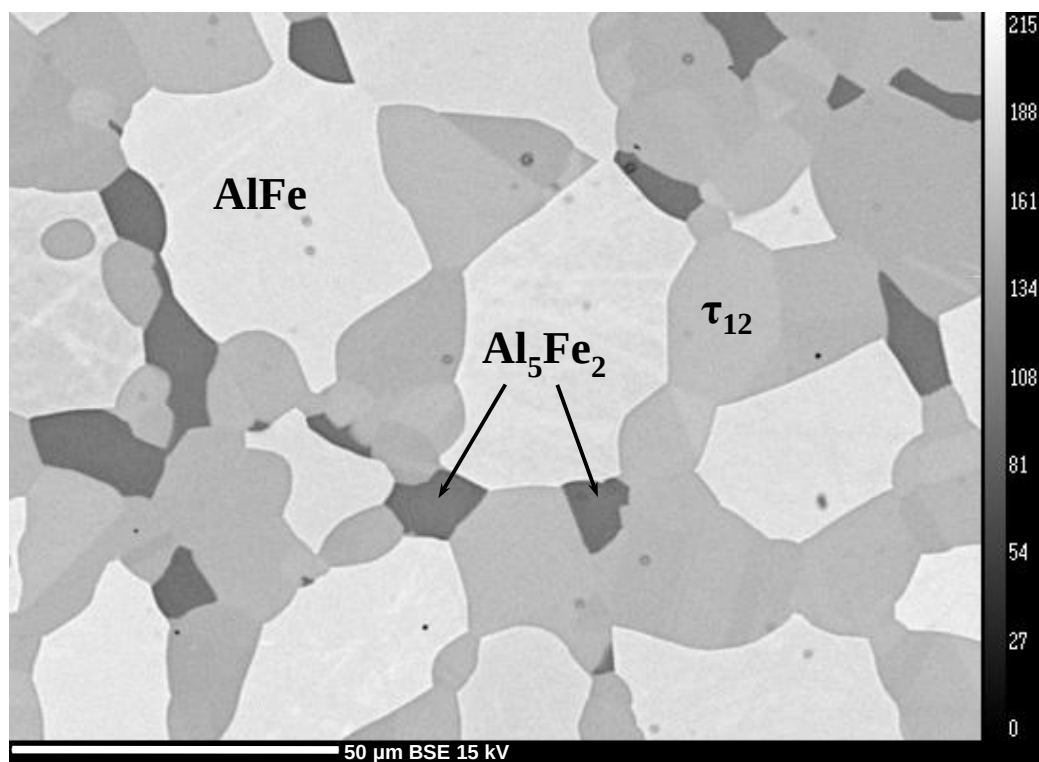


Figure 35. BSE image of a sample with the nominal composition $\text{Al}_{45}\text{Fe}_{40}\text{Si}_{15}$, representing the three-phase field [AlFe + Al_5Fe_2 + τ_{12}].

For characterizing the thermal behavior of the phase, a couple of samples were annealed at different temperature between 700 °C for more than 28 days and 1200 °C for 7 days. In the present work τ_{12} was found to be stable from about 720 to 1005 °C. At 1010 °C and above the pattern of this phase could not be observed anymore. Instead the three phases, AlFe, Al₅Fe₂ and τ_1 were found to be present in these samples. There is no indication of the formation of the liquid phase during the decomposition of τ_{12} . Additional experiments on primary crystallization confirmed these findings. A series of as cast samples in the composition area was investigated to find a possible primary crystallization field of τ_{12} .

However, τ_{12} was not found in any of the as cast samples, confirming its formation in a solid state reaction. The reversibility of the formation / decomposition reaction of τ_{12} was checked and confirmed by annealing experiments. Therefore the proposal for the formation of τ_{12} is a peritectoid-type reaction at around 1005 °C [AlFe + Al₅Fe₂ + $\tau_1 \rightarrow \tau_{12}$] and a eutectoid-type reaction at around 720 °C [$\tau_{12} \rightarrow$ AlFe + Al₅Fe₂ + τ_1].

As τ_{12} does not crystallize directly from the melt, but is formed in a solid state reaction, a long procedure was necessary to get a single crystal of suitable quality. Some crystals from a sample with the composition Al₄₈Fe₃₆Si₁₆ could be obtained after an annealing time of more than eight weeks. The crystal structure of τ_{12} was determined from a small crystal chip. Data collection was performed based on trigonal symmetry. The crystal structure was solved by direct methods [131]. During refinement successively it turned out that the actual symmetry is cubic, space group $Fd\bar{3}m$ (Pearson symbol *cF96*), and belongs to the NiTi₂-type structure. The crystal was twinned; the twin plane is (112). During final refinement based on cubic symmetry, the twin components were obtained as 0.232:0.767(2). Details on data collection and structure refinement are given in Tables 9 and 10 final interatomic bond distances in Table 11. Further details of the crystal structure investigation can be obtained from the *Fachinformationszentrum Karlsruhe*³ on quoting the depository number CSD 422341.

³ 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de)

Table 9. Single crystal data collection and structure refinements of τ_{12} .

Empirical formula	$\text{Al}_3\text{Fe}_2\text{Si}$
Z	16
Crystal system, Space group	$Fd\bar{3}m$
Structure type	NiTi_2
Cell parameters ($\text{\AA}$)	10.806(2)
Cell volume ($\text{\AA}^3$)	1261.8(6)
Crystal dimensions (μm)	20×40×50
2 θ range for data collection	3 – 70
Reflections collected / unique	1790 / 1201
Extinction coefficient	0.0002(2)
$R1 = \Sigma(F_o - F_c) / \Sigma F_o$ (164 merged reflections)	0.042
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$	1.104
Final difference Fourier map / $\text{e}\text{\AA}^{-3}$	-0.92 to +1.09

Table 10. Fractional atomic coordinates and displacement parameters of Al₃Fe₂Si (τ₁₂).

Position	Wykoff symbol	Fractional coordination			Displacement parameters						
		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{equiv.}
Fe	32	0.21402(3)	= <i>x</i>	= <i>x</i>	0.0092(2)	= <i>U</i> ₁₁	= <i>U</i> ₁₁	0.0005(1)	= <i>U</i> ₂₃	= <i>U</i> ₂₃	0.0092(2)
Al	48	0.42756(9)	1/8	1/8	0.0075(5)	0.0070(3)	= <i>U</i> ₂₂	0.0011(3)	0	0	0.0072(2)
Si	16	0	0	0	0.0089(3)	= <i>U</i> ₁₁	= <i>U</i> ₁₁	0.0015(3)	= <i>U</i> ₂₃	= <i>U</i> ₂₃	0.0089(3)

The anisotropic displacement parameters are defined as: $\exp [-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$ [147].

Table 11. Interatomic bond lengths (Å) of Al₃Fe₂Si (τ₁₂).

Al—Fe	2.4915(8), 2x	Fe—Si	2.3771(9), 3x	Si—Fe	2.3771(9), 6x
Al—Fe	2.6787(11), 2x	Fe—Al	2.4915(8), 3x	Si—Al	2.7075(10), 6x
Al—Si	2.7075(10), 2x	Fe—Al	2.6787(11), 3x		
Al—Al	2.8184(11), 4x	Fe—Fe	2.7207(9), 3x		
Al—Al	3.0172(16), 4x				

The NiTi₂-type was found to exist in several binary systems and also in some ternary systems like e.g. Mn₃Ni₂Si, Ni₂SiV₃, Nb₃Ni₂Si, Ni₂SiTa₃, Ni₂SiZn₃, GeNi₂Zn₃ or Co₂Nb₃Si. [122]. The basic structure contains 96 atoms per unit cell; the three independent positions Ti1, Ni and Ti2 exhibit multiplicities of 16, 32 and 48; i.e. in the ratio 1:2:3. Ni and Ti2 sites are icosahedrally coordinated, while the site Ti1 has fourteen neighbors. In τ_{12} , Si occupies the Ti1 site, Al the Ti2 and Fe the Ni site.

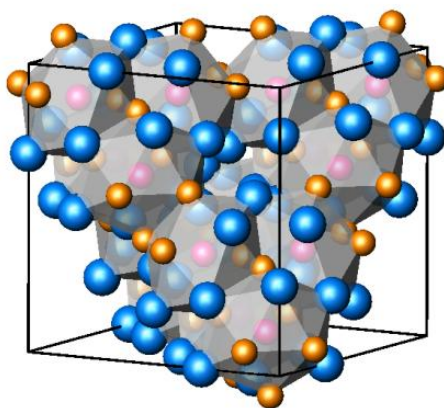


Figure 36. Polyhedron with the centered Fe-atoms coordinated by Al (blue colored) and Fe-atoms (orange colored) in the unit cell of τ_{12} with NiTi₂-structure type.

The ideal composition of τ_{12} based on the crystal structure is therefore Al₃Fe₂Si; i.e. 50 at.% Al, 33.3 at.% Fe and 16.7 at.% Si. This deviates slightly from the real composition of the phase as determined by EPMA which is 48 at.% Al, 36 at.% Fe and 16 at.% Si. It is not completely clear what mechanism is responsible for this shift towards the Fe-rich side. The most significant mechanism of non-stoichiometry of the different phases in the system Al–Fe–Si is the Al / Si substitution. This is reflected in the usual extension of ternary phases which show fixed Fe composition but often variable Al / Si ratio (compare Figures 27 and 28). This mechanism is obviously not responsible for the composition shift in this case. It is not possible to constitute conclusive evidence on this issue with the information from Rietveld refinement, and the single crystal structure refinement using different models of substitution mechanism and vacancies mechanism are not unambiguous.

Some authors report on the possible stabilization of the NiTi₂-type structure by hetero-atoms like oxygen [152]. There are strong indications that this is not the case for τ_{12} . Firstly the phase

can be completely decomposed and formed again by annealing in the proper temperature range, and secondly, not any significant residual electron density could be found in the single crystal refinement (compare with Table 9). Therefore it can be concluded that τ_{12} is not stabilized by oxygen, but is a true ternary compound.

For high-temperature applications potentially the mechanical properties could be of interest and therefore microhardness measurements were performed. A Vickershardness of $HV = 1317(16)$ (50mN for 20s) and an indentation modulus of $E_{IT} = 236(3) \text{ N}\cdot\text{mm}^{-2}$ for τ_{12} were determined. In Figure 37 the microstructure of the ternary sample No. 12. shows the three-phase equilibrium with τ_{12} as the main phase, grains of AlFe and Al_5Fe_2 .

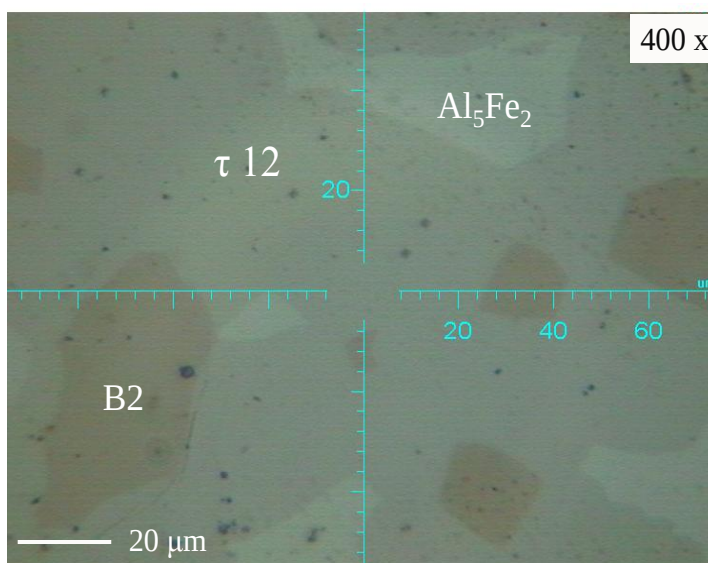


Figure 37. Microstructure of the three phase equilibrium [τ_{12} + B2 + Al_5Fe_2] of sample No. 12. with the nominal composition $\text{Al}_{48}\text{Fe}_{37}\text{Si}_{15}$.

In addition during these investigations two more single crystal data were collected for τ_7 ($\text{Al}_3\text{Fe}_2\text{Si}_3$) and τ_8 ($\text{Al}_2\text{Fe}_3\text{Si}_4$ or $\text{AlFe}_{1.5}\text{Si}_2$). Selected single crystal data are given in Tables 12 – 14. Further details of the crystal structure investigation can be obtained from the *Fachinformationszentrum Karlsruhe*⁴ on quoting the depository numbers CSD 426321 for $\text{Al}_3\text{Fe}_2\text{Si}_3$ (τ_7) and CSD 426322 for $\text{AlFe}_{1.5}\text{Si}_2$ (τ_8).

⁴ 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de)

Table 12. Single crystal data collection and structure refinements of τ_7 and τ_8 .

	τ_7	τ_8
Empirical formula	$\text{Al}_3\text{Fe}_2\text{Si}_3$	$\text{Al}_2\text{Fe}_3\text{Si}_4$
Z	8	4
Crystal system, Space group	$P2_1 / n$	$Cmcm$
Structure type	$\text{Al}_3\text{Fe}_2\text{Si}_3$	$\text{Al}_2\text{Fe}_3\text{Si}_4$
Cell parameters ($\text{\AA}$)	$a = 7.243(1)$ $b = 8.336(1)$ $c = 14.512(2)$ $\beta = 93.89(1)$	$a = 3.670(1)$ $b = 12.429(3)$ $c = 10.162(2)$
Cell volume ($\text{\AA}^3$)	874.2(2)	463.6(2)
Crystal dimensions (μm)	18×36×40	14×20×25
2 θ range for data collection	3 – 75	3 – 75
Reflections collected / unique	4672 / 3976	716 / 674
Extinction coefficient	0.0056(7)	0.0106(9)
$R1 = \Sigma(F_o - F_c) / \Sigma F_o$	0.033 / 0.028	0.022 / 0.020
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$	1.083	1.128
Final difference Fourier map / $\text{e}\text{\AA}^{-3}$	-0.88 to +1.35	-0.75 to +1.22

Table 13. Fractional atomic coordinates and displacement parameters of Al₃Fe₂Si₃ (τ_7).

Position	Wykoff symbol	Fractional coordination			Displacement parameters						
		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{equiv.}
Fe1	4(<i>e</i>)	0.55673(2)	0.11652(2)	0.72911(2)	0.0087(1)	0.0086(7)	0.0077(1)	-0.0003(1)	0.0009(1)	-0.0003(1)	0.0084(1)
Fe2	4(<i>e</i>)	0.55563(2)	0.63594(2)	0.73049(2)	0.0086(1)	0.0089(1)	0.0078(1)	0.0003(1)	0.0009(1)	0.0004(1)	0.0084(1)
Fe3	4(<i>e</i>)	0.75186(3)	0.13044(2)	0.46441(2)	0.0097(1)	0.0088(1)	0.0073(1)	-0.0000(1)	0.0005(1)	-0.0002(1)	0.0086(1)
Fe4	4(<i>e</i>)	0.76481(2)	0.62004(2)	0.46849(2)	0.0086(1)	0.0099(1)	0.0078(1)	-0.0000(1)	0.0006(1)	0.0004(1)	0.0087(1)
Al1	4(<i>e</i>)	0.17605(6)	0.04580(5)	0.66758(3)	0.0163(2)	0.0168(2)	0.0150(2)	-0.0032(2)	0.0045(2)	0.0036(2)	0.0159(1)
Al2	4(<i>e</i>)	0.18848(5)	0.70269(5)	0.67674(3)	0.0141(2)	0.0162(2)	0.0132(2)	0.0021(2)	0.0036(2)	-0.0030(2)	0.0144(1)
Al3	4(<i>e</i>)	0.45029(6)	0.13689(4)	0.55071(3)	0.0102(2)	0.0110(2)	0.0112(2)	0.0012(2)	0.0008(2)	0.0002(1)	0.0108(1)
Al4	4(<i>e</i>)	0.45578(6)	0.61396(4)	0.55612(3)	0.0104(2)	0.0101(2)	0.0105(2)	-0.0008(2)	0.0007(2)	-0.0000(2)	0.0103(1)
Al5	4(<i>e</i>)	0.55303(6)	0.12444(4)	0.17411(3)	0.0120(2)	0.0120(2)	0.0095(2)	-0.0001(2)	0.0015(2)	0.0001(2)	0.0111(1)
Al6	4(<i>e</i>)	0.29086(7)	0.62329(4)	0.23101(4)	0.0132(2)	0.0091(2)	0.0258(2)	0.0001(2)	-0.0067(2)	-0.0001(2)	0.0164(1)
Si1	4(<i>e</i>)	0.90796(5)	0.12490(4)	0.17385(3)	0.0107(2)	0.0120(2)	0.0097(2)	-0.0004(1)	-0.0005(2)	0.0001(1)	0.0109(1)
Si2	4(<i>e</i>)	0.96943(5)	0.62251(4)	0.15281(3)	0.0115(2)	0.0092(2)	0.0096(2)	0.0001(1)	-0.0014(2)	0.0002(1)	0.0102(1)
Si3	4(<i>e</i>)	0.79046(5)	0.13942(4)	0.62325(3)	0.0106(2)	0.0176(2)	0.0079(2)	0.0001(1)	0.0005(2)	-0.0000(1)	0.0120(1)
Si4	4(<i>e</i>)	0.79364(5)	0.61495(4)	0.62592(3)	0.0107(2)	0.0180(2)	0.0075(2)	-0.0001(1)	0.0005(2)	-0.0002(1)	0.0121(1)
Si5	4(<i>e</i>)	0.39893(5)	0.12814(4)	0.01038(3)	0.01043(2)	0.0090(2)	0.0127(2)	0.0002(1)	-0.0004(2)	0.0001(1)	0.0108(1)
Si6	4(<i>e</i>)	0.39926(6)	0.62147(4)	0.03141(3)	0.0142(2)	0.0125(2)	0.0178(2)	-0.0002(2)	0.0001(2)	0.0001(1)	0.0149(1)

The anisotropic displacement parameters are defined as: $\exp [-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$ [147].

Table 14. Fractional atomic coordinates and displacement parameters of $\text{Al}_2\text{Fe}_3\text{Si}_4$ (τ_8).

Position	Wyckoff symbol	Fractional coordination			Displacement parameters						
		x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	$U_{equiv.}$
Fe1	8(f)	0	0.14943(1)	0.12522(2)	0.0096(1)	0.0080(2)	0.0064(1)	-0.0001(1)	0	0	0.00798(7)
Fe2	4(c)	0	0.35190(2)	1/4	0.011(2)	0.0089(2)	0.0066(2)	0	0	0	0.00882(7)
Al	8(f)	0	0.05775(4)	0.60846(4)	0.0100(2)	0.0095(2)	0.0094(2)	0.0006(2)	0	0	0.0096(1)
Si1	8(f)	0	0.31919(3)	0.01553(4)	0.0081(2)	0.0093(2)	0.0085(2)	-0.0007(2)	0	0	0.0086(1)
Si2	4(c)	0	0.54471(4)	1/4	0.0103(2)	0.0093(2)	0.0157(3)	0	0	0	0.0118(2)
Si3	4(c)	0	0.73899(4)	1/4	0.0084(2)	0.0112(2)	0.0108(2)	0	0	0	0.0101(2)

The anisotropic displacement parameters are defined as: $\exp [-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$ [147]

4.1.5. Vertical sections

The ternary phase reactions in the system Al–Fe–Si were studied by DTA analysis of samples situated in six different vertical sections at 5 at.% Al and at constant iron contents of 27, 35, 40, 50 and 60 at.% (given as red lines in Figure 38). Experimental results of thermal analysis are given in Appendix-Table 3. Two heating- and cooling-cycles were performed in each measurement. The starting temperature was 800 and 900 °C i.e. the respective annealing temperature of the samples. The maximum temperature reached in these experiments was 1450 °C. The results of thermal analyses are shown in Figures 39 and 40. The experimental data points for thermal effects shown in Figures 39 and 40 (large and small circles) represent mainly DTA results obtained on first heating of the annealed samples. The liquidus values (triangles) were evaluated from heating- and cooling-curves, respectively. These figures contain the experimental data points and the evaluated phase equilibria.

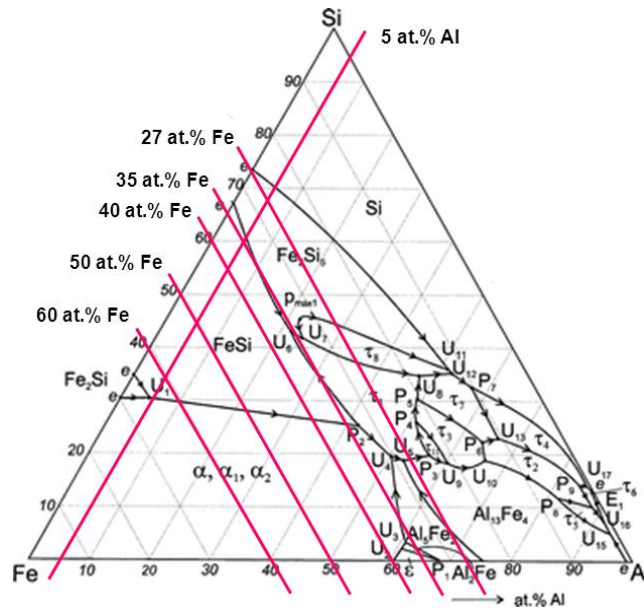


Figure 38. Investigated vertical sections (isopleths) situated in the ternary system Al–Fe–Si outlined on the liquidus projections.

The reaction scheme from Krendelsberger *et al.* [46] was used as input for interpretation. The phase boundaries were adapted according to the own experimental data (phase compositions) determined in the two isothermal sections at 800 °C and 900 °C. Generally, the

phase reactions observed in this study are in good agreement with the reaction scheme and the liquidus surface given in [46], although some changes of phase boundaries were necessary to fit the experimental results.

As already discussed in the previous sections, the presence of LT-FeSi₂ and HT-FeSi₂ was observed, while [45, 96] reported only about the existence of LT-FeSi₂ at 800°C. In the area of τ_1 and the additional ternary phase τ_{12} , the new three-phase fields [AlFe + τ_1 + τ_{12}] and [AlFe + Al₅Fe₂ + τ_{12}] were detected. These facts are included in the corresponding vertical sections shown in Figures 39 and 40.

The phase reactions listed in literature [46] were confirmed. In addition, the solid state reactions connected with the formation and decomposition of τ_{12} (compare section 4.1.4) were introduced as well as solid state equilibria connected with the ternary solubility of HT-FeSi₂ (compare section 4.1.3).

The situation of the liquidus valleys found in the various sections in Figures 39 and 40 match reasonably well with the liquidus projection given in [46]. For the liquidus curve and liquidus valleys a trend to significantly higher temperature could be observed in the isopleths at 40, 50 and 60 at.% Fe in this work compared to the vertical sections calculated by Du et al. [45]. Due to the results in the FeSi₂ area, the vertical section at 5 at.% Al (Figure 41a) deviates in terms of some additional phase fields. A comparison of the experimental results with the sections at 5 at.% Al and at 40, 50, 60 at.% Fe calculated with the thermodynamic model of Du et al. [45] is shown in Figure 41. Given the significant differences of the liquidus lines, a re-assessment of this phase diagram appears to be necessary.

During the current investigation, also some binary Fe–Si samples were prepared in order to check consistency with the literature phase diagram given by [153]. These data are included in Figures 39b and c. In case of the congruent melting point of FeSi a slight difference to the literature value is found: according to the DTA results (compare Appendix-Table 3) this value is 1421 °C while the assessed phase diagram [50] gives 1410 °C.

A full list of thermal effects observed by DTA in this study is provided as supplementary material in Appendix-Table 3.

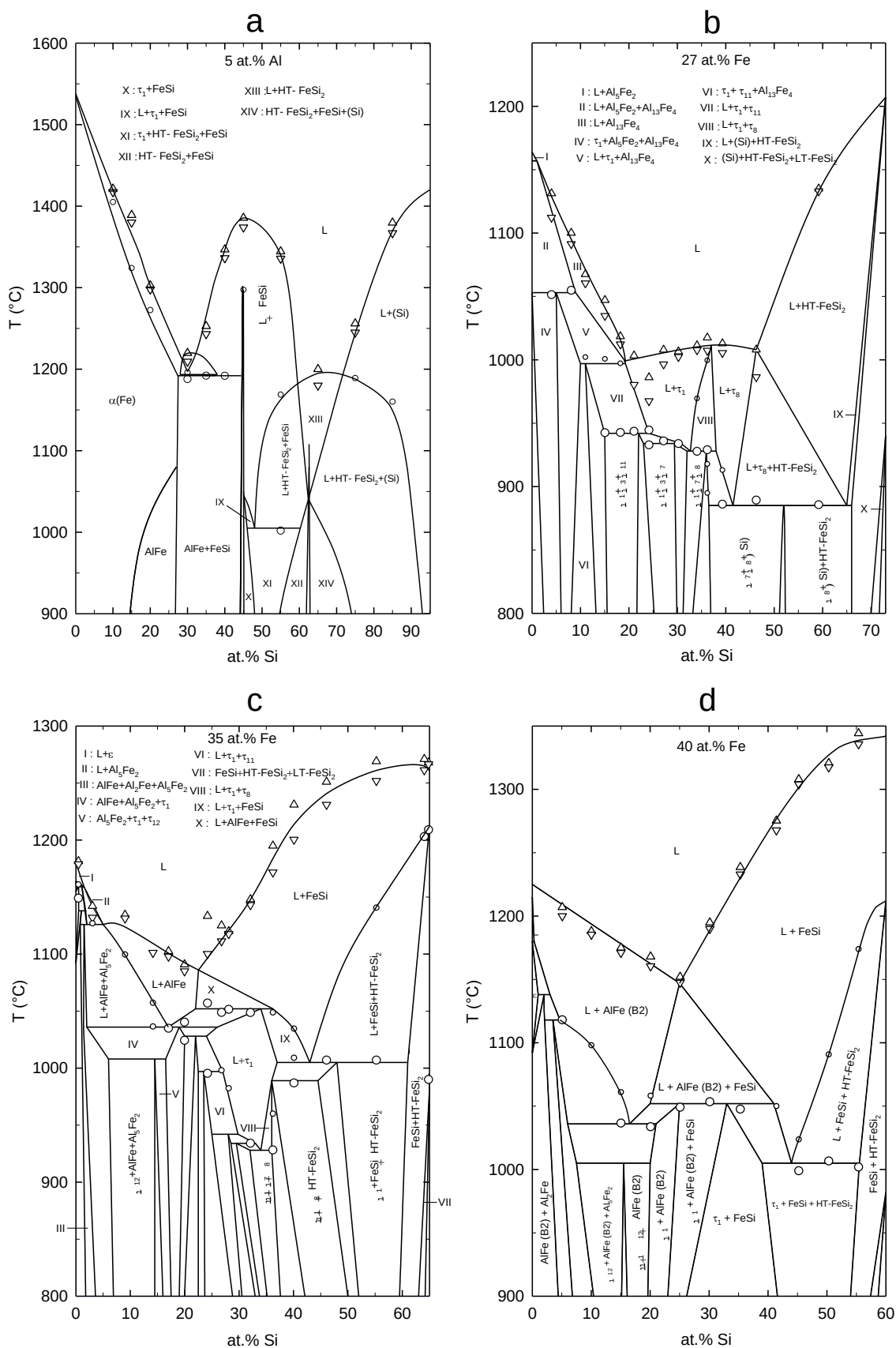


Figure 39. Vertical sections of Al–Fe–Si at (a) 5 at.%Al, (b) 27, (c) 35 and (d) 40 at.% Fe and Experimental data from DTA experiments are shown as circles (invariant thermal effects), small circles (non-invariant thermal effects), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

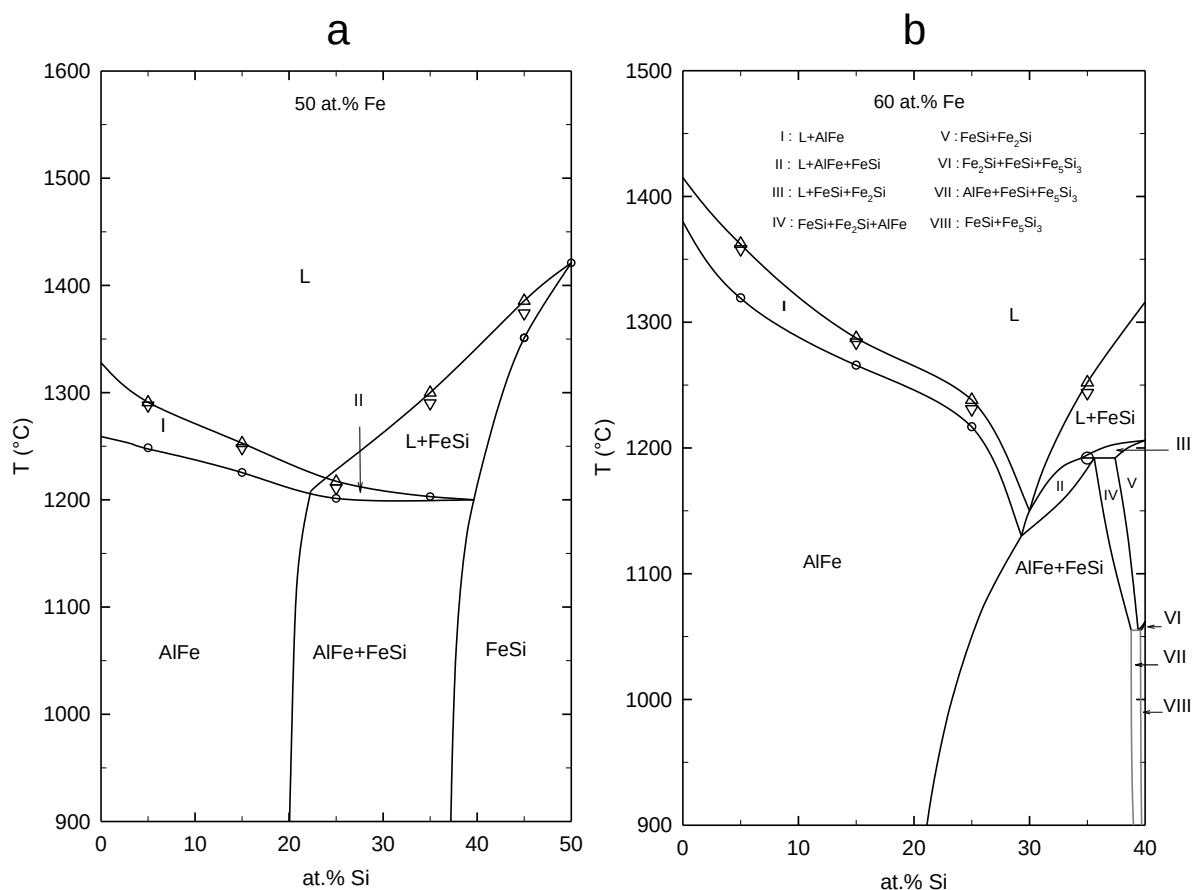


Figure 40. Vertical sections of Al–Fe–Si at (a) 50 and (b) 60 at.%Fe. Experimental Data from DTA experiments are shown as circles (invariant thermal effects), small circles (non-invariant thermal effects), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

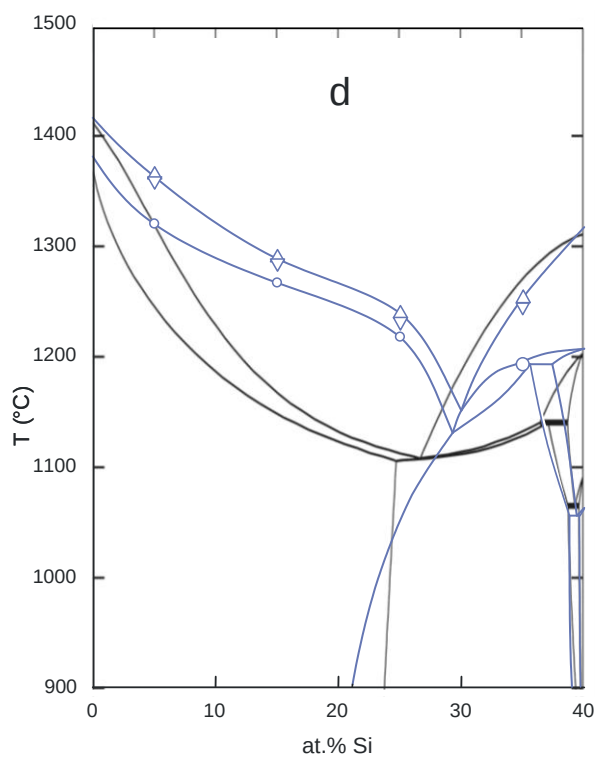
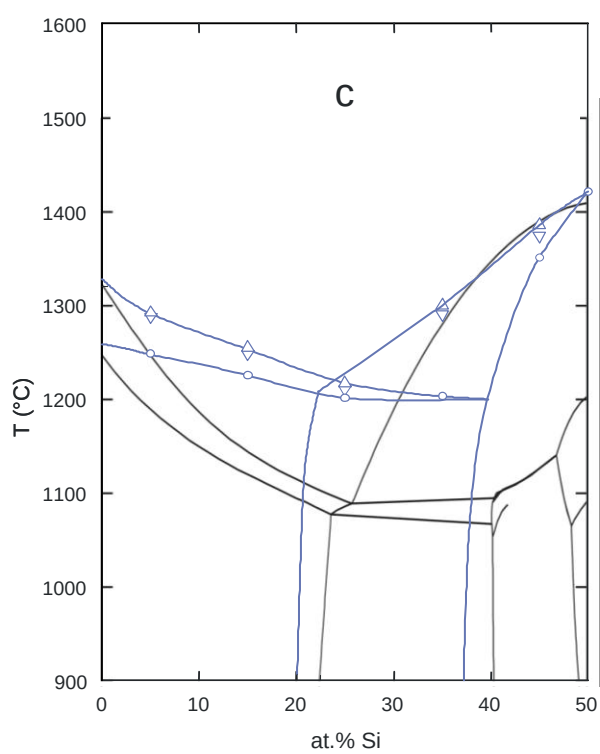
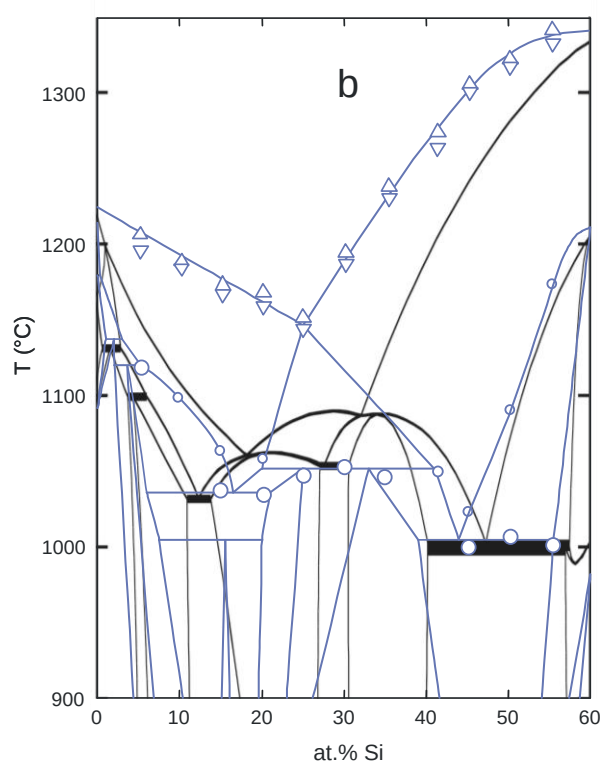
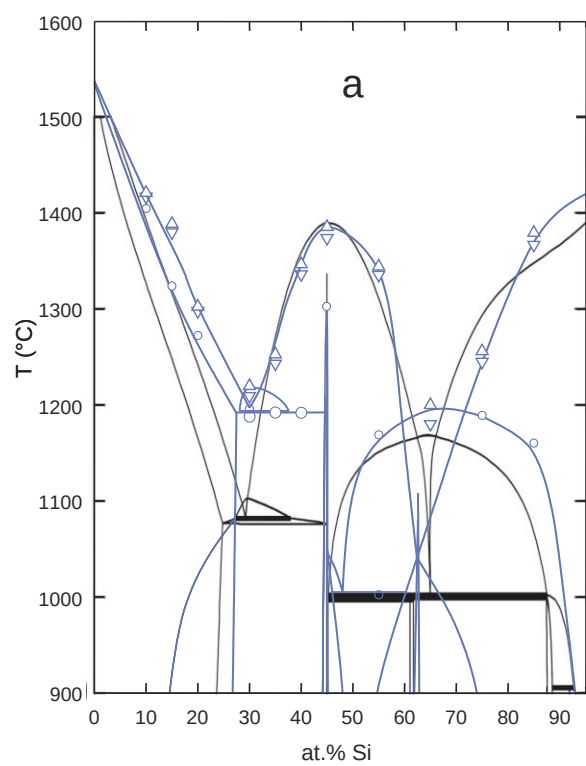


Figure 41. Comparison of vertical sections in Al–Fe–Si at (a) 5 at.% Al, (b) 40, (c) 50 and (d) 60 at.% Fe. Black lines: calculated isopleths from Du et al. [45, 154]; blue lines: constructed isopleths from present investigations. Experimental data from DTA experiments are shown as circles (invariant thermal effects), small circles (non-invariant thermal effects), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

4.2. Results in the quaternary system Al–Fe–Si–Ti

Text and figures of this chapter are taken from the publications: *M.C.J. Marker, L.I. Duarte, C. Leinenbach, K.W. Richter, Characterization of the Fe-rich corner of Al-Fe-Si-Ti, Intermetallics, 39 (2013) 38-4;* and *M.C.J. Marker, K.W. Richter, Partial liquidus projection and vertical sections in the system of Al-Fe-Si-Ti, Intermetallics, D-13-00320 (2013) revised.* A few additional remarks and comments have been added.

In the current work three two-dimensional isothermal sections at 900°C and at fixed Fe-content of 50, 60 and 70 at.% respectively are presented. It should be pointed out, that (similar to e.g. vertical sections in the ternary) these graphical sections do not contain the full phase diagram information, as they refer to phase compositions that usually do not lie within the section. Therefore a full list of experimental results for all investigated samples (including phase compositions measured by EPMA and lattice parameters refined by powder XRD) is given in Appendix-Table 4. The graphical representation of sample composition is given in Figure 42a-c.

Different terms are used in literature for the different bcc-based modifications in the Fe-rich area of the systems. To avoid confusion, they will be labelled subsequently as **A2** for (α Fe) (W-type, *cI2*); **B2** for α_2 (FeAl) and α_2 (Fe₃Si) (CsCl-type, *cP2*); **D0₃** for α_1 (Fe₃Al) and α_1 (Fe₃Si) (BiF₃-type, *cF16*) and the ternary ordered L2₁ variant (Heusler phase) in the system Al–Fe–Ti. Unary, binary and ternary phases of the involved systems, known in the Fe-rich area are listed also in Appendix-Table 1.

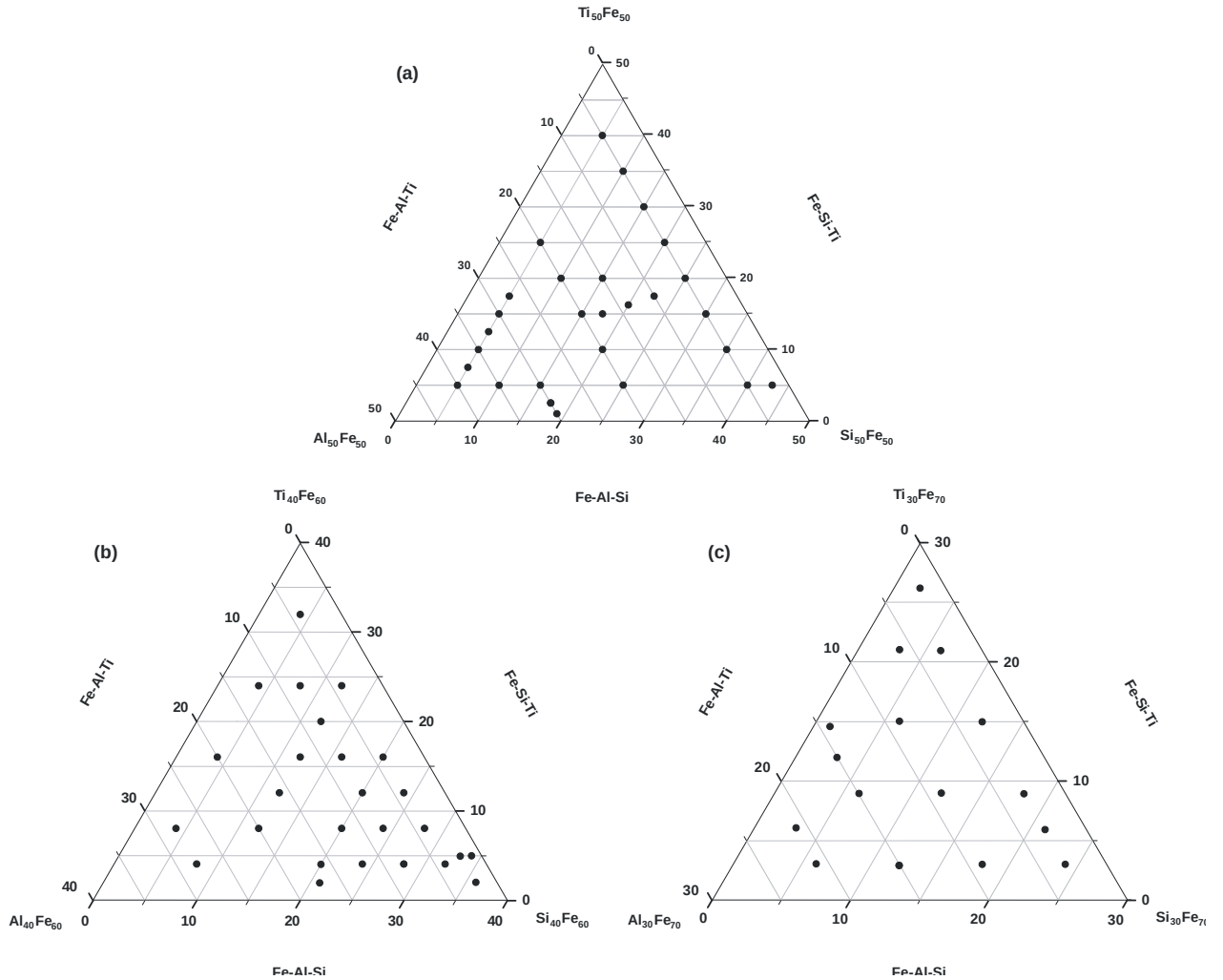


Figure 42. Sample compositions of quaternary samples investigated in the system Al–Fe–Si–Ti at (a) 50, (b) 60 and (c) 70 at.% Fe annealed at 900 °C.

In the beginning of this chapter an explanation how to construct and read phase fields drawn by the measured compositions and their relationship to the ternary subsystems is given.

For the depiction of experimental data in the figures, the projection of the intersection between phase field and section plane is given in the respective figures. This procedure is shown schematically in Figure 43. A four-phase field has the form of a general tetrahedron which may intersect with the section plane in the form of a triangle (if three of the phase compositions lie on one side of the plane, and one on the opposite side), or a quadrangle (if two of the phase compositions lie on each side of the plane).

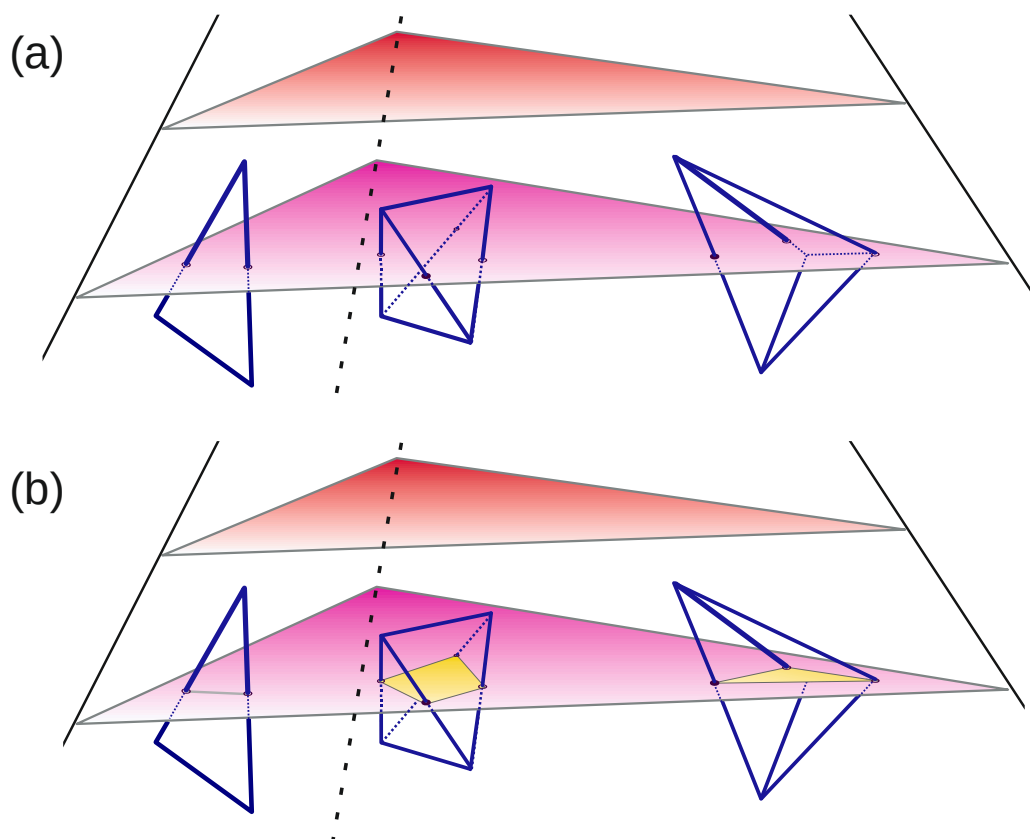


Figure 43. (a) Schematic representation of the intersection of three- and four-phase equilibria with a two-dimensional section within a composition tetrahedron. Intersection lines and planes to be shown within the two-dimensional section are highlighted in (b).

Likewise, the projection of a three-phase field in the plane is a line, and the projection of a two-phase field is a point within the plane (not shown in Figure 43). Knowing the composition of the phases (Appendix-Table 4), the piercing points within the section plane can be easily determined by vector calculation. A detailed graphical explanation of the procedure on basis of sample No. 31 is shown in Figures 44 - 46.

Figure 44 shows the situation for sample No. 31 (compare also Appendix-Table 4) situated in the section at 60 at.% Fe in the Si-rich corner. The connecting line (part of a tie-triangle) inside the red square represents the phase boundary of the three-phase field $[D0_3 + \tau_2 + Fe_2Ti]$, determined by vector calculation.

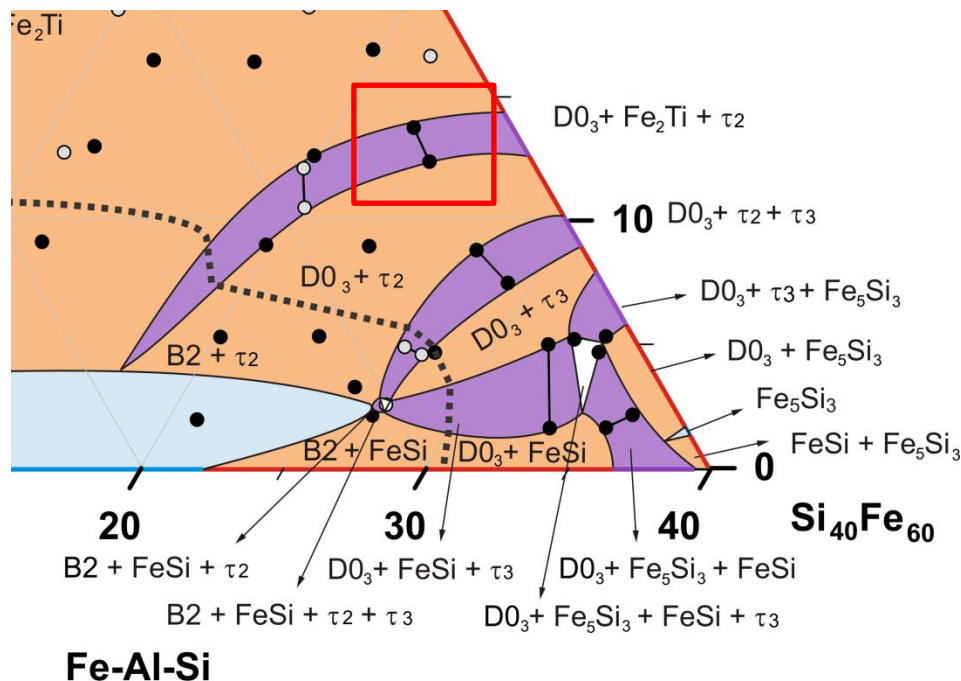


Figure 44. Detail of the intersection at 60 at.% Fe in the Si-rich corner. Focus is on the tie-line of sample No. 31 (red square). This tie-line represents the phase boundary of the three-phase field, determined by vector calculation.

The tie-triangle was measured experimentally, i.e. the three compositions are known from EPMA measurements with the usual error bars and given below:

Fe₂Ti: Al 1.8(1) Fe 49.1(3) Si 24.9(3) Ti 24.1(1)

D0₃: Al 4.8(1) Fe 67.4(3) Si 21.2(2) Ti 6.6(2)

τ₂: Al 0.0(1) Fe 34.7(4) Si 32.9(2) Ti 32.3(2)

These three composition points exactly define the position of the tie triangle in space (in the same way as two composition points define the position of a tie line in a ternary isothermal section). By vector calculation, the intersection line between the tie triangle and the composition plane (Fe = 60at.%) can be calculated. This is again an exact procedure. The endpoints of the intersection line exactly show the measured phase boundary (zero fraction line) for this specific sample.

They are in fact the only way to fix the course of the phase boundary (zero fraction line) from experimental data. Thus the line and the points in Figure 45 (outlined in red) can be drawn. The phase boundary (zero fraction line) must go through the point. The first one is the limit of the $[D0_3 + \tau_2]$ equilibrium with zero fraction of Fe_2Ti , the second is the limit $[D0_3 + Fe_2Ti]$ equilibrium with zero fraction of τ_2 . The line shows the intersection of the two triangles. The nominal sample composition must lie on this line. None of the measured phases of the three phase field $[D0_3 + \tau_2 + Fe_2Ti]$ has a composition at 60 at.% Fe.

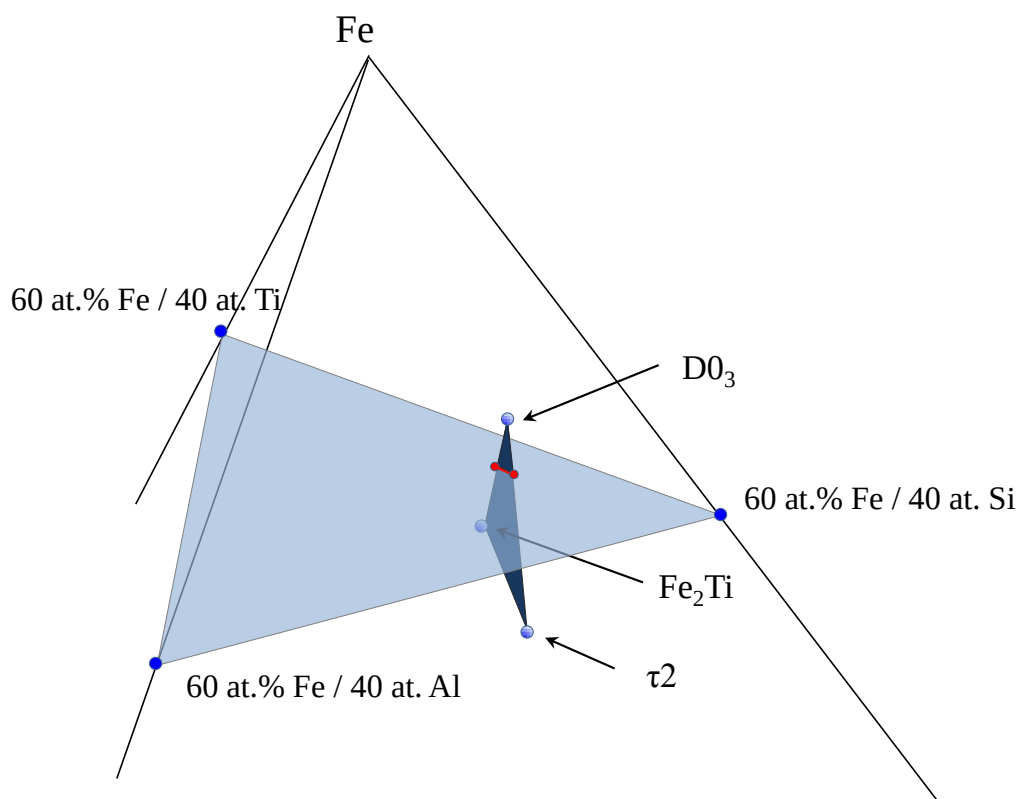


Figure 45. Detail of the intersection at 60 at.% Fe in the Si-rich corner. Focusing is on the tie-line of sample No. 31 (red square).

With the same procedure it is also possible to exactly determine the phase boundary lines in the limiting ternary systems. The correlation of a tie-triangle in the three-phase field $[D0_3 + \tau_2 + Fe_2Ti]$ in the sub-system Fe–Si–Ti and the corresponding line in the quaternary intersection is shown in Figure 46. The phase Fe_3Si in Figure 46 (b) is identical with $D0_3$.

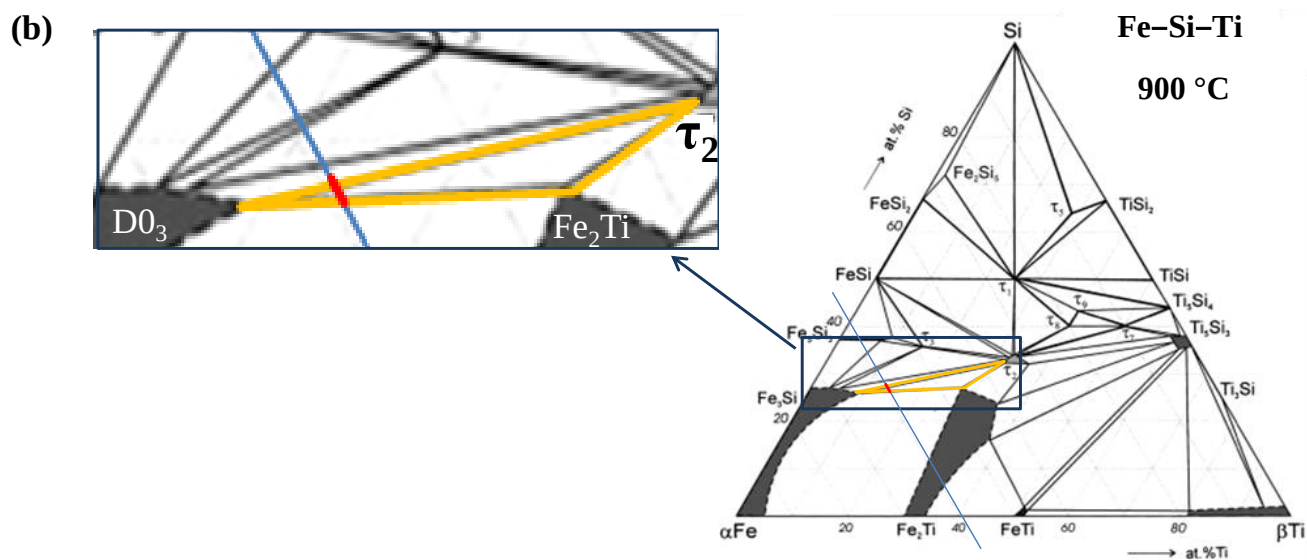
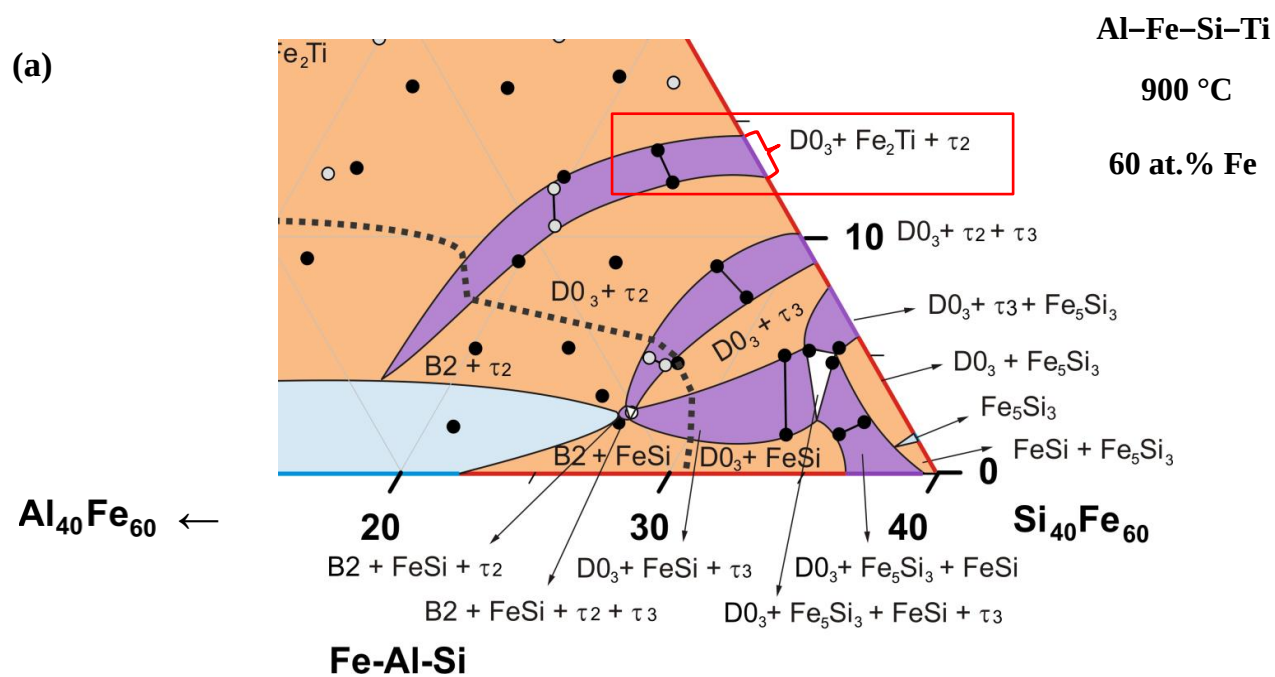


Figure 46. (a) Detail of the intersection at 60 at.% Fe in the Si-rich corner. (b) Correlation of tie-lines in the quaternary intersection and in the ternary isothermal section.

In the quaternary system Al–Fe–Si–Ti the three-phase field [$D0_3 + \tau_2 + Fe_2Ti$] (violet) shows an extension from the ternary limiting system Fe–Si–Ti to the quaternary intermetallic B2 phase. In Figure 46 (b) the red tie-line show the boundary at 60 at.% Fe which is the same as in Figure 46 (a) highlighted by the red curly bracket.

All experimental data points shown in the Figures 49 - 51 (sections at 50, 60 and 70 at.% Fe) were determined by this procedure. Furthermore it should be pointed out, that the projection of a specific equilibrium may show up in more than one section. For example, sample number 05 in Appendix-Table 4 contains phases with Fe-contents of 34 ($\tau_2 = FeSiTi$), 46 (Fe_2Ti) and 66 ($D0_3$) at.% Fe. Thus, the projection of this specific three-phase equilibrium can be drawn in the sections at 50 as well as at 60 at.% Fe.

Besides the investigation of phase compositions by EPMA, the crystallographic structures of all coexisting phases were identified by X-ray powder diffraction as already discussed in 3.1 & 3.2. Cell parameters and other crystallographic parameters were refined by the Rietveld method. These data are of special importance for the identification of phases with extended composition range and allow furthermore the distinction between A2, B2 and $D0_3$ phase regions, which form a common phase field in the quaternary system. It should be emphasized, however, that the distinction of A2, B2 and $D0_3/L2_1$ is not always unambiguous. It is known that the ordering transitions cannot always be suppressed by quenching, and that A2 disorder can be attained by pulverizing B2 or $D0_3$ -ordered samples for powder XRD investigations. Thus, the course of the lines separating these fields has to be taken with some caution. To confirm these results, additional experiments, e.g. with transmission electron microscopy would be helpful. A more detailed discussion of the A2/B2/ $D0_3$ phase region will be given in section 4.2.1.

For an improved graphical illustration the combined three intersections at 50, 60 and 70 at.% situated in the tetrahedron is given in Figure 47 below.

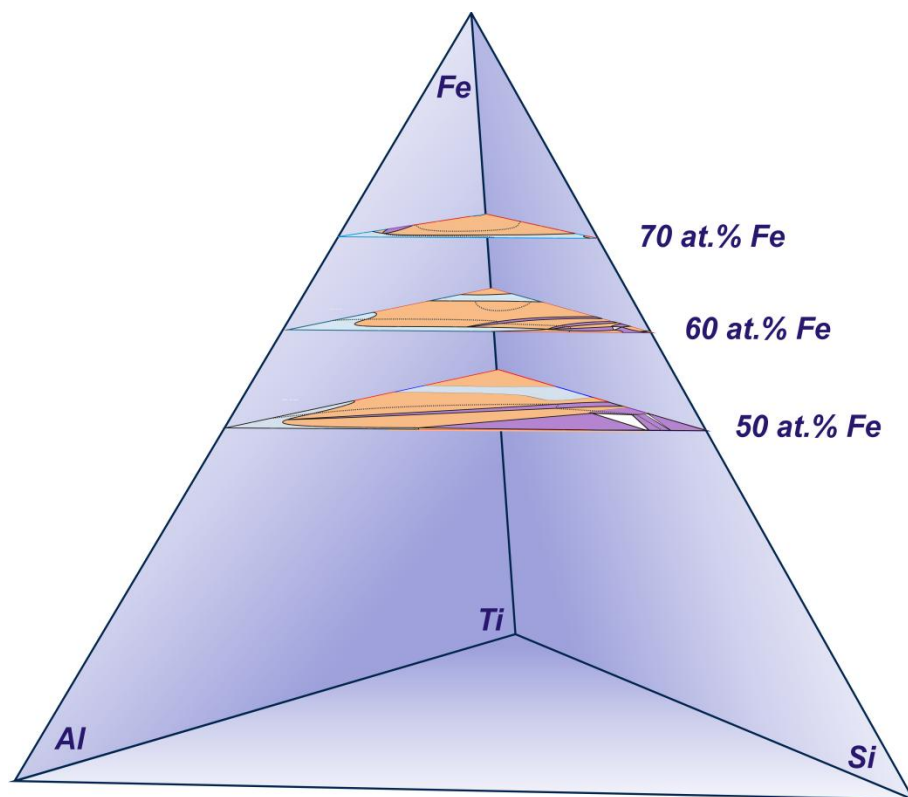


Figure 47. Graphical representation of the three sections at 50, 60 and 70 at.% Fe situated in the isothermal tetrahedron of the quaternary system Al-Fe-Si-Ti.

To see the correlation of these sections with the limiting ternary isothermal sections and phase boundaries respectively, an attempt of a graphical representation is given in Figure 48, selected section at 50 at.% Fe.

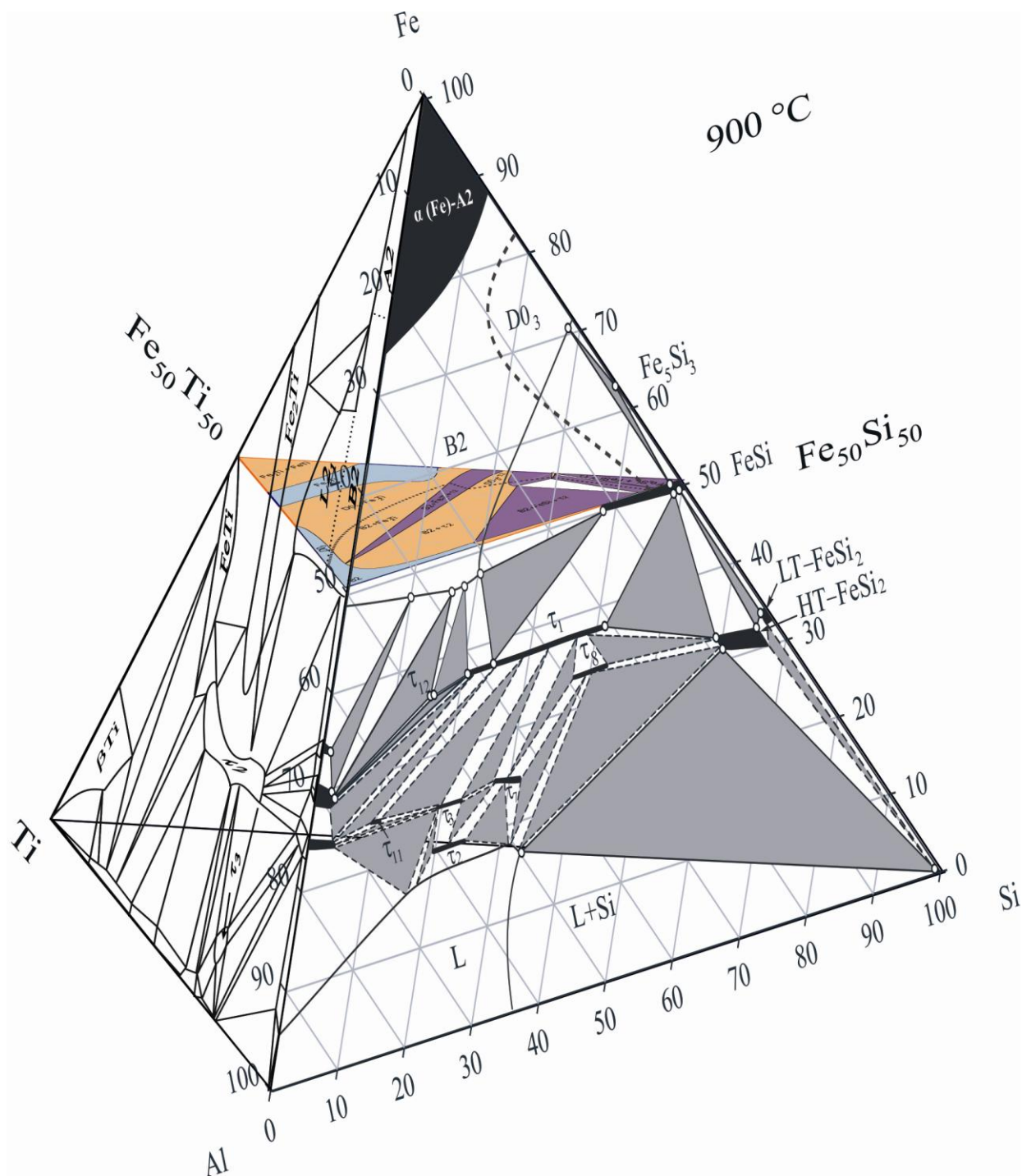


Figure 48. Graphical representation of the quaternary section at 50 at.% Fe correlated with the ternary isothermal sections of the two sub-systems Al–Fe–Si [48] and Al–Fe–Ti [107].

Boundaries of the respective phase fields from the ternary limiting isothermal sections (only two are shown at front of the tetrahedron) form the outer lines of the quaternary section (triangle).

Figures 49 – 51 show the sections at 50, 60 and 70 at.% Fe, respectively. Different colouring was used to distinguish single-, two-, three- and four-phase regions. Experimental data points (piercing points) are given as small circles, which are connected with lines in case of three- and four-phase fields. Black circles correspond to samples lying within the section; while white circles correspond to samples lying in an adjacent section. The course of the second order transition lines between A2, B2 and D0₃ (L2₁) phase fields are shown as dotted lines. All limiting ternary phase equilibria were taken from the isothermal sections at 900°C shown in Figures 6, 10 and 12 (chapter 2.2).

4.2.1. The section at 50 at.% Fe

The section at 50 at.% Fe given in Figure 49 shows two single-phase fields, the Laves phase Fe₂Ti which extends continuously from the ternary Al–Fe–Ti to the ternary Fe–Si–Ti system, and a small V-shaped phase field of B2/D0₃ which is situated around the Al₅₀Fe₅₀ corner. In this section, the Laves phase shows a solubility of about 13 - 19 at.% Al and 13 - 23 at.% Si. In addition, the solid solution of Al in FeSi is situated at 50 at.% Fe in the limiting ternary system Al–Fe–Si. This phase does not have a significant solubility for Ti. Six two-phase fields were observed in the section, including the extended fields [B2/D0₃ + Fe₂Ti] and [B2/D0₃ + τ 2]. Four of the six three-phase fields found in the section originate from the ternary Fe–Si–Ti system. In the Si-rich part, two four-phase equilibria, [B2 + FeSi + τ 2 + τ 3] and [D0₃ + Fe₅Si₃ + FeSi + τ 3] are observed. These four-phase equilibria touch the limiting Al–Fe–Si system at the solid solution of Al in FeSi. Note that the four-phase equilibrium [B2 + FeSi + τ 2 + τ 3] was found in two samples (No. 07 and No. 08) which differ significantly regarding the composition of B2. The compositions determined from sample No. 08 were found to be more reliable due to better homogeneity of the sample and also due to much better agreement with the results from the section at 60 at.% Fe, so these values were taken to draw the section in Figure 49.

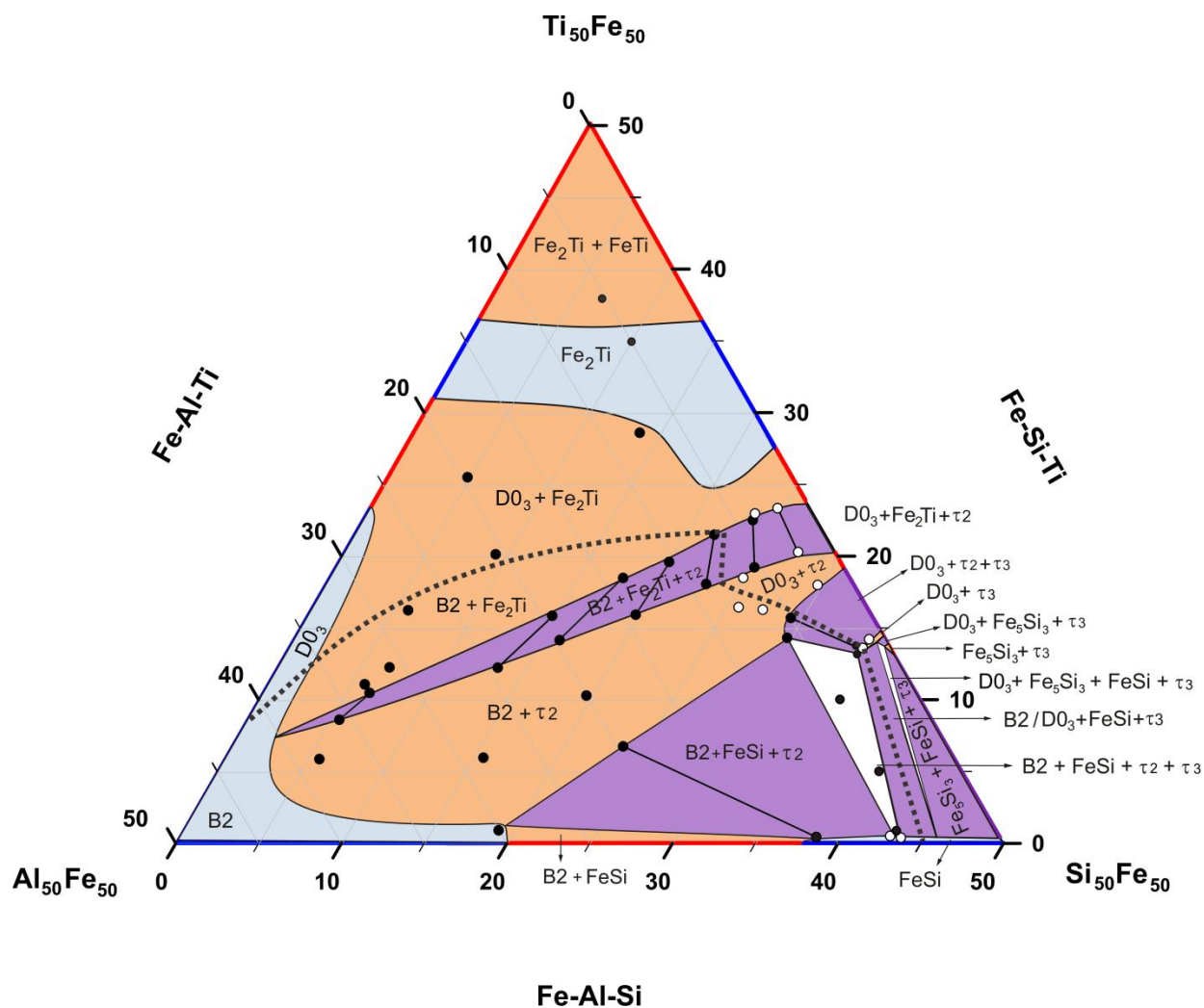


Figure 49. Isothermal section of Al–Fe–Si–Ti at 900°C and 50 at% Fe. Single-phase field: blue, two-phase field: orange, three-phase field: violet, four-phase field: white. Experimental intersection points from samples situated within the section are shown as filled circles, points from samples situated in other sections are shown as open circles. The dotted line separates B2 and $D0_3$ phase fields. Values of phase boundaries from the ternary sub-systems drawn at the edges were taken from literature [48, 107, 112]. Note that the lines shown in the three-phase fields are projections of the measured tie-triangles within the plane. They should not be confused with tie-lines.

4.2.2. The section at 60 at.% Fe

The section at 60 at.% Fe given in Figure 50 is dominated by the two-phase field $[A2/B2/D0_3 + Fe_2Ti]$ which covers a large part of the section. It is bordered by the single-phase field of $B2/D0_3$ and the Laves phase Fe_2Ti in the Ti-rich corner. The latter again shows a continuous extension from the ternary Al–Fe–Ti to the ternary Fe–Si–Ti system. Three samples in the section at 60 at.% Fe show the equilibrium $A2 + Fe_2Ti$. Supplemented by the tie lines of samples from the section at 70 at.% Fe, the course of the line separating the A2 and $D0_3$ fields was assessed (Figure 50). Equilibria with A2 do not extend to the limiting ternaries but form an island in the quaternary. Fe_5Si_3 does not show a significant extension to the quaternary. The same two four-phase equilibria as in the previous section are found in the Si-rich corner. The phase field $[B2 + FeSi + \tau_2 + \tau_3]$ is already very small in the section at 60 at.% Fe. The phase field $[D0_3 + Fe_5Si_3 + FeSi + \tau_3]$ was confirmed in two samples (numbers 53 and 54) by XRD, but the exact composition of FeSi could not be determined due to the fine microstructure of the samples.

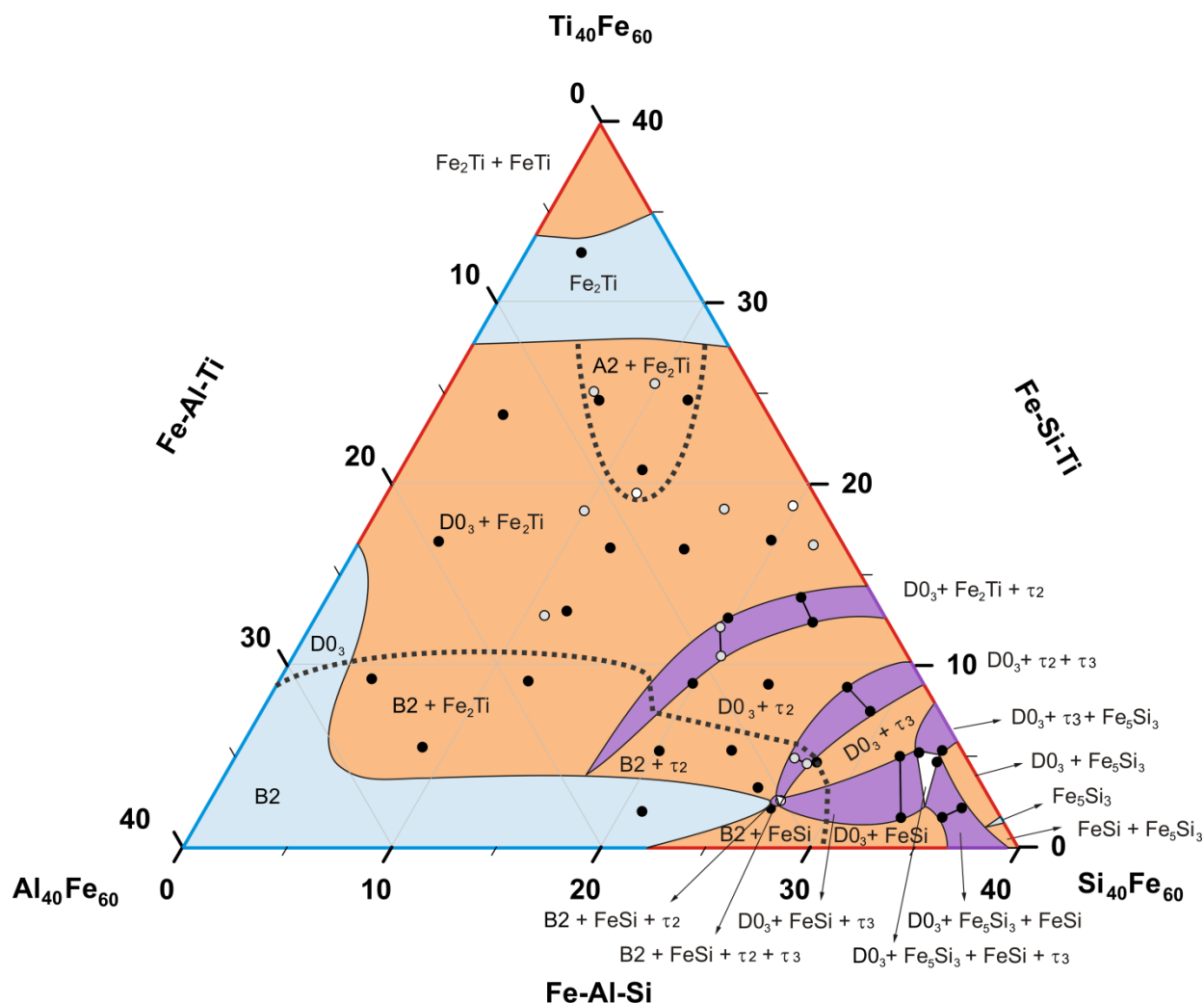


Figure 50. Isothermal section of Al–Fe–Si–Ti at 900°C and 60 at% Fe. Single-phase field: blue, two-phase field: orange, three-phase field: violet, four-phase field: white. Experimental intersection points from samples situated within the section are shown as filled circles, points from samples situated in other sections are shown as open circles. The dotted lines separate A2, B2 and D0₃ phase fields. Note that the lines shown in the three-phase fields are projections of the measured tie-triangles within the plane. They should not be confused with tie-lines.

4.2.3. The section at 70 at.% Fe

Phase equilibria at 70 at.% Fe (Figure 51) are comparably simple. The section is dominated by a large single-phase field B2/D0₃ originating from the phase field in the ternary Al–Fe–Si system, and by the two-phase field [A2/D0₃ + Fe₂Ti]. The solubility of Ti in B2/D0₃ within the section varies between 5 and more than 10 at.%. In agreement with the ternary Al–Fe–Ti phase diagram shown in Figure 10, the second order B2/D0₃ transition is drawn to open up into a two-phase field near the ternary system. However, the extension of this phase field is only tentative, as none of our samples was situated within the two-phase field. Several samples in the section at 70 at.% Fe show the equilibrium A2+ Fe₂Ti. The respective tie lines connect the Laves phase with A2 at Fe-contents higher than 75 at.%. The extensions of the single-phase field of Fe₂Ti, the two-phase field [D0₃ + Fe₅Si₃] and the three-phase field of [B2 + Fe₂Ti + D0₃] are only small; no samples were situated within them. In agreement with [112], the Fe-rich phase Fe₇Si₂Ti was not found in any of the samples annealed at 900 °C.

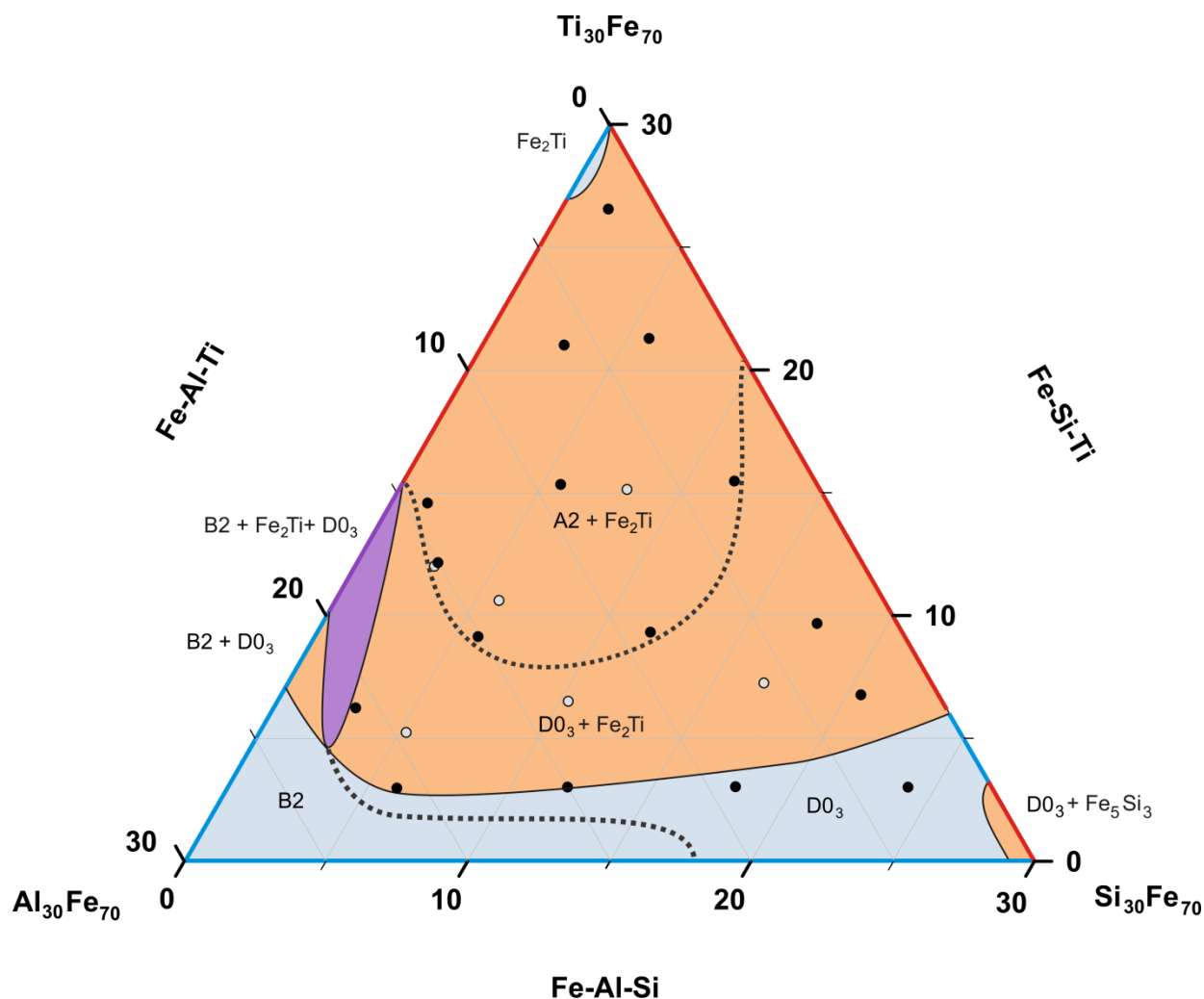


Figure 51. Isothermal section of Al–Fe–Si–Ti at 900°C and 70 at% Fe. Single-phase field: blue, two-phase field: orange, three-phase field: violet, four-phase field: white. Experimental intersection points from samples situated within the section are shown as filled circles, points from samples situated in other sections are shown as open circles. The dotted lines separate A2, B2 and D0₃ phase fields. Note that the lines shown in the three-phase fields are projections of the measured tie-triangles within the plane. They should not be confused with tie-lines.

In Figure 52 a graphical representation of the correlation between the respective quaternary sections and the ternary limiting systems is shown.

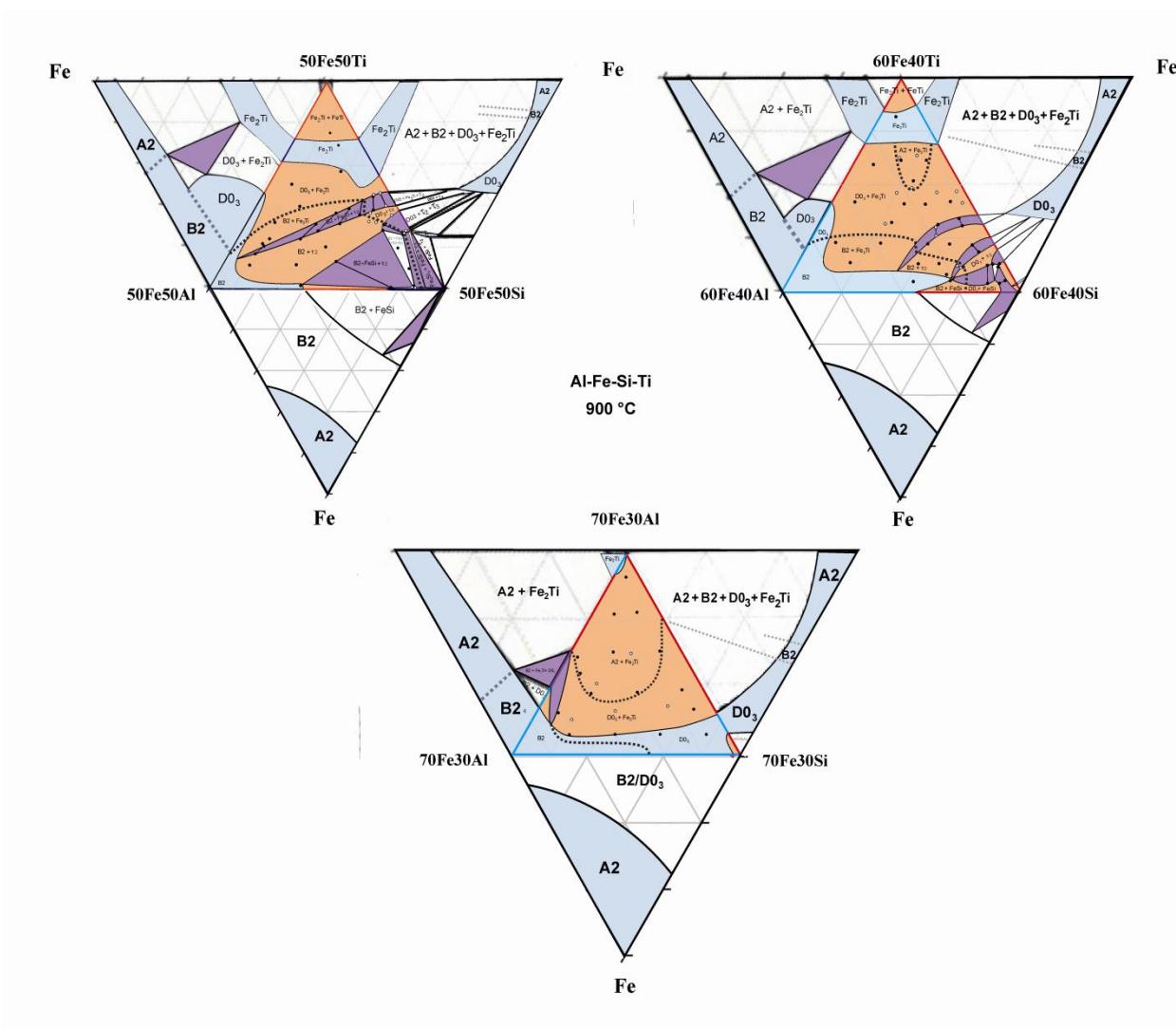


Figure 52. Quaternary intersections at 50, 60 and 70 at% Fe at 900°C surrounded by the three ternary limiting isothermal sections Al–Fe–Si, Al–Fe–Ti and Fe–Si–Ti.

4.2.1. Crystallographic Parameters and Homogeneity Ranges

The phase field A2 / B2 / D0₃

It is well known that the B2 structure (CsCl-type, $Pm\bar{3}m$) can be formed in a second order transition from a disordered A2 (W-type, $Im\bar{3}m$) solid solution, e.g in the binary Al–Fe system [57]. Ordering occurs between nearest neighbour atoms where the Fe-atoms occupy the corners of the cubic cell, while the body-centered sites are occupied statistically by Fe- and Al-atoms. Another ordering transition leads to the D0₃ structure (BiF₃-type, $Fm\bar{3}m$). This transition is connected with a doubling of the cubic cell parameter (i.e. the cell volume is increased by a factor of 8). In ideal Fe₃Al (D0₃), the Fe-atoms occupy the crystallographic 8c and 4a sites, while the Al-atoms occupy the 4b sites. The Fe-atom in the 4a site has eight Fe-atoms as nearest neighbours, while the Fe-atom in the 8c site has four Fe-atoms and 4 Al-atoms, as nearest neighbours [57]. Further ternary ordering may lead to the formation of the L2₁ structure (Heusler phase, AlCu₂Mn-type, $Fm\bar{3}m$), where the 4a and 8c sites are occupied by different transition metals, or at least different mixtures of atoms. This structure type has been reported in the ternary Al–Fe–Ti system [107].

First order transition A2→D0₃ and second order transitions A2→B2 and B2→D0₃ have been reported in the binary Fe–Al and Fe–Si systems and the respective phase fields extend to the ternary systems Al–Fe–Si, Fe–Si–Ti and Al–Fe–Ti, so it is clear that they are also present in the quaternary Al–Fe–Si–Ti system. These transitions have significant impact on the mechanical and physical properties of the materials and are therefore important from the application point of view. In the current work, the powder diffraction patterns of all samples containing A2/B2/D0₃-type phases were carefully analyzed in order to identify the structure type and to determine reliable cell parameters. The main diffraction lines of A2, B2 and D0₃ are identical, so identification is only possible based on a few, relatively weak superstructure reflections (compare Figure 53). Thus it is often difficult to detect the extra reflections, especially if the phase is only present as minority component in a multi-phase sample. No attempt was made to distinguish L2₁ and D0₃ ordering and all samples showing the corresponding superstructure lines are listed as D0₃ in Appendix-Table 4. The superstructure identification performed on all

samples was used to fix the second order transition lines shown dotted in Figures 49 – 51. The possible limitations of this method have been discussed in the previous section.

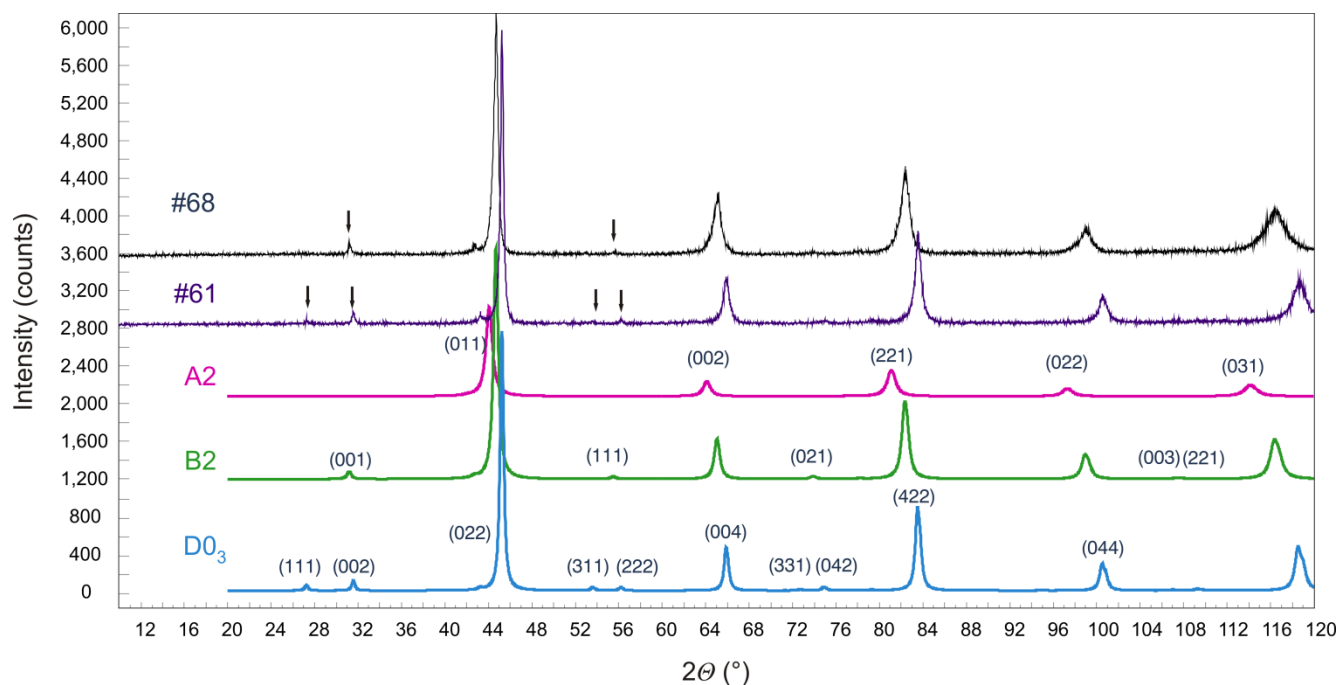


Figure 53. X-ray powder diffractograms of sample No. 68 ($\text{Al}_{15}\text{Fe}_{70}\text{Si}_{12}\text{Ti}_3$; single-phase B2) and No. 61 ($\text{Al}_3\text{Fe}_{70}\text{Si}_{24}\text{Ti}_3$; single-phase D0_3). The calculated patterns for A2, B2 and D0_3 structures are shown below.

Most of the samples investigated in the current study contain more than one phase. So the refined lattice parameters of A2/B2/ D0_3 phases listed in Appendix-Table 4 correspond to a rather arbitrary selection of quaternary phase compositions, mostly situated at the phase boundary of this phase. Therefore it is not possible to systematically discuss the change of lattice parameters with the composition. Nevertheless, by sorting our data according to certain fixed element ratios it was still possible to reveal some trends of lattice parameter variation. It can be stated that the change of the lattice parameter with the composition is in excellent agreement with size considerations based on the covalent radii of Al (1.25 Å), Fe (1.16 Å), Si (1.17 Å) and Ti (1.32 Å); i.e. the lattice parameter decreases with increasing content of Fe and Si.

An example is given in Figure 54, showing the experimentally observed lattice parameters of B2 for several samples at fixed Fe- and Al- content.

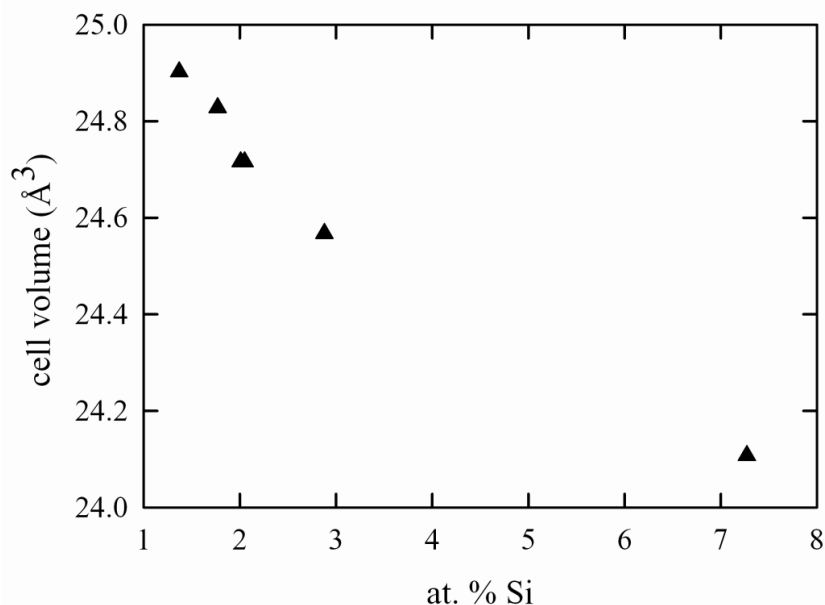


Figure 54. Change of cell volume of the B2-type phase as a function of the Si-content. The content of Al and Fe is fixed to 40(2) at.% and 52(1) at.% respectively.

Rietveld analysis of site occupations was tried for selected samples containing more than 80 % of the B2 phase. Although it is principally not possible to make an unambiguous statement on site occupations in the case of multi-component substitution, it can be stated that our refinements largely support a simple substitution model extrapolated from the ternary and binary subsystems. Considering stoichiometric “FeAl” as ideally ordered B2 phase, Fe substitution on the Al sublattice is the principal mechanism for deviation of the composition to the Fe-rich side. A similar statement can be made for the B2 phase in the binary Fe–Si system. In the ternary system Al–Fe–Ti it was found that Ti-atoms preferentially occupy the Fe-sublattice [155, 156]. Thus the substitution model $(\text{Fe,Ti})_1(\text{Al,Si,Fe})_1$ is suggested for the quaternary system which is generally in good agreement with the results from Rietveld refinement.

The Laves phase

An important group of intermetallic phases is represented by the Laves phases⁵ which form compounds of stoichiometry AB_2 . The phases are classified on the basis of geometry and exist in the three structure types (compare Figure 55): cubic $MgCu_2$ (C15, $cF24$, $Fd\bar{3}m$) [157-159], hexagonal $MgZn_2$ (C14, $hP12$, $P6_3 / mmc$) [159, 160] and hexagonal $MgNi_2$ (C36, $hP24$, $P6_3 / mmc$) [161-163]. The structures are topologically tetrahedrally close-packed (tcp, tetrahedral interstices) and belongs to the Frank-Kasper phases. The A-atoms (Mg) are surrounded by a Frank-Kasper polyhedron coordinated by 4 A- and 12 B-atoms (Ni, Cu or Zn) (compare Figure 55a) which form a network of linked tetrahedrons (compare Figure 55b and c). B-atoms are coordinated icosahedrally by 6 A-atoms in chair conformation and 6 B-atoms (compare Figure 55c).

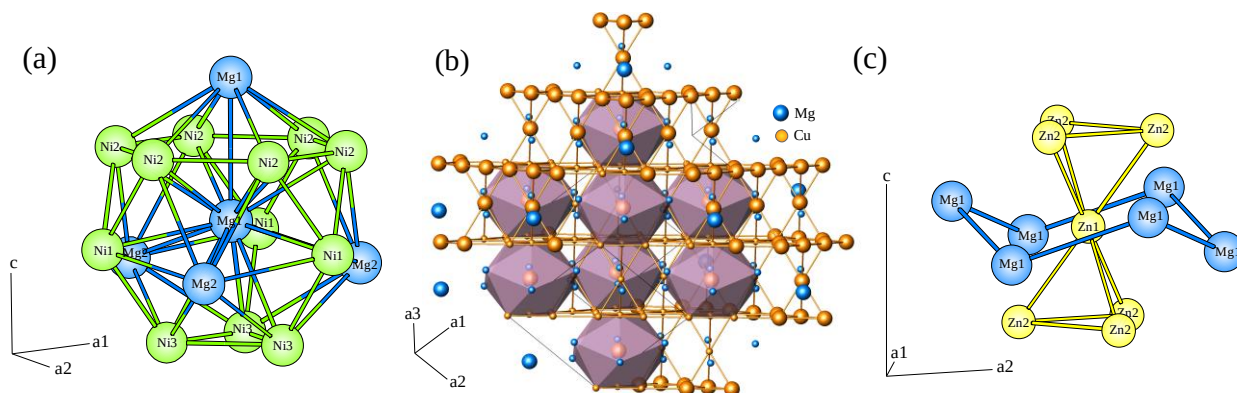


Figure 55. The structures of Laves phases (a) Frank-Kasper polyhedron of centered Mg in $MgNi_2$ (C36), (b) icosahedrons with centered Cu and its network in $MgCu_2$ (C15) and coordination sphere of Zn in $MgZn_2$ (C14).

Laves phases show also a deviation from the stoichiometric composition AB_2 [93, 164-168]. The extension to the B-rich side can be explained by substitution of the larger B atoms by smaller A atoms. The extension to the A-rich side can be caused by vacancies on the B sublattice [93, 165, 166, 168-170]. The stability of Laves phases is affected by atomic size ratio and electronegativity [86, 163].

⁵ With respect to Fritz Laves 1906-1978, a German mineralogist who first described them.

Provided a perfect hard sphere model in each of the three classes of Laves phase, the ideal size ratio is defined by $r_A / r_B = \sqrt{3/2} \approx 1.225$. At this size ratio, the structure has an overall packing volume density of 0.710. In case of the binary C14 Laves phase Fe_2Ti the size ratio is 1.167.

Laves phases are of particular interest in modern metallurgical research because of their unusual physical and chemical properties. Among others, they are used for superconducting devices or hydrogen storage materials. A review of applications is given in [171].

The Laves phase C14 (*hP12*, $P6_3/mmc$ MgZn_2 -type) is found in the binary Fe–Ti system (Figure 4, section 2.1.) around the composition Fe_2Ti and shows considerable ternary homogeneity ranges in the Al–Fe–Ti (Figure 10) as well as in the Fe–Si–Ti system. In the current work, a continuous connection of these ternary phase fields was observed. Two of the quaternary samples investigated in the current study were single-phase Fe_2Ti (samples No. 2 and No. 28) and many more were situated in various two- and three- phase fields containing Fe_2Ti in equilibrium with A2/B2/D0_3 , FeTi and τ_2 . The hexagonal lattice parameters were evaluated for all samples and are listed in Appendix-Table 4 together with the respective phase compositions. General trends of cell parameter variation with the composition are consistent with the respective covalent radii and are discussed in more detail below. The c/a ratio is varying between approx. 1.65 and 1.60 and appears to decrease with increasing Si-content.

Fe_2Ti has three crystallographically independent positions: $2a$ and $6h$ occupied by Fe-atoms and $4f$ occupied by Ti-atoms (Figure 56). Binary Fe_2Ti shows a significant homogeneity range which is mainly found at the Fe-rich side of the stoichiometric composition and was found to be due to excess of Fe-atoms on the Ti-sites [93]. In the ternary system Al–Fe–Ti a solubility of 47.5 at.% Al in Fe_2Ti is reported at 1000 °C [94] and the investigation of site preferences by Yan et al. [172] showed that Al enters both Fe-sites at different mixing levels with site preference of Al for the $2a$ site. The corresponding mechanism in Fe–Si–Ti was not studied in detail, but given the extension of the phase in the ternary (at more or less constant Ti-content) it is likely that Si primarily enters the Fe-sites. The simplified site occupation model for the quaternary phase is thus $(\text{Fe,Al,Si})_2(\text{Fe,Al,Si})_6(\text{Ti,Fe})_4$. Rietveld refinements of selected samples constrained by the overall phase composition are generally in line with such model. However, it is impossible to distinguish between Al and Si, due to their similar scattering factors.

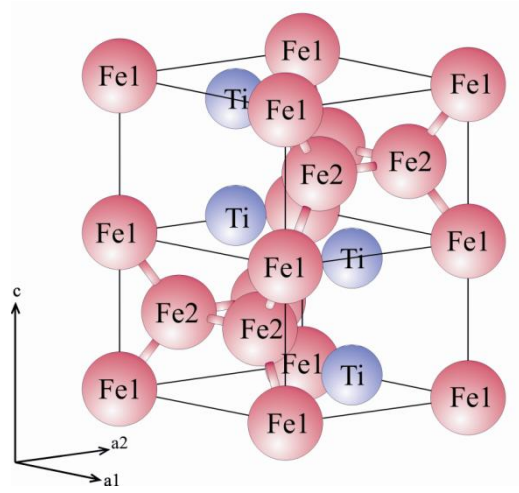


Figure 56. Graphical representation of the Laves phase Fe_2Ti ($hP12$, $P6_3/mmc$, MgZn_2 -type).

For a more detailed evaluation of the cell parameter variation with the composition, the crystallographic data for the Laves phase listed in Appendix-Table 4 were used for a non-linear regression fit using the fit equation:

$$p = v1 \cdot x(\text{Al}) + v2 \cdot x(\text{Si}) + v3 \cdot \Delta x(\text{Ti}) - p(\text{Fe}_2\text{Ti}) \quad \text{Eq. (3)}$$

where p denotes the cell parameters a , c in Å and the cell volume V in Å³, $x(\text{Al})$ and $x(\text{Si})$ are the contents Al and Si in at.% and $\Delta x(\text{Ti})$ denotes the deviation of the Ti content from the ideal composition Fe_2Ti , i.e. $33 - x(\text{Ti})$ in at.%. This fit equation reflects the basic mechanism of non-stoichiometry discussed above: Al- and Si- substitution on the Fe sublattice and Fe- substitution on the Ti-sublattice. The fit of data shows reasonable correlation between measured and predicted cell parameters as shown in Figure 57.

Table 15. Coefficients for non-linear regression fit on cell parameters of the quaternary Laves phase according to Eq. 3.

Cell Parameter	Coefficient v1	Coefficient v2	Coefficient v3
$a / \text{\AA}$	0.00398(26)	0.000680(95)	0.00256(26)
$c / \text{\AA}$	0.00466(76)	-0.00405(28)	0.00378(76)
$V / \text{\AA}^3$	0.335(23)	-0.0495(90)	0.241(23)

The regression parameters v1, v2, v3 listed in Table 15 may be interpreted as follows: the cell parameter a increases considerably with the Al-content and weakly with the Si-content, and it decreases considerably when Ti is exchanged by Fe. The cell parameter c increases with the Al-content and decreases with the Si-content, and it also decreases when Ti is exchanged by Fe. The cell volume increases with the Al-content, decreases when Ti is exchanged by Fe and is independent from the Si-content. This behaviour is in agreement with the proposed substitution mechanism considering the covalent radii of Al (1.25 Å), Fe (1.16 Å), Si (1.17 Å) and Ti (1.32 Å). However, it should be emphasized that the regression parameters give only general trends and are certainly not suitable to reliably predict cell parameters of the quaternary Laves phase. A systematic investigation of cell parameters of single-phase samples would be necessary for a deeper understanding of the substitution mechanism.

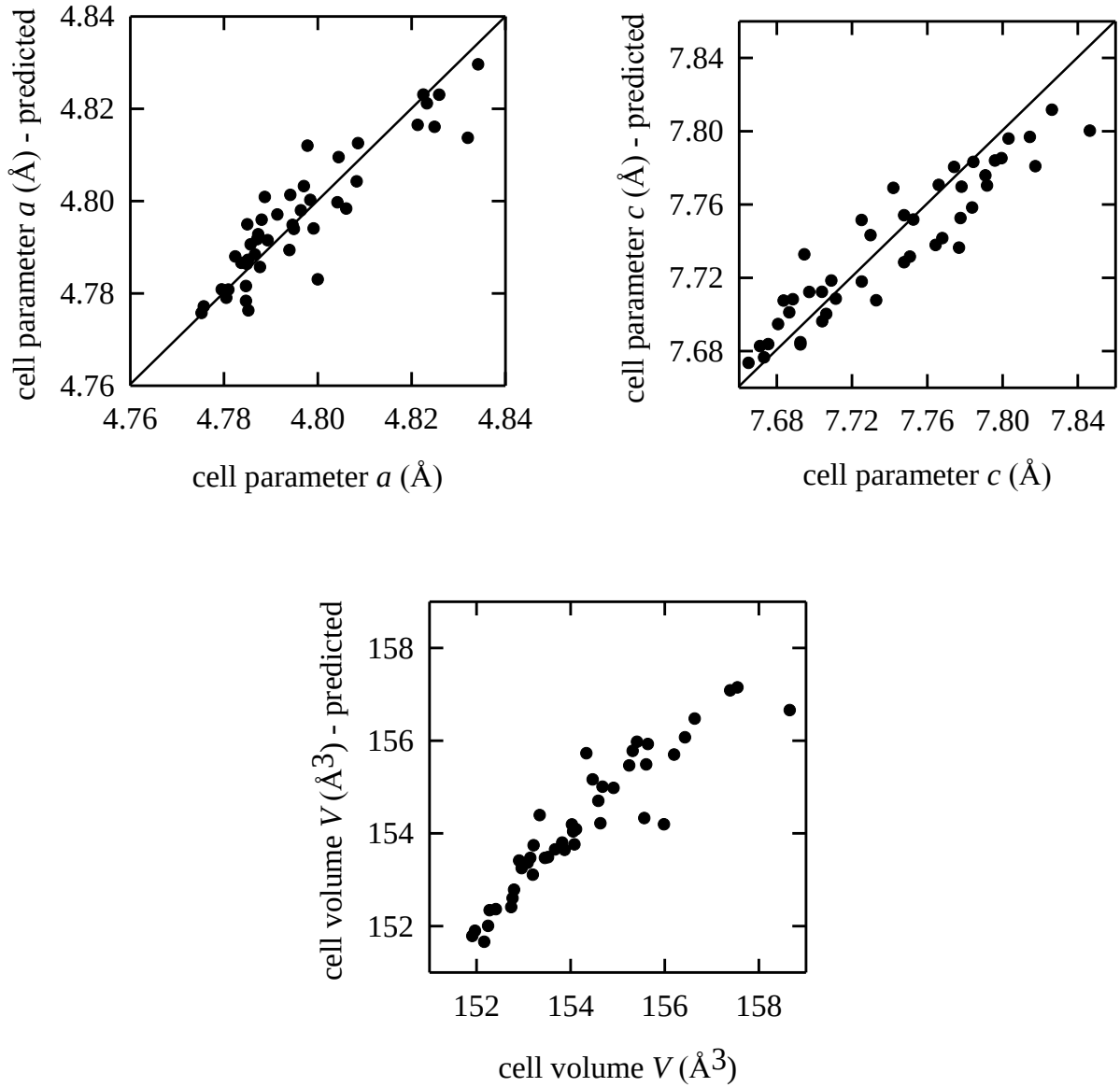


Figure 57. Correlation of experimental cell parameters for the quaternary Laves phase with predicted values based on a non-linear fit according to Eq. (3). Fit parameters are listed in Table 15.

The extension of the quaternary Laves phase field exhibits an unexpected feature highlighted in Figure 58 which shows all measured phase compositions of the Laves phase in the two-phase field $[\text{Fe}_2\text{Ti}+\text{A2/B2/D0}_3]$.

It can be seen that the phase boundary of the Laves phase in the quaternary is significantly curved towards the Fe–Al–Si system. According to the phase boundary data listed in Appendix-Table 4, the simultaneous substitution of Al and Si to Fe_2Ti strongly shifts the Ti-poor phase boundary. Ti-contents of less than 20 at.% have been found in some of the quaternary samples (e.g. No. 46 and No. 69), which is much lower than any value reported for the binary and ternary systems. During this study no explanation could be found for this behaviour, but it might be interesting to study this effect in more detail in future studies.

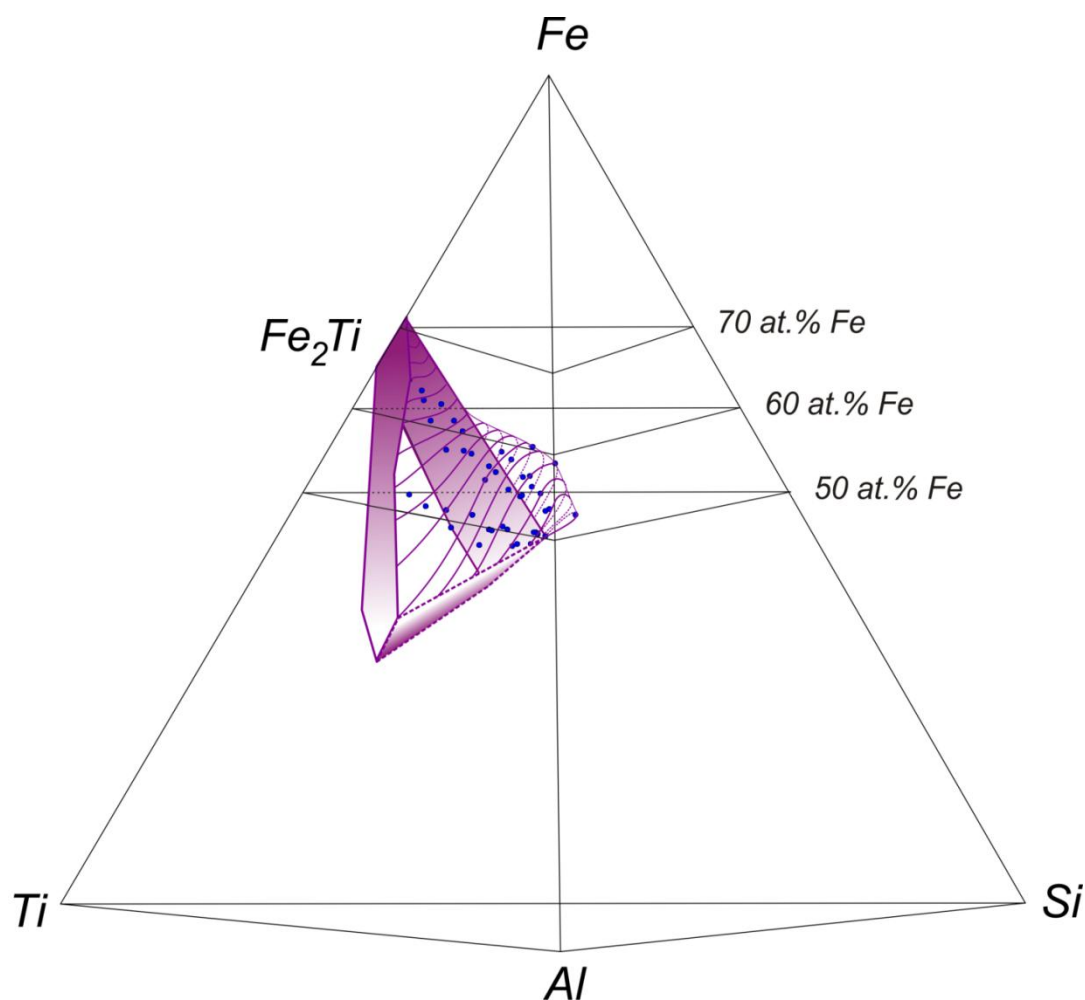


Figure 58. Fe-rich phase boundary of the Laves phase in the quaternary system Al–Fe–Si–Ti showing a pronounced curvature towards the Ti-poor side.

4.2.2. Microhardness measurements

Microhardness measurements were performed and evaluated for the Vickers hardness HV on selected metallographic samples containing either the Laves phase or the B2 phase. The results of these measurements are compiled in Table 16 (Laves phase) and Table 17 (B2 phase). Samples have been selected to cover a wide range of compositions within the respective homogeneity area. However, it should be pointed out that the phase compositions are spread out more or less randomly over the homogeneity area and thus do not correspond to certain well defined composition lines. Therefore it is only possible to evaluate rough trends of hardness with the composition.

For the Laves phase (Table 16), the measured values at room temperature vary between 1100 and 1500 HV (50mN for 20s), depending on the composition. Binary Fe_2Ti was also prepared and tested with the same experimental procedure as a reference. For this compound a value of 1242 HV was measured. The composition dependence of the Vickers hardness was evaluated with a similar substitution-model based non-linear regression equation as used for the cell parameters:

$$HV = w1 \cdot x(\text{Al}) + w2 \cdot x(\text{Si}) + w3 \cdot \Delta x(\text{Ti}) - HV(\text{Fe}_2\text{Ti}) \quad \text{Eq. (4)}$$

The correlation between the measured and predicted values for HV is shown in Figure 59. The coefficients $w1 = -17.1 \pm 5.4$, $w2 = 11.7 \pm 2.3$ and $w3 = 11.0 \pm 6.1$ show that Al decreases the Vickers hardness while Si increases HV. This is in a good agreement with the results found by Löffler et al. [114]. The substitution of Ti with Fe on the Ti-sublattice decreases the Vickers hardness. In addition, with regard to the above described correlation between the cell parameters and the Al, Si and Ti amount it can be stated that HV increases with decreasing cell-volume and decreasing c/a ratio. Sauthoff et al. observed different correlations during hardness and compression tests of the ternary C14 Laves phases $(\text{Ni},\text{Al})_2\text{Nb}$ and $(\text{Fe},\text{Al})_2\text{Ta}$, for which the hardness and yield strength, respectively, increased with increasing cell volume and increasing Al [173, 174]. However, the standard errors for the parameters $w1$ (Al) and $w3$ (Ti) are relatively large, so the trends observed in this study have to be taken with some caution.

Table 16. Vickers hardness of the Laves phase in selected quaternary samples and binary Fe₂Ti

Sample No.	Phase composition, Laves Phase				HV (50mN/20s)	Standard deviation
	Al at.%	Si at.%	Ti at.%	Fe at.%		
01	5.4	8.3	35.6	50.7	1210	–
02	4.0	11.	35.2	49.4	1390	170
03	2.3	17.	32.0	48.5	1472	70
04	2.4	21.	29.3	46.6	1295	86
10	8.2	16.	28.4	46.4	1219	30
11	6.9	22.	25.7	44.7	1349	130
28	4.9	2.1	32.6	60.5	1145	36
29	2.2	13.	28.5	55.7	1296	38
30	1.2	22.	24.9	51.9	1480	32
34	4.9	9.5	29.5	56.1	1302	35
35	3.4	16.	28.1	52.6	1280	25
36	2.6	20.	26.0	50.6	1385	–
40	7.8	5.0	28.0	59.3	1160	65
41	4.3	18.	25.9	51.4	1253	130
55	1.4	1.9	29.6	67.0	1139	40
56	1.5	7.9	28.9	61.7	1210	–
57	0.9	17.	26.0	56.1	1326	180
Fe ₂ Ti	0.0	0.0	34.0	66.0	1242	59

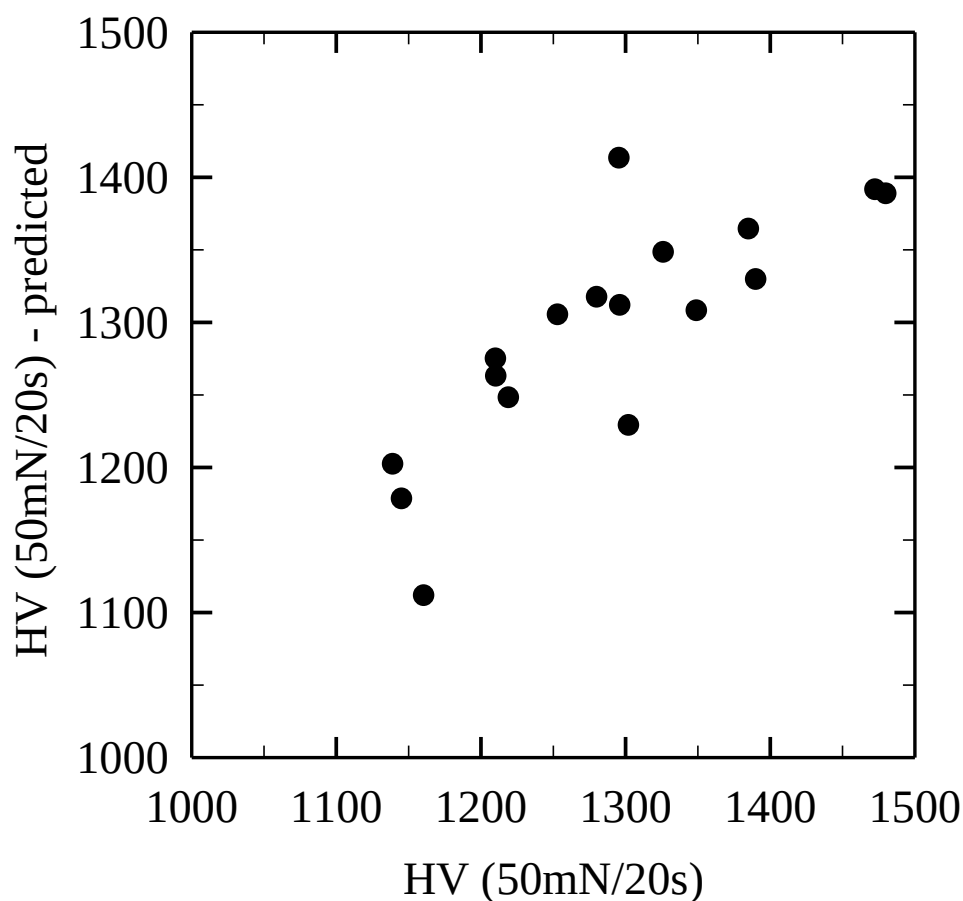


Figure 59. Correlation of experimental Vickers hardness for the quaternary Laves phase with predicted values based on a non-linear fit according to Equation (4).

In the B2 phase, the Vickers hardness was found to vary between 500 and 1000 HV (50mN/20s). The graphical representation of all data shown in Figure 60 again shows a considerable increase of the Vickers hardness with the Si-content. This general trend is in good agreement with the results of Shin et al., who observed a linear increase of HV with increasing Si amount in Fe-(9-12 at%)Si alloys with B2 structure [175].

Table 17. Vickers hardness of the B2 phase in selected quaternary samples

Sample No.	Phase composition, B2 phase				HV (50mN/20s)	Standard deviation
	Al at.%	Si at.%	Ti at.%	Fe at.%		
11	33.6	6.1	4.4	56.0	875	28
12	27.0	14.9	2.4	55.8	776	8
13	23.5	21.9	1.9	52.8	916	43
14	38.9	2.0	6.9	52.2	512	33
15	38.5	7.3	1.9	52.2	659	45
16	33.1	1.2	14.4	51.4	701	63
17	35.5	1.3	11.3	52.0	733	70
19	39.7	1.8	6.7	51.8	734	68
20	40.3	2.1	5.7	51.9	722	53
22	33.4	12.5	1.6	52.4	816	30
23	32.9	16.4	0.9	49.9	922	25
23	30.3	18.9	0.7	50.1	870	43
24	30.6	6.9	3.7	58.9	755	64
26	17.6	13.4	3.9	65.0	923	–
50	10.5	28.2	2.2	59.1	905	7
51	16.8	22.0	2.0	59.2	876	29
52	11.2	27.0	2.3	59.5	955	23
69	21.6	5.3	2.2	70.9	586	21

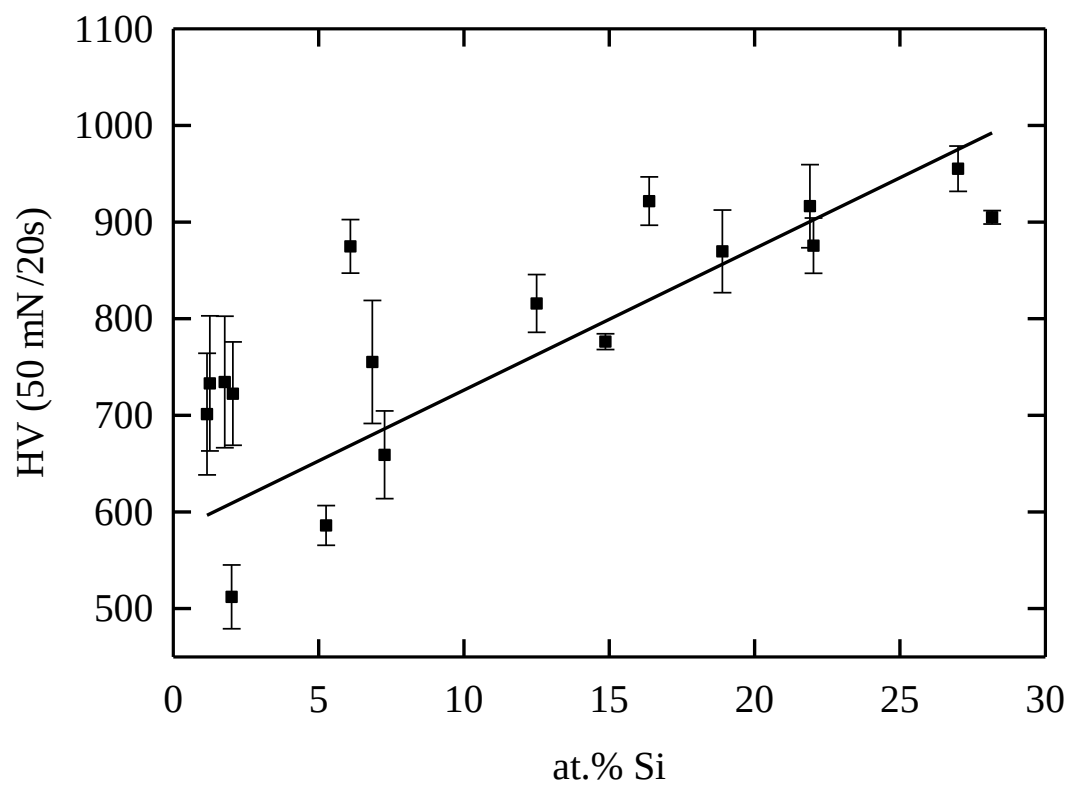


Figure 60. Vickers hardness HV (50mN/20s) for selected compositions of the B2 phase shown as a function of the Si-content.

4.2.3. Partial liquidus projection and vertical sections in the system Al–Fe–Si–Ti

An extensive description of isothermal phase equilibria at 900 °C in the iron-rich area of the quaternary system Al–Fe–Si–Ti was given above. In this section a partial liquidus projection based on DTA studies and the analysis of as-cast microstructures is given.

For a first orientation, the liquidus surfaces of the four ternary sub-systems from literature are given in Figure 61. Interpretation of the thermal effects in the quaternary system Al–Fe–Si–Ti were done on the basis of the investigations in ternary systems Al–Fe–Si by Krendelsberger et al. [46] and [45, 48], Al–Fe–Ti [106, 107, 109] and Fe–Si–Ti [112]. Reaction scheme and liquidus temperatures for these ternary systems in general are well-established.

The isotherms shown in the liquidus projection of the ternary system Al–Fe–Si have been adopted from the calculation by Du et al. [45] and were adapted in some details on basis of the experimental data measured by DTA (given in Appendix-Table 3., discussed in chapter 4.1.5 and published by Marker et al. [48]). It should be mentioned that the primary crystallization of disordered A2 and ordered B2 from the melt has not been studied experimentally. Therefore no details are given in Figure 61 and the primary crystallization field is designated as A2/B2. For the Fe-rich part (≥ 50 at.% Fe) only the transition-reaction U1: $L + \text{Fe}_2\text{Si} \rightleftharpoons (\text{A2/B2}) + \text{FeSi}$ is of importance.

Selected invariant reactions which are relevant for the iron-rich part of the quaternary system Al–Fe–Si–Ti of the ternary sub systems Al–Fe–Si, Al–Fe–Ti and Fe–Si–Ti are listed in Table 18. An extended graph of the ternary liquidus projections in the relevant area of 50 at.% Fe and more is shown in Figure 62. Isotherms in the system Fe–Si–Ti were added by the authors and are only tentative. Regarding the preparation of as-cast alloys and their characterization at ambient temperature, it should be expressed that during solidification of the liquid, the order/disorder transformation of the modifications A2, B2 and D0₃ cannot be quenched [108, 176]. So these fields are generally designated as A2/B2 in the liquidus projection.

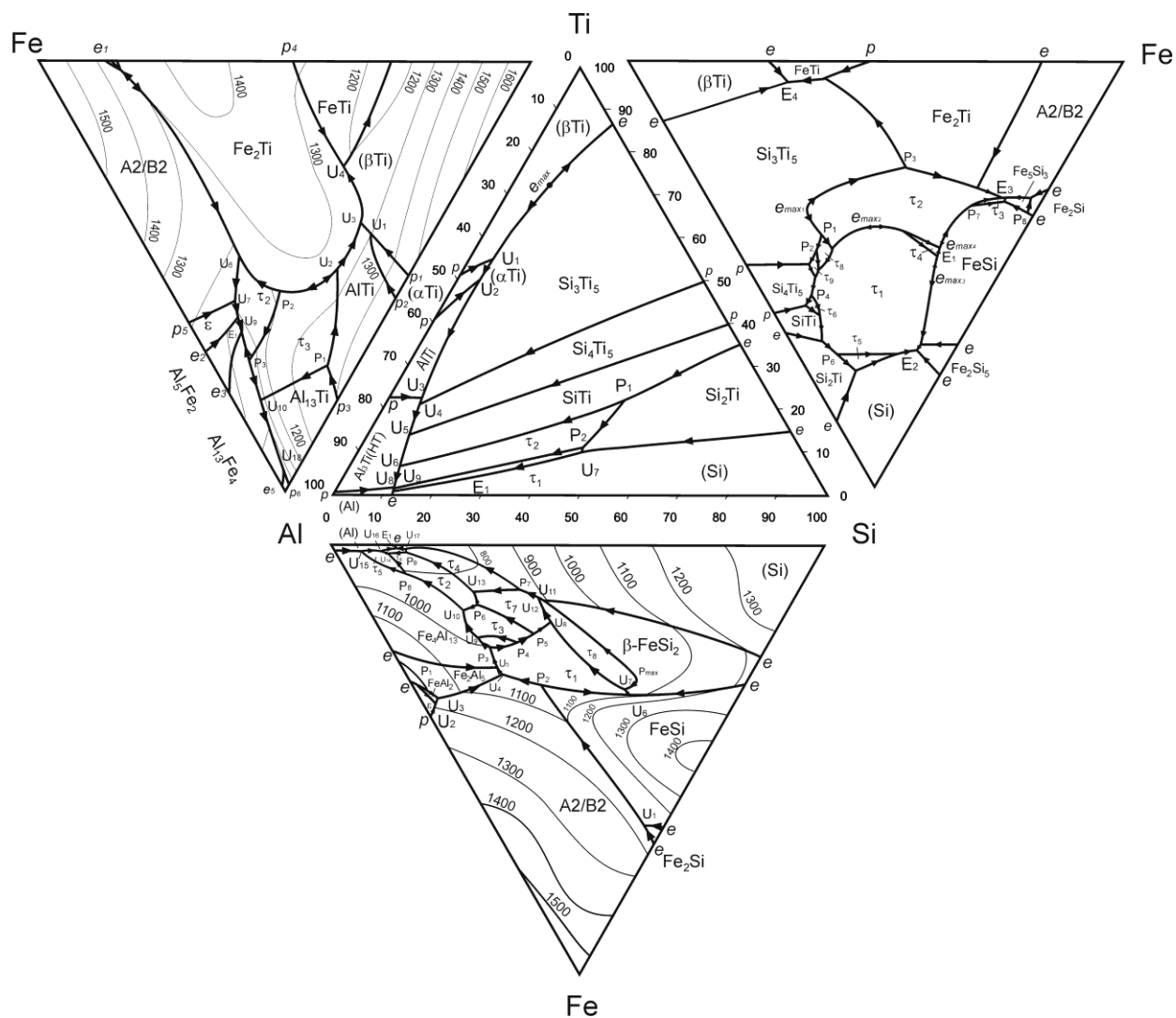


Figure 61. Graphical arrangement of the liquidus projections of the four ternary subsystems from literature of the systems Al-Fe-Si [45, 46, 48], Al-Fe-Ti [106, 107, 109], Fe-Si-Ti [112] and Al-Si-Ti [177].

Table 18. Ternary and binary invariant phase reactions relevant for the iron-rich part of Al–Fe–Si–Ti.

Ternary invariant reaction	T (°C)	Reference
Al–Fe–Si		
U1: $L + \text{Fe}_2\text{Si} \rightleftharpoons \alpha_2 + \text{FeSi}$	1052 < U1 < 1200; 1178	[46, 178]
Al–Fe–Ti		
Max1: $L \rightleftharpoons (\alpha\text{Fe}) + \text{Fe}_2\text{Ti}$	1305	[109]
Fe–Si–Ti		
E1: $L \rightleftharpoons \tau_2 + \tau_4 + \text{FeSi}$	1254	[112]
P7: $L + \text{FeSi} + \tau_2 \rightleftharpoons \tau_3$	1241	[112]
U10: $L + \text{Fe}_2\text{Ti} \rightleftharpoons \tau_2 + \alpha_2(\text{Fe}_3\text{Si})$	1202	[112]
P8: $L + \text{Fe}_2\text{Si} + \text{FeSi} \rightleftharpoons \text{Fe}_5\text{Si}_3$	1201	[112]
U12: $L + \text{FeSi} \rightleftharpoons \text{Fe}_5\text{Si}_3 + \tau_3$	1199	[112]
U13: $L + \text{Fe}_2\text{Si} \rightleftharpoons \text{Fe}_5\text{Si}_3 + \alpha_2(\text{Fe}_3\text{Si})$	1194	[112]
U12: $L + \text{FeSi} \rightleftharpoons \text{Fe}_5\text{Si}_3 + \tau_3$	1199	[112]
E3: $L \rightleftharpoons \tau_3 + \alpha_2(\text{Fe}_3\text{Si}) + \text{Fe}_5\text{Si}_3$	1151	[112]

Binary invariant reaction	T (°C)	Reference
Fe–Si		
$L \rightleftharpoons \text{FeSi}$	1409	[179]
e: $L \rightleftharpoons \text{Fe}_2\text{Si} + \text{FeSi}$	1203	[179]
Fe–Ti		
$L \rightleftharpoons \text{Fe}_2\text{Ti}$	1427	[84]
p: $L + \text{Fe}_2\text{Ti} \rightleftharpoons \text{FeTi}$	1317	[84]
e: $L \rightleftharpoons (\alpha\text{Fe}) + \text{Fe}_2\text{Ti}$	1289	[84]

$(\alpha\text{Fe}) \rightleftharpoons \text{A2}$, W-type; $\alpha_2 = \text{B2}$, CsCl-type,

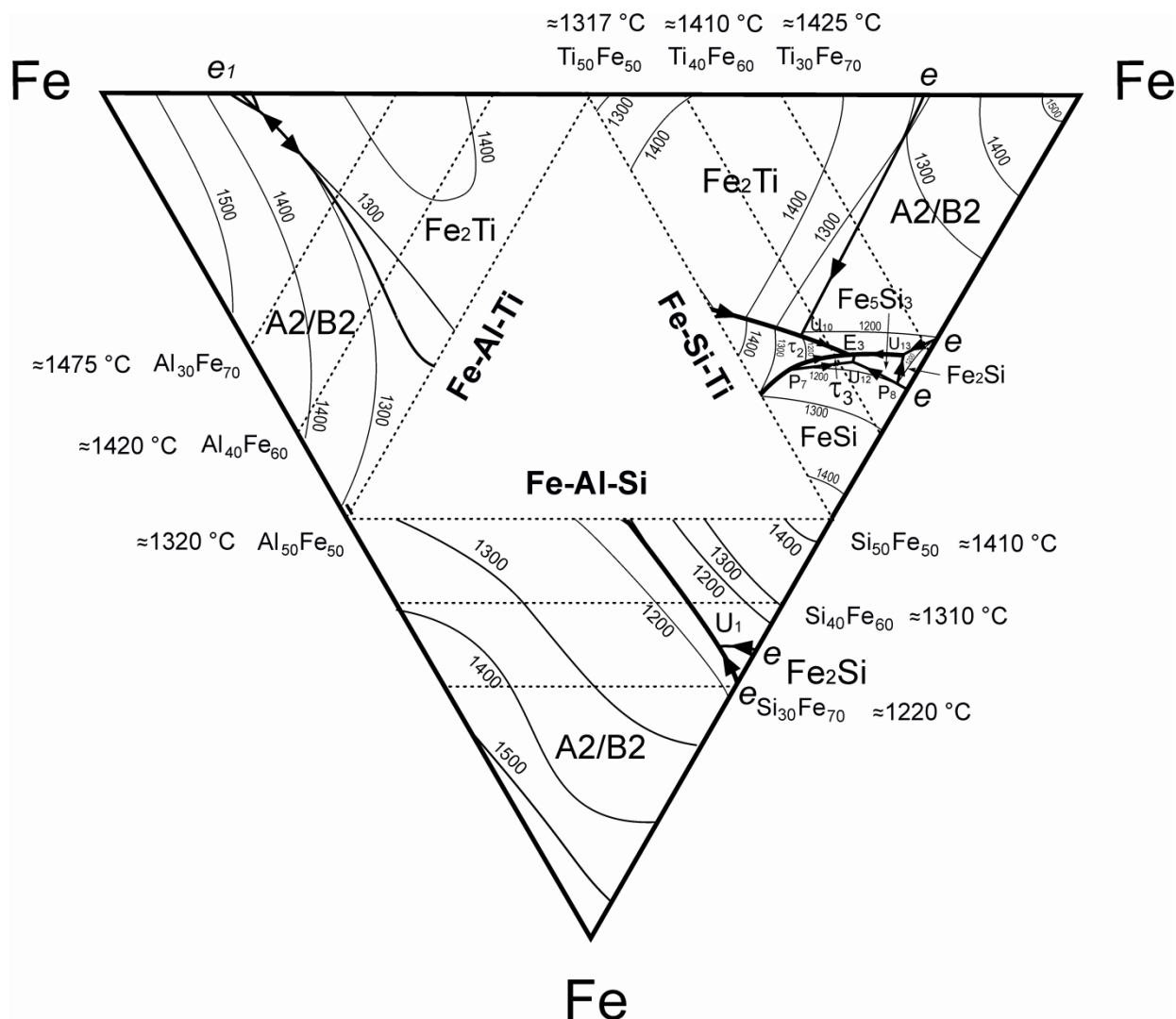


Figure 62. Liquidus surfaces in the Fe-rich area (≥ 50 at.% Fe) of the three ternary sub-systems Al–Fe–Si [45, 46, 48], Al–Fe–Ti [106, 107, 109], and Fe–Si–Ti [112]. Isotherms of the liquidus surface in Fe-rich area of the Fe–Si–Ti system drawn by the authors and are tentative. Dashed lines designate the compositions 50, 60 and 70 at.% Fe studied here. The respective temperatures at the corners label the liquidus temperatures in the binary systems.

The quaternary phase reactions were studied by DTA up to a maximum temperature of 1490 °C, which was the limit of experiment in the current study. All thermal effects were evaluated from the heating curves. Usually the first heating curves, starting from the well equilibrated samples were evaluated. The second heating was considered for comparison and for the determination of very weak effects. The cooling curves were evaluated for effects with regard to a corresponding effect in the heating curve and the liquidus values; other effects were not considered, due to supercooling effects and the possibility to observe metastable phase equilibria on cooling. All measured DTA data are listed in Appendix-Table 5 together with the respective type of effect (invariant, onset, maximum or step, and liquidus). The DTA curve of sample No. 67 shown in Figure 63 may serve as an example for the evaluation.

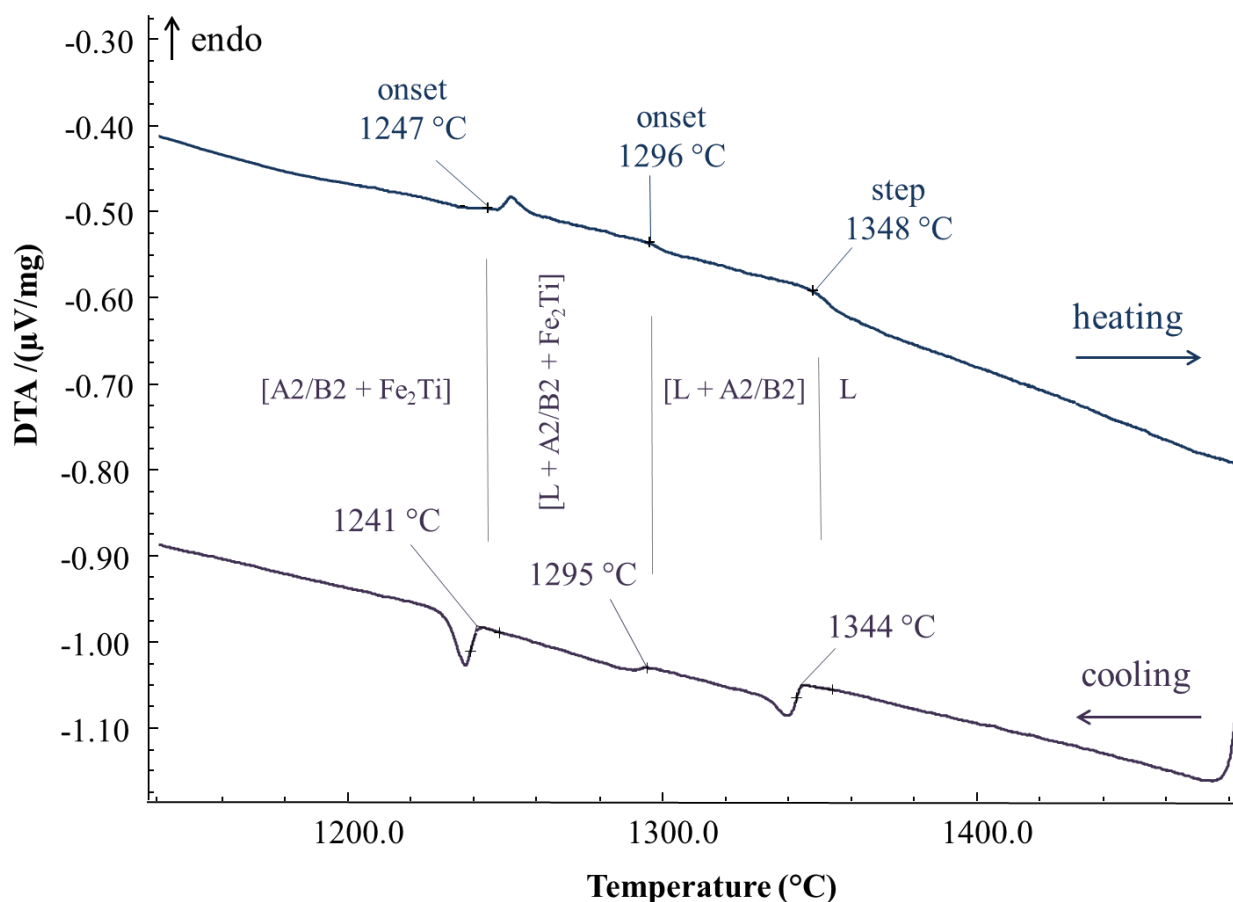


Figure 63. DTA-curves for sample No. 67 (nominal composition $\text{Al}_{15}\text{Fe}_{70}\text{Si}_{12}\text{Ti}_3$) showing different thermal effects and their interpretation.

The as-cast samples were investigated by EPMA after metallographic preparation and the primary crystallisation was determined for approximately 40 samples. The primary crystallizing phases and the respective phase compositions are listed in Appendix-Table 6.

Liquidus data observed by DTA were combined with primary crystallization data and available literature data from the binary and ternary subsystems to construct the partial liquidus projection in the Fe-rich corner. It should be mentioned that a full liquidus projection of a quaternary system can only be displayed in three dimensions within a composition tetrahedron. Three sections through this liquidus projection at 50, 60 and 70 at.% Fe are presented. These sections differ from a ternary liquidus projection, in particular by the fact that the points connecting three monovariant lines do not correspond to an invariant reaction. This fact should be considered on interpreting the figures shown below.

In addition several vertical sections were constructed to interpret the thermal effects observed in DTA. This was only done for selected sections, as some of the phase equilibria (especially at 50 at.% Fe) are too complex to be interpreted unambiguously based on the available data. A full list of thermal effects is given in Appendix-Table 5 in order to allow comparison and interpretation in future studies, including thermodynamic modelling of the quaternary system.

4.2.3.1. Liquidus projection

The three sections at 70, 60 and 50 at.% Fe through the quaternary liquidus projection are shown in Figures 64 – 66.

Section at 70 at.% Fe

Commencing with the iron-rich part at 70 at.% Fe Figure 64, the projection shows the two primary phase fields of the Laves phase (Fe_2Ti) and A2/B2. In the Ti-rich corner (primary crystallization Fe_2Ti) a maximum melting temperature was found above 1460 °C. The A2/B2 primary crystallization field is flatter and the melting points increase with the Al-content.

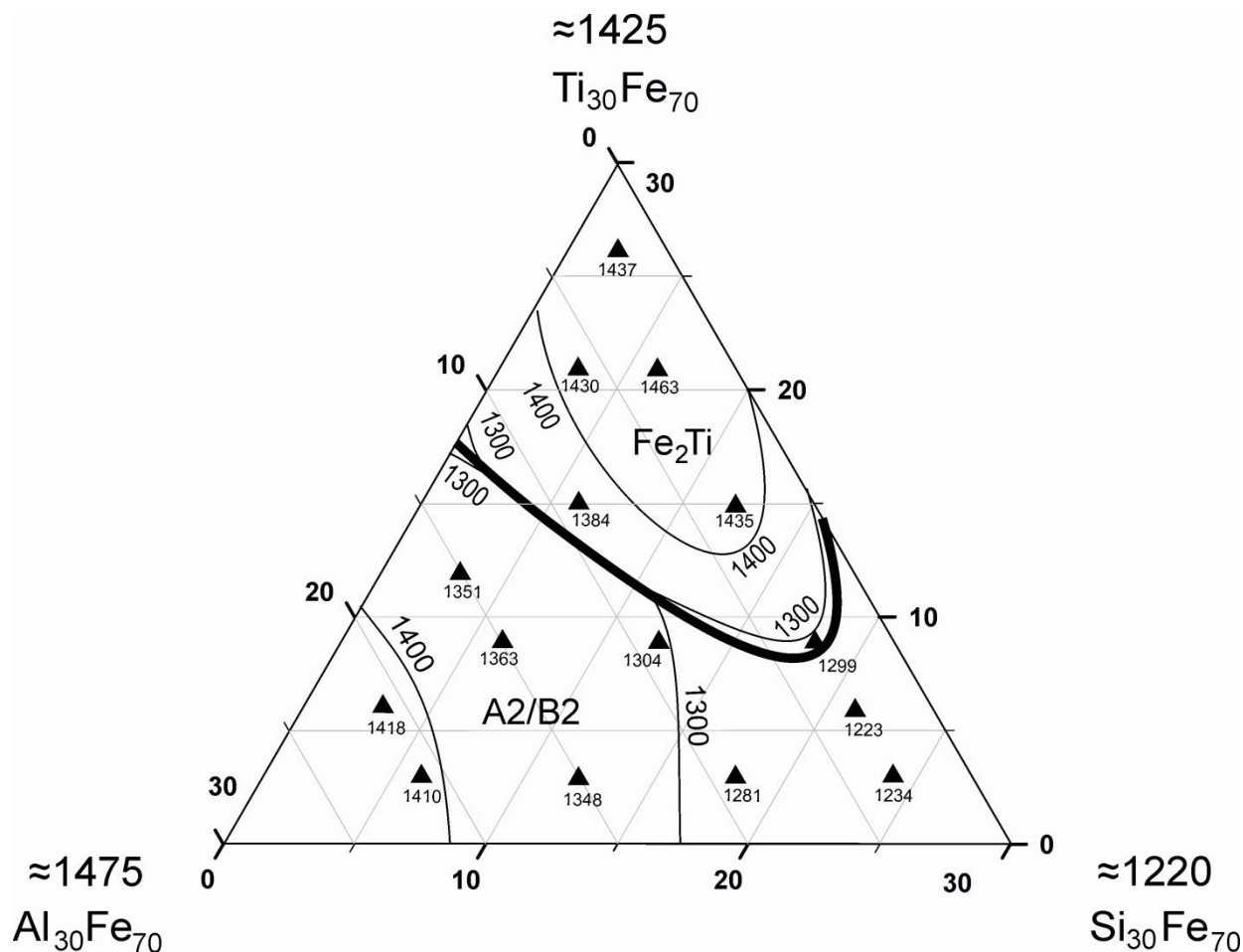


Figure 64. Partial liquidus projections at 70at.% Fe. Experimental data from DTA experiments are shown as black triangles up (liquidus on heating).

Section at 60 at.% Fe

Within the range of 60 at.% Fe (Figure 65) liquidus surface is dominated by the two primary phase fields of the Laves phase and A2/B2. In the Si-rich area the primary phase field of FeSi is found. The primary phase fields of τ_2 , τ_3 and Fe_5Si_3 could not be accurately determined due to lack of samples in the area, but they should be present according to the liquidus projection of the ternary Fe-Si-Ti system. The maximum in the melting temperature is observed above 1490 °C in the primary crystallization field of the Laves phase. The separation line of Laves

phase and A2/B2 ranges from the ternary limiting systems Fe–Si–Ti and should end in the primary phase field of τ_2 which is only assessed in this section.

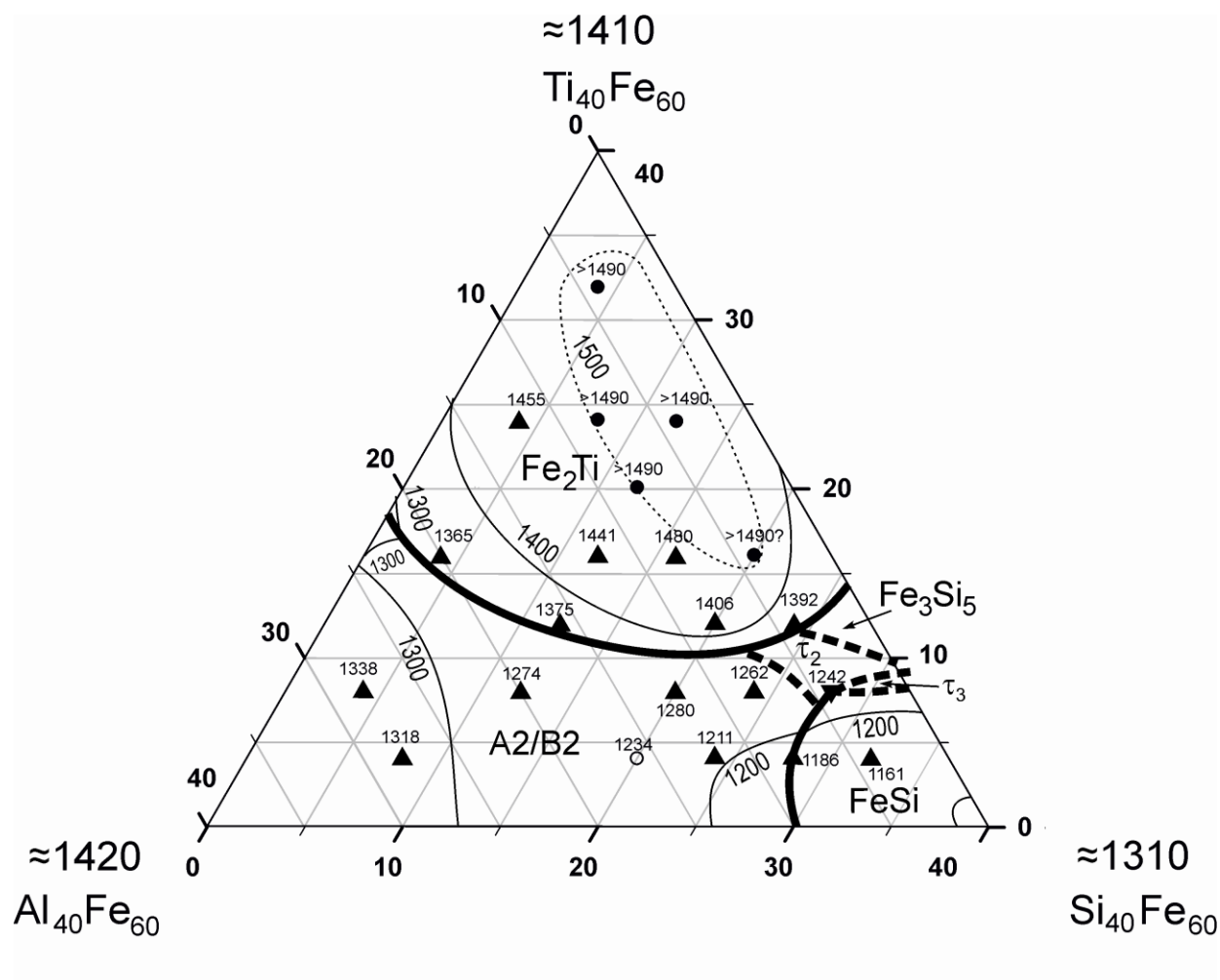


Figure 65. Partial liquidus projections at 60 at.% Fe. Experimental data from DTA experiments are shown as black circles (liquidus above detecting limit), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

Section at 50 at.% Fe

At the content of 50 at.% Fe (compare Figure 66) four primary crystallization fields are found: Laves phase, τ_2 , FeSi and A2/B2. Separation lines meet close to sample No. 12 with nominal composition $\text{Al}_{20}\text{Fe}_{50}\text{Si}_{20}\text{Ti}_{10}$. In the Al-rich corner the primary crystallization of A2/B2 can be observed and the liquidus projection shows a flat shape. Near the separation line of the primary crystallization fields of A2/B2 and the Laves phase a local maximum of about 1350 °C can be observed, represented by the alloy No. 17 with the nominal composition $\text{Al}_{30}\text{Fe}_{50}\text{Si}_5\text{Ti}_{15}$. Sample No. 13 with nominal composition $\text{Al}_{20}\text{Fe}_{50}\text{Si}_{25}\text{Ti}_5$ is very close to the separation line A2/B2 and FeSi. The microstructure of this sample is also given and discussed in section 4.2.3.3. The primary crystallization of τ_2 could be determined in the Si-rich corner of this section (sample No. 6). The liquidus of this sample was not determined in DTA due to a melting temperature above 1490 °C. The melting of τ_2 (FeSiTi) was not determined in DTA due to a melting temperature above 1490 °C. The melting temperature of τ_2 given in literature is found at $1700 \pm 20^\circ\text{C}$ and was determined by [115].

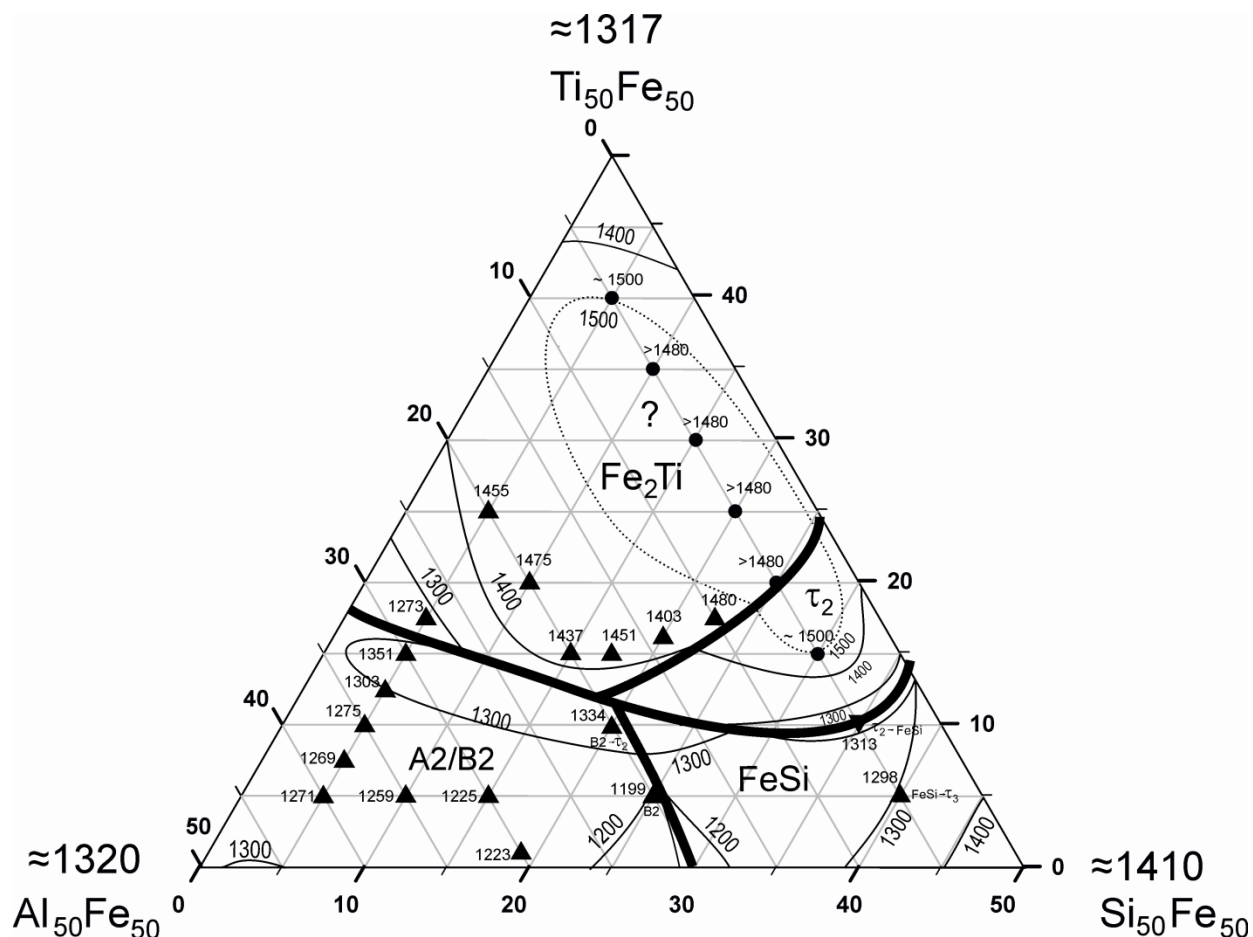


Figure 66. Partial liquidus projections at 50 at.% Fe. Experimental data from DTA experiments are shown as black circles (liquidus above detecting limit), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

4.2.3.2. Phase reactions and vertical sections

Two groups of thermal effects were identified as invariant reactions: an effect at $\approx 1160^\circ\text{C}$, observed in alloy No.07 and No.08 connected with the four-phase equilibrium $[\text{B2} + \text{FeSi} + \tau_2 + \tau_3]$ and a probable interpretation of the observed thermal effects is given in Figure 67. A second effect at 1150°C was observed in alloy No.32 and 33 connected with the four-phase equilibrium $[\text{FeSi} + \text{Fe}_5\text{Si}_3 + \tau_3 + \text{B2}]$. It is not possible to suggest a conclusive reaction type

based on the current data. Several other effects observed by DTA could be invariant based on the shape of the effect and these have been marked with an asterisk in Appendix-Table 5.

Five selected vertical sections at 60 and 70 at.% Fe, were constructed based on DTA data and these are shown in Figures 68 and 69. The additional composition constraints for the sections at 70 at.% Fe are: 3at.%Al (Figure 68a), 6 at.% Si (Figure 68b) and 3 at.% Ti (Figure 68c). For the section at 60 at.% Fe the additional constraints are 4 at. % Si (Figure 69a) and 16 at.% Ti (Figure 69b). For the construction of these sections the known isothermal equilibrium at 900 °C given in Figures 49 - 51 (discussed above in the sections 4.2.1 - 4.2.3) were used and the liquidus projection and the information available from the subsystems. The course of the second order transition lines A2/B2/D0₃ at higher temperatures are not known in detail and are therefore not drawn in the figures.

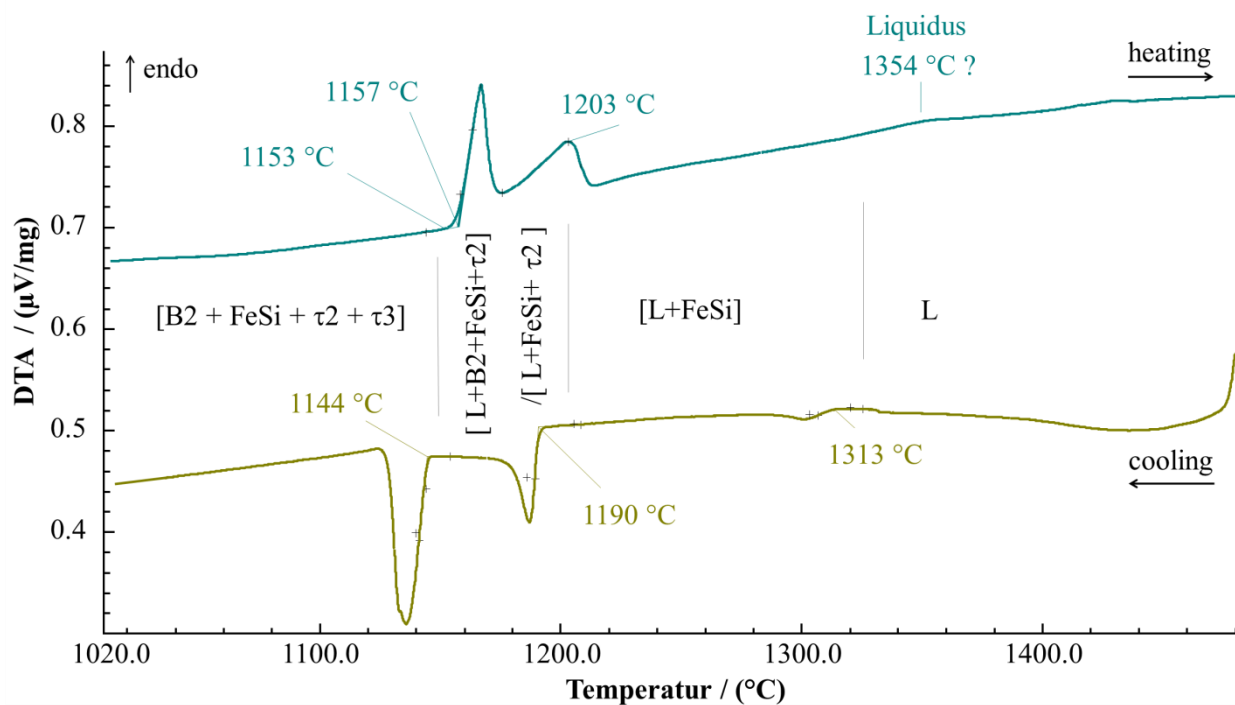


Figure 67. DTA-curves for sample No. 07 (nominal composition $\text{Al}_5\text{Fe}_{50}\text{Si}_{35}\text{Ti}_{10}$) showing different thermal effects and their interpretation).

Results and discussion

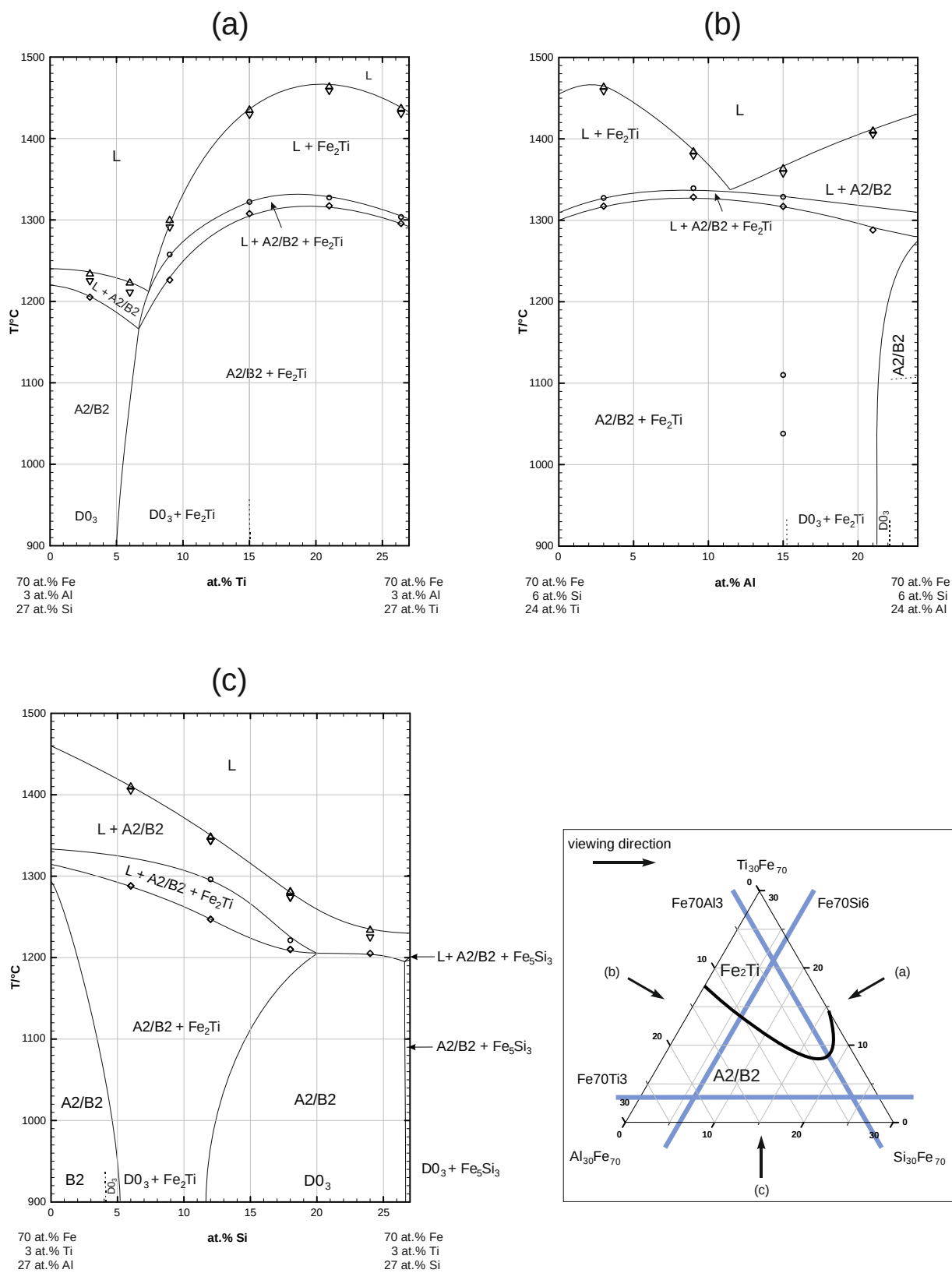


Figure 68. Vertical sections of Al–Fe–Si–Ti at 70 at.% Fe and (a) 3at.%Al, (b) 6 at.% Si and (c) 3 at.% Ti. Experimental data from DTA experiments are shown as diamonds (onset, non-invariant thermal effects), small circles (max/peak, non-invariant thermal effects), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

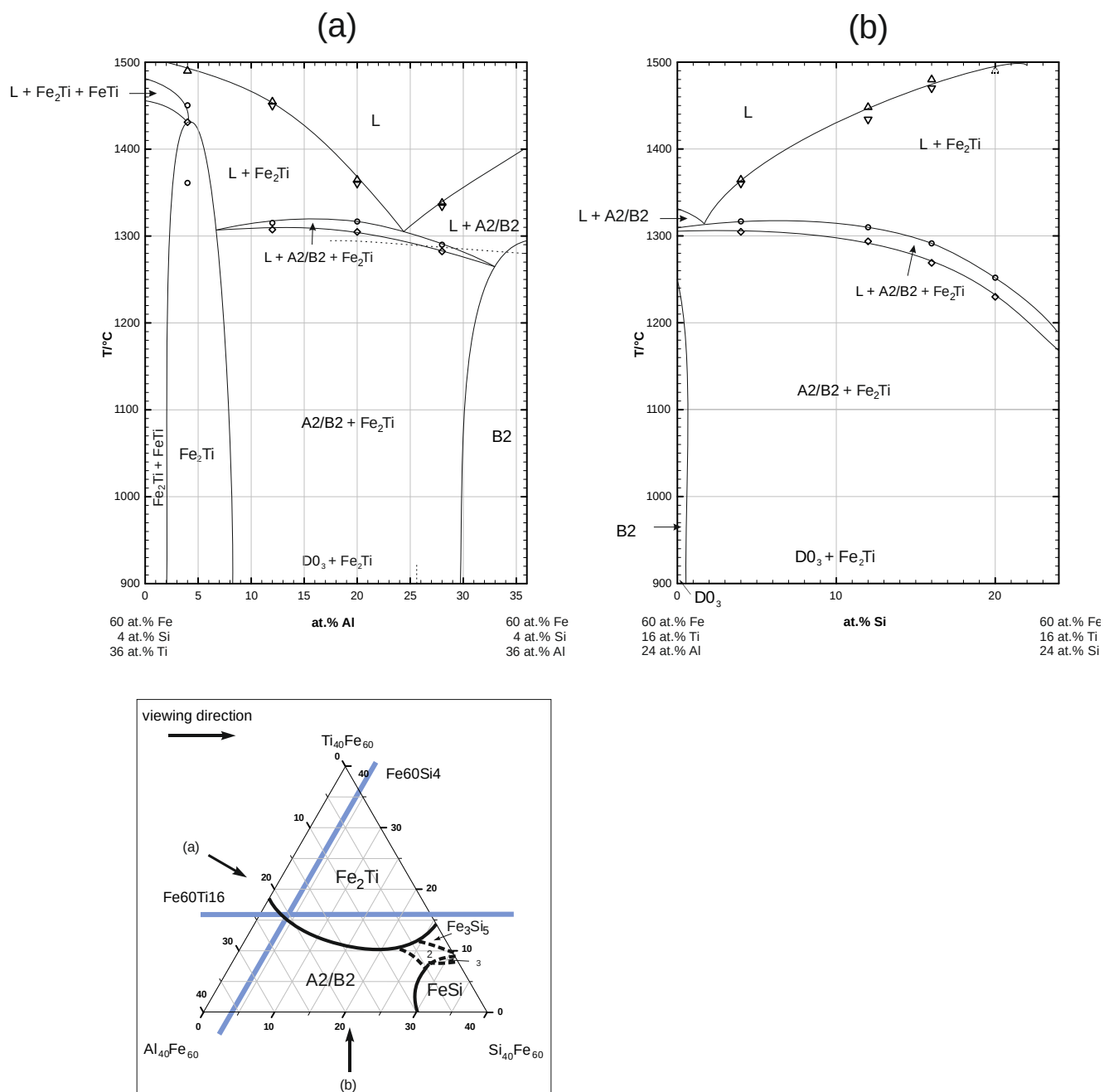


Figure 69. Vertical sections of Al–Fe–Si–Ti at 60 at.% Fe and (a) 4 at. % Si; (b) 16 at.% Ti. Experimental data from DTA experiments are shown as diamonds (onset, non-invariant thermal effects), small circles (max/peak, non-invariant thermal effects), triangles up (liquidus on heating) and triangles down (liquidus on cooling).

4.2.3.3. Microstructures of selected alloys

Primary crystallization of Fe₂Ti

The melting temperature of the binary Laves phase Fe₂Ti increases by substitution of Fe by Si in the ternary Laves phase (Fe_{1-x}Si_x)₂Ti from 1427 °C [180] to an incongruent melting point at 1591 °C [113]. In the quaternary system maximal melting points of Fe₂Ti were found above 1500 °C in the sections at 60 and 50 at.% Fe with a tendency for higher melting points at higher Si content. The primary phase composition of the quaternary Laves phase generally shows low content of Al, mostly < 10 at.% (compare Appendix-Table 6).

The microstructure of sample No. 11, given in Figure 70 shows primary dendrites of the Laves phase and the assumed secondary crystallization of τ_2 is incorporated in the matrix of A2/B2. At the equilibration temperature of 900 °C a phase content of around 47 % Laves phase, 49 % B2 and $\approx$ 4 % τ_2 was found by Rietveld refinement.

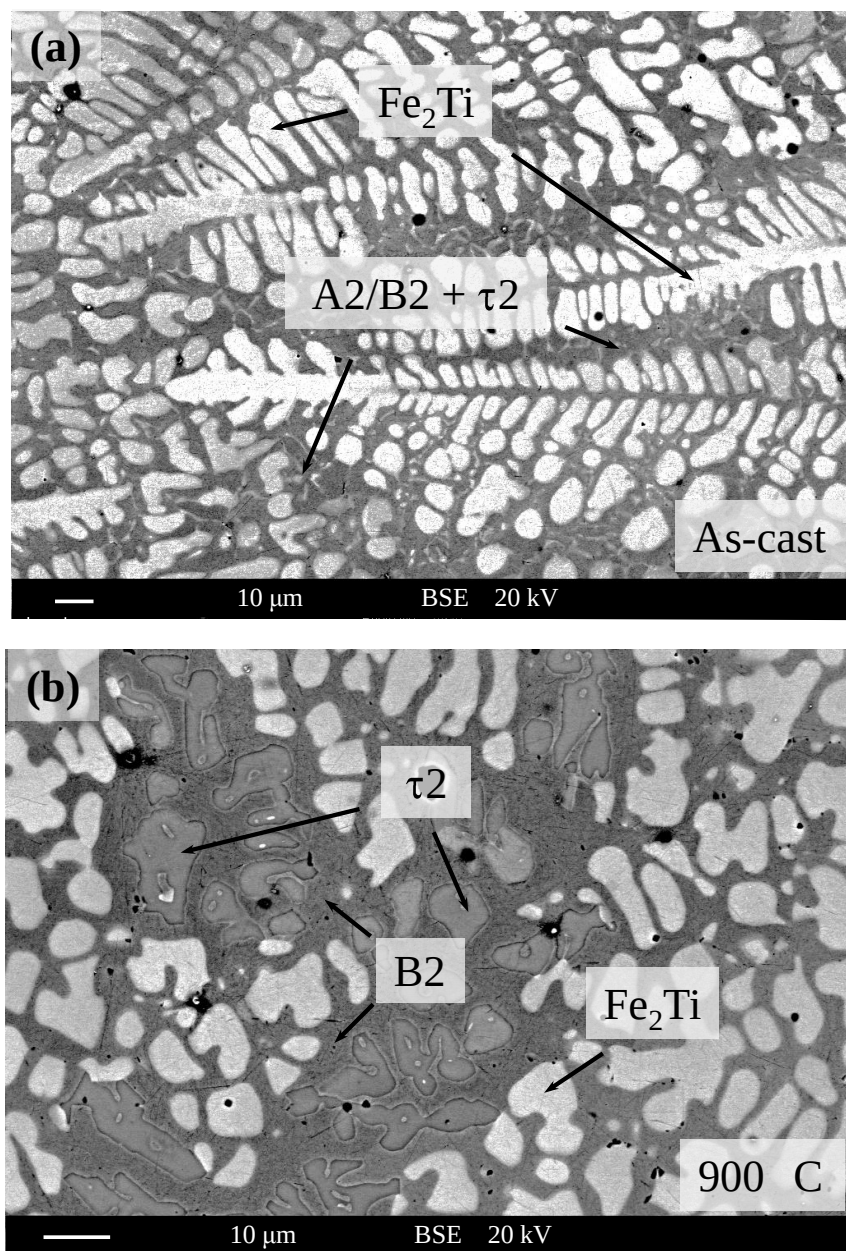


Figure 70. Back scattered electron images of alloy No. 11 with the nominal composition $\text{Al}_{20}\text{Fe}_{50}\text{Si}_{15}\text{Ti}_{15}$ at (a) as-cast condition and (b) equilibrated at 900 °C.

In sample No. 58 (Figure 71) the microstructure shows primary dendrites of Laves phase and a binary eutectic mixture of Laves phase and A2/B2 due to the fact that this alloy is situated nearby the eutectic reaction $\text{L} \rightleftharpoons \text{A2} + \text{Fe}_2\text{Ti}$. The binary eutectic reaction is found at 1289 °C [84], whereas the maximum $[\text{L} \rightleftharpoons \text{A2} + \text{Fe}_2\text{Ti}]$ in the system Al–Fe–Ti is found at 1305 °C

[109]. In the quaternary system this reaction seems to take place around 1219 °C (compare thermal effect in alloy No.58 and Figure 68a), but due to the shape of the liquidus curve given in Figure 68a, the reaction should be found at or above 1340 C.

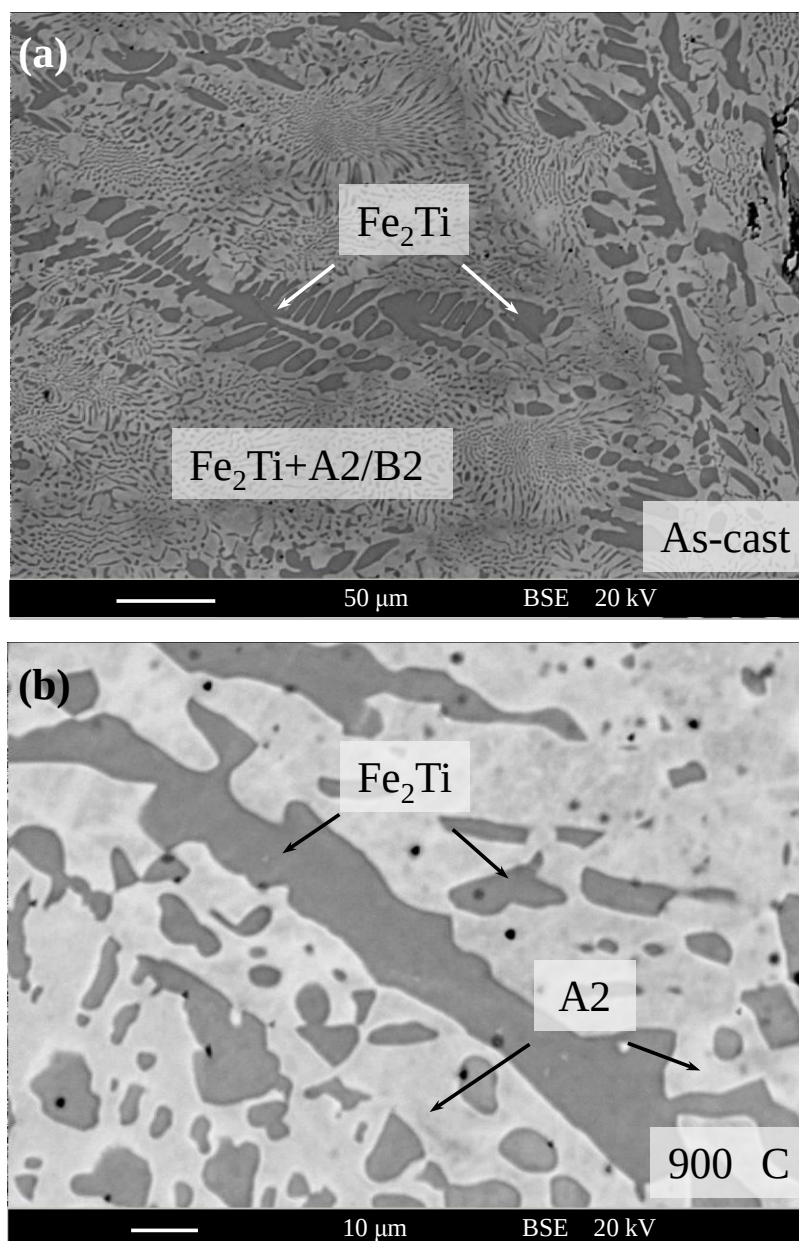


Figure 71. Back scattered electron images of the alloy No. 58 with the nominal composition $\text{Al}_9\text{Fe}_{70}\text{Si}_6\text{Ti}_{15}$; (a) as-cast, (b) equilibrium at 900 °C. The microstructure of the as-cast alloy shows a matrix of primary solidified Laves phase and binary eutectic mixture of Laves phase and A2/B2.

Primary crystallization of A2/B2

In the Al-rich corner of the three liquidus projections the primary crystallization field of A2/B2 is situated. The micrograph of alloy No. 13, Figure 72, is formed by primary grains of A2/B2 surrounded by a fine mixture of FeSi and τ_2 . At 900 °C the three-phase equilibrium of [B2 + FeSi + τ_2] was found in this alloy [47]. Alloy No. 46 with a content of 60 at.% (Figure 73) shows primary crystallization of A2/B2 and a fine mixture of A2/B2 and Fe₂Ti at the phase boundaries. In both as-cast alloys, the A2/B2 primary crystals show very finely dispersed

inhomogeneities which may be due to precipitation of a second phase (Fe₂Ti) during quenching. On annealing, clear precipitates of Fe₂Ti are formed within the primary crystals (Figure 73b), suggesting a decrease of Ti-solubility in the A2/B2 phase at lower temperature. This is in agreement with the phase diagram at 900 °C given in Figure 50 (section 4.2.2, page 84).

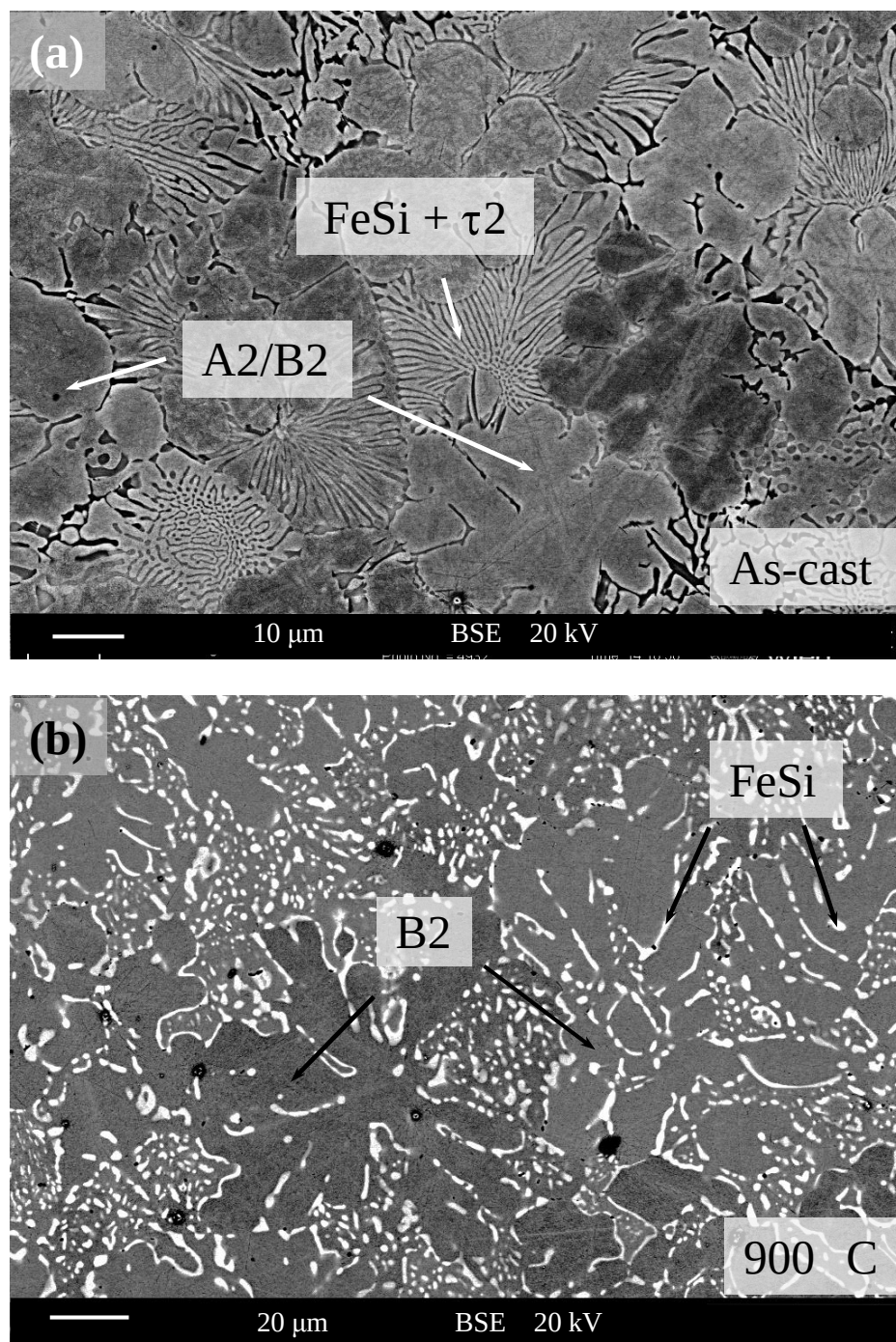


Figure 72. Back scattered electron images of the alloy No. 13 with the nominal composition $\text{Al}_{20}\text{Fe}_{50}\text{Si}_{25}\text{Ti}_5$; (a) as-cast and (b) equilibrium at 900 °C; the microstructure shows primary grains of A2/B2 surrounded by a fine mixture of FeSi and τ_2 .

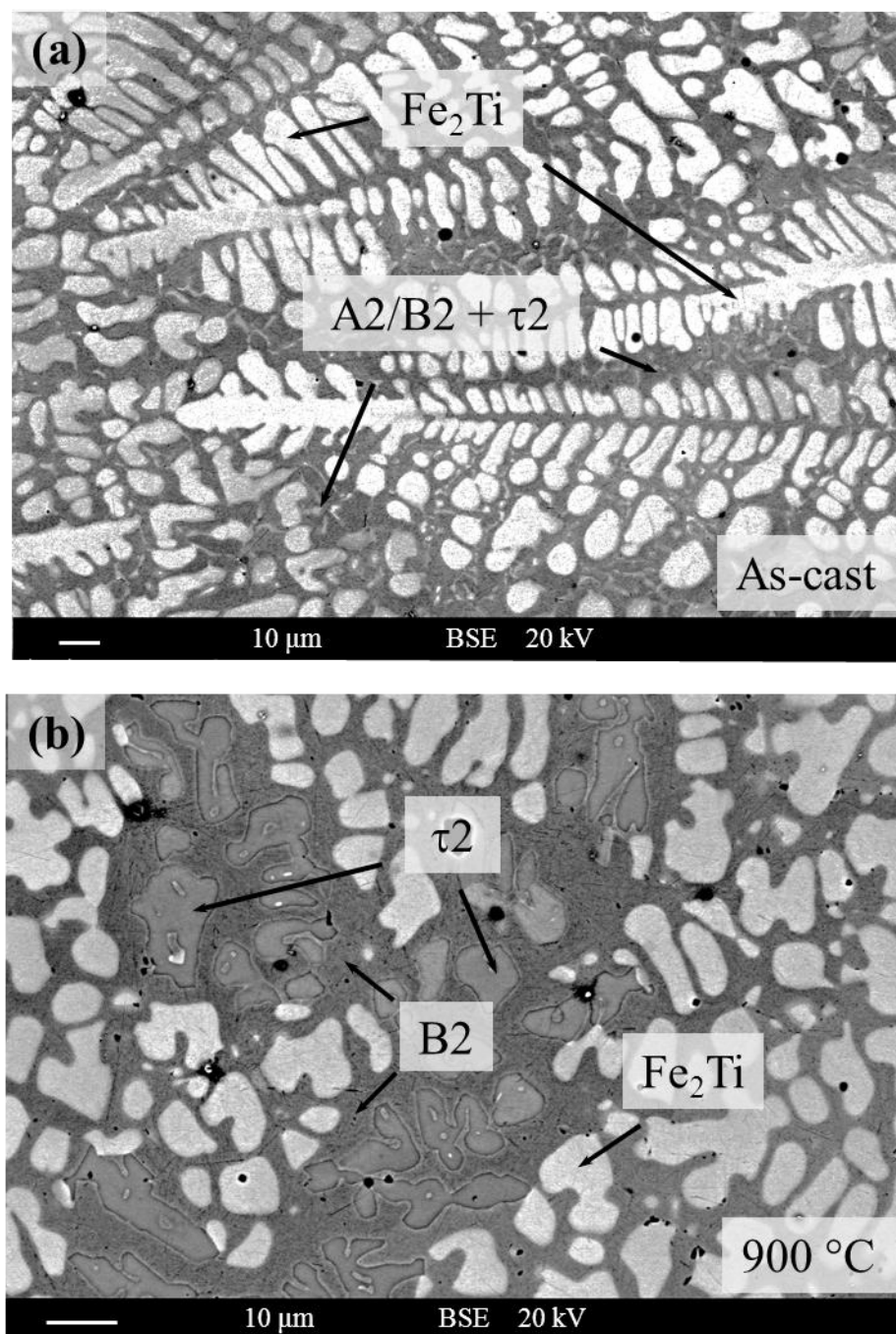


Figure 73. Back scattered electron images of alloy No. 46 with the nominal composition $\text{Al}_{20}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_8$ at (a) as-cast condition and (b) equilibrated at 900 °C.

Primary crystallization of FeSi

In alloys No. 07 (Figure 74) and No. 08 (Figure 75) dark-grey grains were determined as primary crystals of FeSi with a solubility of about 3.5 - 5 at.% Al and a maximum of 1.4 at.% Ti. In the as-cast samples grey grains of τ_3 form a majority of the matrix. At 900 °C the following situation can be found: large grains of FeSi, in a matrix of τ_3 and precipitation of B2 and traces of τ_2 from the matrix. The observed liquidus temperatures of both alloys No. 07 and No. 08 tend to lower temperature with substitution of Si by Al. This is in agreement with the composition of FeSi in the primary crystals given in Appendix-Table 6.

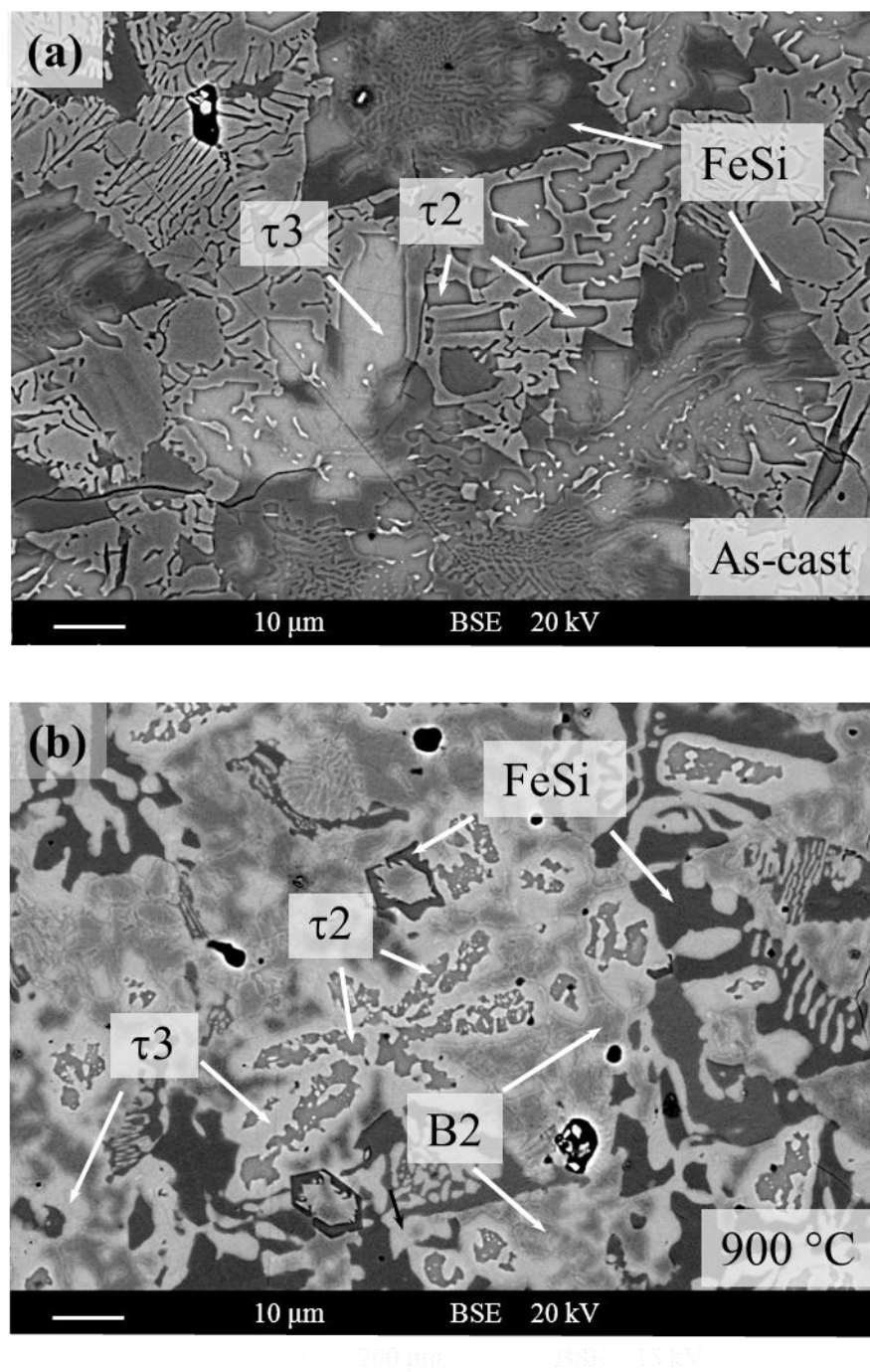


Figure 74. Back scattered electron images of the alloy No. 07 with the nominal composition $\text{Al}_5\text{Fe}_{50}\text{Si}_{35}\text{Ti}_{10}$ at (a) as-cast condition and (b) thermal equilibrium at 900 °C.

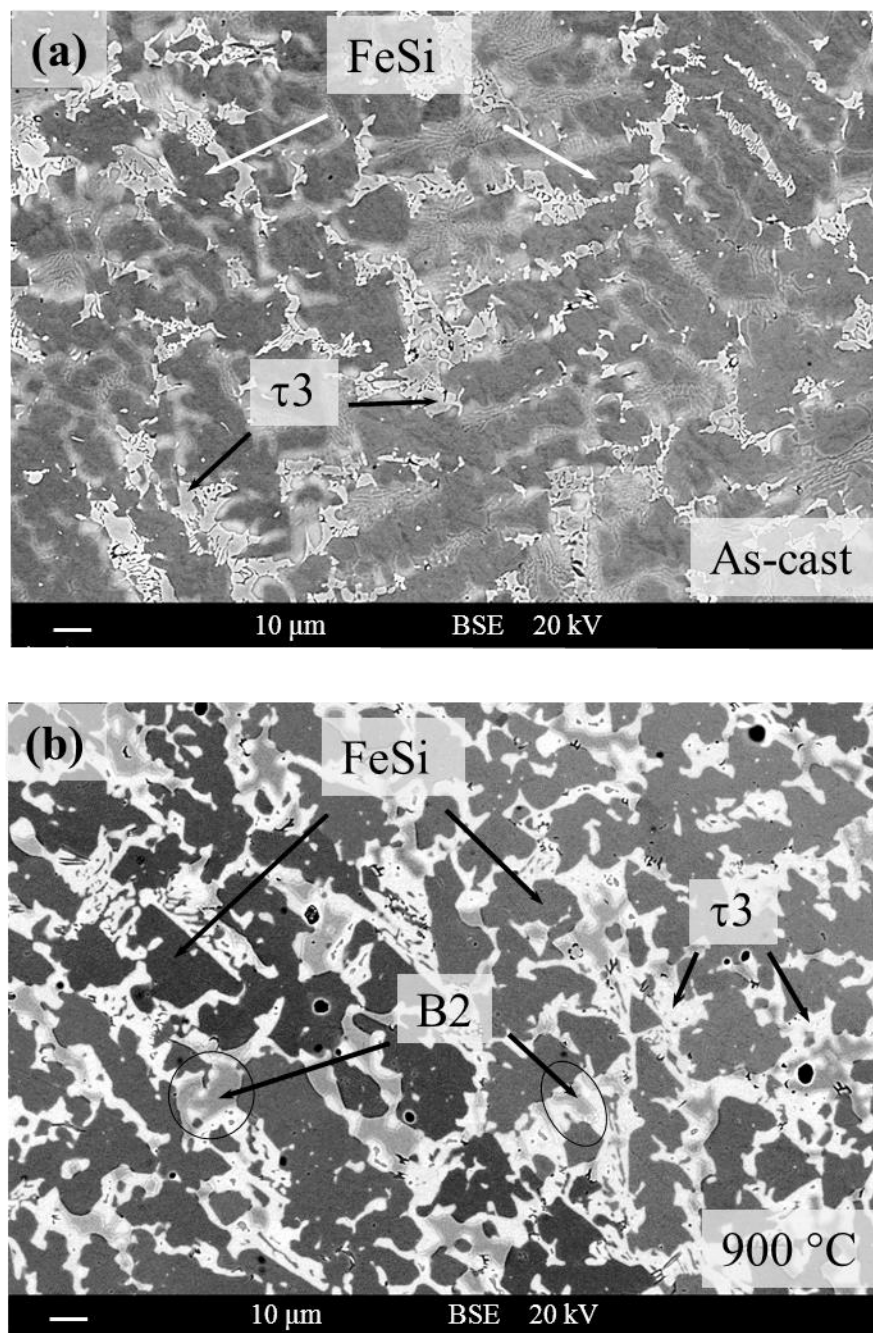


Figure 75. Back scattered electron images of the alloy No. 08 with the nominal composition $\text{Al}_5\text{Fe}_{50}\text{Si}_{40}\text{Ti}_5$ at (a) as-cast condition and (b) thermal equilibrium at 900 °C.

Primary Crystallization of τ_2

The primary crystallization field of τ_2 was found in sample No. 06 with a Fe-content of 50 at.% (compare Figure 76). The microstructure of the as-cast alloy shows dark-grey grains of primary phase τ_2 . The matrix is formed by B2 and traces of τ_3 . At 900 °C τ_2 and B2 are both present at a content of $\approx 45\%$ (found by Rietveld refinement). Traces of precipitations of τ_3 are found inside the matrix as well as along the grain boundaries of τ_2 . This implies that τ_3 is formed by a reaction of the primary phase τ_2 and the liquid phase in this specific alloy.

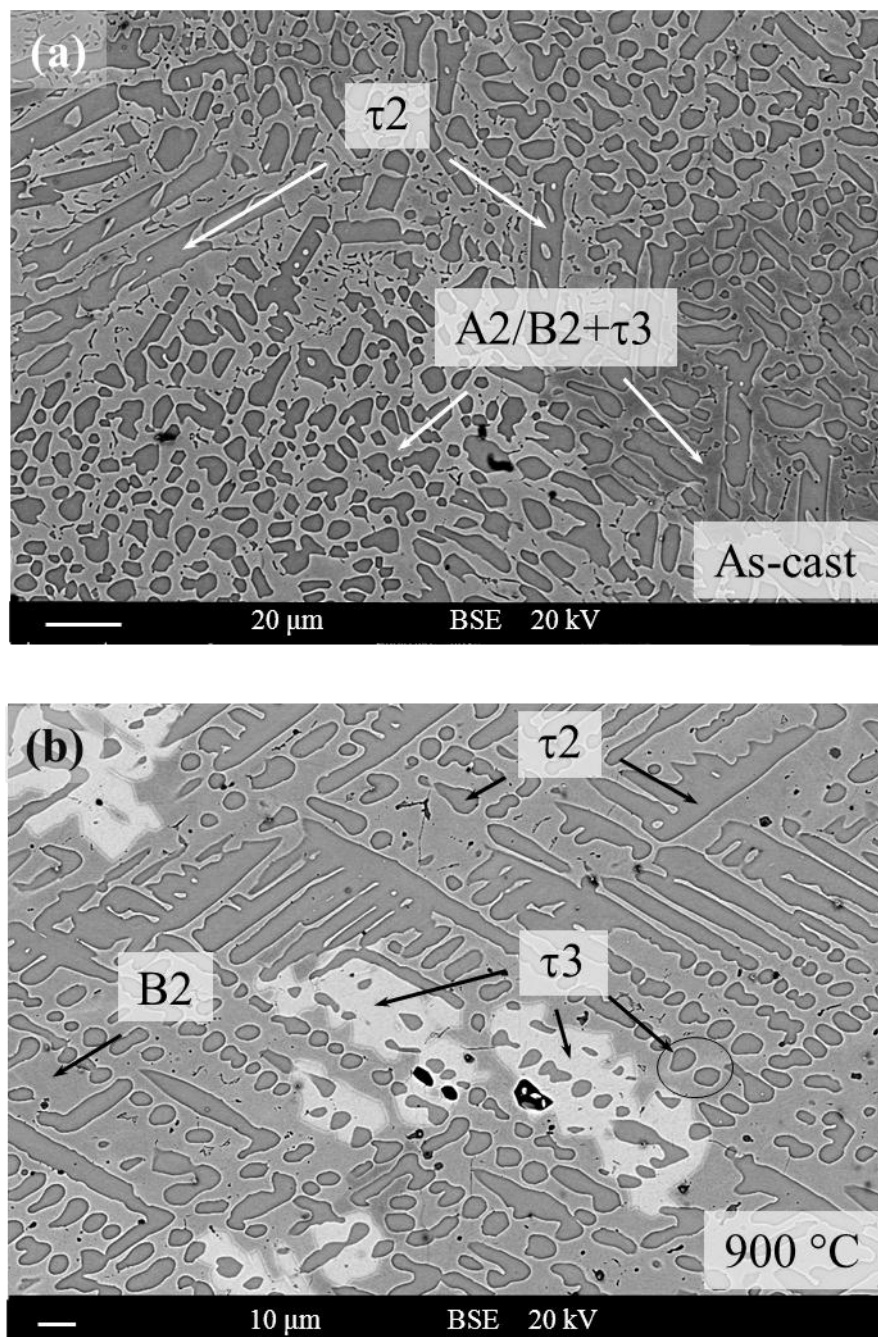


Figure 76. Back scattered electron images of the alloy No. 06 with the nominal composition $\text{Al}_5\text{Fe}_{50}\text{Si}_{30}\text{Ti}_{15}$; (a) as-cast, (b) equilibrated at 900 °C.

5. Summary

5.1. Summary (English version)

The present investigation was part of a research project with the aim to systematically investigate phase equilibria of transition metals like Co, Cu, Fe, Mo, Ti, V with Al and Si. Some phases existing in this system are highly important for industrial application because of their advantageous properties. It is necessary to understand alteration of intermetallic phases under the influence of temperature, mechanical stress and composition. Phase equilibria in the Al–Fe–Si–Ti system are of potential interest for the development of new structural alloys based on Fe- and Ti-aluminides and composites with Ti-silicides for high temperature applications. The aim of the investigation was to determine the phase equilibria and to characterize selected physical properties.

Optical microscopy and powder X-ray diffraction (XRD) followed by Rietveld refinement was used for initial sample characterization. Electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) of the annealed samples were used to determine the exact phase compositions. Thermal reactions were studied by Differential Thermal Analysis (DTA). Characterization of mechanical properties was done and performed by microhardness measurements.

The ternary subsystem Al–Fe–Si system was studied with an isothermal section at 800 °C in the Al-rich part and at 900 °C in the Fe-rich part and with half a dozen vertical sections at 27, 35, 40, 50 and 60 at.% Fe and 5 at.% Al. Our experimental results are generally in good agreement with the most recent phase diagram versions of the system Al–Fe–Si. A new ternary high-temperature phase τ_{12} (*cF96*, NiTi_2 -type) with the composition $\text{Al}_{48}\text{Fe}_{36}\text{Si}_{16}$ was discovered and structurally characterized by means of single crystal and powder XRD. The variation of the lattice parameters of the trigonal phase τ_1 with the composition $\text{Al}_{2+x}\text{Fe}_3\text{Si}_{3-x}$ ($-0.73 < x < 1.3$) was studied in detail. Only small solubility of Al in the low temperature modification LT- FeSi_2 (ζ_β) but significant solubility in the high temperature modification HT- FeSi_2 (ζ_α) (8.5 at.% Al) was found. The high temperature modification of FeSi_2 is stabilized to much lower temperature in the ternary. A partial reaction scheme (Scheil Diagram) was established. DTA results in four selected vertical sections at 40, 50 and 60 at.% Fe and 5 at.% Al were compared with calculated sections based on a recent CALPHAD

assessment. The deviations of liquidus values are significant, suggesting the need for improvement of the thermodynamic models.

The quaternary system Al–Fe–Si–Ti was studied in the iron rich corner in the sections at 50, 60 and 70 at.% Fe at 900°C. All experimental data were evaluated and combined with available sections of the ternary subsystems Al–Fe–Si, Al–Fe–Ti and Fe–Ti–Si to yield a consistent description of isothermal phase equilibria presented in three sections at 50, 60, and 70 at.% Fe. Special efforts were made to distinguish between the disordered A2 and ordered B2 and D0₃ structures by analysis of the XRD powder patterns. Trends of cell parameter and site occupations with the composition were discussed for the B2 and Laves phase. Microhardness measurements were performed on selected samples at different compositions throughout their quaternary homogeneity range in order to determine Vickers hardness (HV) of the B2 and Laves phase in the quaternary. For the Laves phase an increase of HV with decreasing cell-volume and decreasing c/a ratio was found because of the correlation between the cell parameters and the Al-, Si- and Ti-amount. The substitution of Ti by Fe on the Ti-sublattice decreases the Vickers hardness for the Laves phase. A considerable increase of the HV with the Si-content was found for the B2 phase.

Thermal reactions of the quaternary system Al–Fe–Si–Ti were investigated in the Fe-rich area. The interpretation of effects is presented in the form of three partial liquidus projections at 50, 60 and 70 at.% Fe and five selected vertical sections at 60 and 70 at.% Fe. On the basis of the microstructure of selected alloys the primary crystallization fields of the Laves phase, τ_2 , FeSi and A2/B2 were discussed. Due to the problem of quenching a second-order transition, it was not possible to distinguish A2 and B2 domains in the liquidus projection. Anti-phase-domains (ABDs) characterization by TEM measurements would be necessary investigate this topic. It was not possible to interpret all experimental data from DTA, so a thermodynamic modeling of the system would be helpful for a full understanding of phase reactions in the Fe-rich corner.

5.2. Zusammenfassung (Deutsche Fassung)

Die hier dargelegte Arbeit entstand aus einem Forschungsprojekt das zum Ziel hatte, Phasengleichgewichte und Eigenschaften von Aluminiumsiliziden in Kombination mit 3d-Übergangsmetallen wie Co, Cu, Fe, Mo, Ti oder V zu untersuchen. Legierungen auf Basis von Fe- und Ti-Aluminiden und Komposita mit Ti-Siliziden sind für die Entwicklung neuer Materialien für Hochtemperaturanwendungen von großer potentieller Bedeutung. Für die technische Anwendung von Legierungen und die Entwicklung von neuen Werkstoffen sind genaue Kenntnisse von Phasengleichgewichten, der Stabilität von Phasen in Abhängigkeit von Temperatur und der mechanischen Eigenschaften nötig. Die Zielsetzung der vorliegenden Arbeit war deshalb eine detaillierte Beschreibung der Phasengleichgewichte im ternären System Al–Fe–Si und die Untersuchung von Phasengleichgewichten bzw. spezieller physikalischer Eigenschaften im quaternären System Al–Fe–Si–Ti.

Die qualitative Charakterisierung aller Proben wurde mittels optischer Mikroskopie und Pulver-Röntgendiffraktometrie mit anschließender Rietveld-Verfeinerung durchgeführt. Die Quantifizierung der Gleichgewichtszusammensetzung wurde mittels Elektronenstrahlmikroanalyse (ESMA) bzw. Raster-Elektronenmikroskopie (REM) durchgeführt. Die Untersuchung von thermischen Effekten wurde unter Verwendung von Differenzthermoanalyse (DTA) durchgeführt. Die Bestimmung der mechanischen Eigenschaften ausgewählter Phasen erfolgte mittels Härtemessungen. In Abhängigkeit der Zusammensetzung wurde die sogenannte Vickershärte (HV) bestimmt.

Bei genauer Betrachtung und Vergleich der Literatur ergaben sich für das ternäre System Al–Fe–Si trotz zahlreicher Untersuchungen einige Unstimmigkeiten und ungeklärte Bereiche. Aus diesem Grund wurde eine detaillierte Untersuchung dieser Bereiche durchgeführt. Charakterisiert wurde das ternäre System Al–Fe–Si mittels zwei isothermer Schnitte, bei 800 °C im aluminiumreichen Teil und bei 900 °C im eisenreichen Teil. Im Zuge der detaillierten Untersuchungen wurde eine neue Hochtemperaturphase τ_{12} (*cF96*, NiTi_2 -Typ) mit der Zusammensetzung $\text{Al}_{48}\text{Fe}_{36}\text{Si}_{16}$ entdeckt. Die genaue Charakterisierung der Struktur wurde mittels Röntgen-Einkristallstrukturanalyse und Pulverdiffraktometrie vorgenommen. Außerdem wurde die genaue Änderung der Gitterparameter mit der Zusammensetzung für die trigonale Phase τ_1 : $\text{Al}_{1+x}\text{Fe}_3\text{Si}_{4-x}$ ($0.7 < x < 2.3$) untersucht. Im Bereich der binären Phase FeSi_2 wurde für die Tieftemperaturmodifikation LT- FeSi_2 (ζ_β) eine nur geringe Löslichkeit von Aluminium, in der Hochtemperaturmodifikation HT- FeSi_2 (ζ_α) hingegen eine Löslichkeit

von 8.5 at.% Al gefunden. Auch ist die Phase HT-FeSi₂ im Vergleich zum binären System zu tieferen Temperaturen stabilisiert. Ein partielles Reaktionsschema (Scheil Diagramm) wurde erstellt. Zusätzlich wurden sechs vertikale Schnitte, sogenannte Isoplethen bei 27, 35, 40, 50 und 60 at.% Fe und 5 at.% Al konstruiert. Vier dieser Isoplethen wurden mit den aus CALPHAD-Berechnungen gewonnene Isoplethen verglichen. Es wurden signifikante Abweichungen der Liquidustemperaturen festgestellt, die eine Anpassung des Modells nahelegen.

Das quaternäre System Al–Fe–Si–Ti wurde im Eisen-reichen Teil bei 50, 60 und 70 at.% Fe bei 900°C untersucht. Im Speziellen wurde auch versucht, anhand der Verfeinerung der Pulverdiffraktogramme die Bereiche mit A2/B2/D0₃-Struktur im eisenreichen Teil zu beschreiben. Der Verlauf der Gitterparameter für die B2-Phase und die Laves Phase wurden untersucht in Abhängigkeit der Phasenzusammensetzung. Zusätzlich wurden Härtemessungen an ausgewählten Proben im gesamten untersuchten Homogenitätsbereich des Systems durchgeführt. Die thermischen Reaktionen im eisenreichen Teil wurden mittels DTA untersucht. Die Interpretation der gemessenen Effekte wurde in Form von drei Schnitten durch die quaternäre Liquidusprojektion bei 50, 60 und 70 at.% Fe und fünf vertikalen Schnitten (Isoplethen) bei einer Konzentration von 60 und 70 at.% Fe dargestellt. Des Weiteren konnten Primärkristallisationsbereiche der Phasen Fe₂Ti (Laves Phase), A2/B2, FeSi und τ_2 identifiziert werden. Die Gefügestruktur der jeweiligen Primärkristallisation wurde anhand von ausgewählten Proben diskutiert.

Im Hinblick auf die Schwierigkeit Phasenübergänge 2. Ordnung beim Abschrecken der Schmelzen “einzufrieren”, würde die Untersuchung der Antiphasen-Domänen mittels Transmissionselektronenmikroskopie (TEM) besseren Aufschluss über den Ordnungsverlauf der Phasenübergänge A2, B2 oder D0₃ geben. Eine vollständige Interpretation aller experimentellen Daten die mittels Differenzthermoanalyse (DTA) erhalten wurden, war nicht möglich. Thermodynamische Modellrechnungen im eisenreichen Teil dieses Systems würden zum besseren Verstehen der Phasenreaktion beitragen.

6. References

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7.3. Appendix III: Appendix-Tables

Appendix-Table 1. Relevant phases in the ternary system Al–Fe–Si and Fe-rich area of the subsystems of Al–Fe–Si–Ti.

Phase	Structure type	Strukturbericht designation	Pearson symbol	Space group	Reference
(α Fe)	W	A2	<i>cI</i> 2	$Im\bar{3}m$	[59-61]
AlFe (α_2)	CsCl	B2	<i>cP</i> 2	$Pm\bar{3}m$	[57, 63-65]
Al ₂ Fe	Al ₂ Fe	B2	<i>aP</i> 18	$P\bar{1}$	[54]
Al ₅ Fe ₂	Al ₅ Fe ₂		<i>oC</i> 16	<i>Cmcm</i>	[55]
Al ₁₃ Fe ₄	Al ₁₃ Fe ₄		<i>mC</i> 102	$C2 / m$	[56]
Al ₈ Fe ₅	Cu ₅ Zn ₈	D8 ₂	<i>cI</i> 52	$I\bar{4}3m$	[53]
AlFe ₃ (α_1)	BiF ₃	D0 ₃	<i>cF</i> 16	$Fm\bar{3}m$	[66, 67]
(Si)		A4		$Fd\bar{3}m$	[72, 73, 81]
Fe ₃ Si (α_1)	BiF ₃	D0 ₃	<i>cF</i> 16	$Fm\bar{3}m$	[181]

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FeSi	FeSi	B20	<i>cP8</i>	<i>P2₁3</i>	[77]
HT-FeSi ₂	FeSi ₂		<i>tP3</i>	<i>P4 / mmm</i>	[78]
LT-FeSi ₂	FeSi ₂		<i>oC48</i>	<i>Cmca</i>	[79]
Fe ₂ Ti	MgZn ₂	C14	<i>hP12</i>	<i>P6₃ / mmc</i>	[94]
Fe ₂ Si	Fe ₂ Si		<i>hP6</i>	<i>P6₃ / mmc</i>	[75]
Fe ₅ Si ₃	Mn ₅ Si ₃	D8 ₈	<i>hP16</i>	<i>P6₃ / mcm</i>	[76]
FeTi	CsCl	B2	<i>cP2</i>	<i>Pm$\bar{3}$m</i>	[91-93]
Fe ₅ Si ₃	Mn ₅ Si ₃		<i>hP16</i>	<i>P6₃ / mcm</i>	[76, 80]
FeSiTi (τ_2)	FeSiTi		<i>oI36</i>	<i>Ima2</i>	[112, 182]
Fe ₄₀ Si ₃₁ Ti ₁₃ , Fe ₄ Si ₃ Ti (τ_3)	Pd ₄₀ Sn ₃₁ Y ₁₃		<i>hP168</i>	<i>P6 / mmm</i>	[112]
Al ₂ Fe ₃ Si ₃ (τ_1)	Al ₂ Fe ₃ Si ₃		<i>aP16</i>	<i>P$\bar{1}$</i>	[48, 149]
Al _{21.5-45} Fe _{36.5-37.5} Si _{8.5-41.5} ¹⁾					
Al ₃ FeSi (τ_2)	Al ₃ FeSi		<i>m**</i>	<i>mC*</i>	[183]
Al _{53.9-65.3} Fe _{19.5-20.5} Si _{15.2-25.6} ¹⁾					
Al ₂ FeSi (τ_3)	Al ₂ FeSi		<i>oC128</i>	<i>Cmma</i>	[184]
Al ₅₃₋₅₆ Fe _{23.5-24.5} Si _{20.5-22.5} ¹⁾					

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Al ₃ FeSi ₂ (τ_4) Al _{45.5–54} Fe _{15.5–16.5} Si _{30.5–38} ¹⁾	GaPd ₅	<i>tI</i> 24	<i>I</i> 4 / <i>mcm</i>	[180]
Al _{7.4} Fe ₂ Si (τ_5) Al _{68–72} Fe _{18–19.5} Si _{10–12.5} ¹⁾	Al _{7.4} Fe ₂ Si	<i>hP</i> 244	<i>P</i> 6 ₃ / <i>mmc</i>	[185]
Al _{4.5} FeSi (τ_6) Al _{64.5–67.5} Fe _{15.5–16.5} Si _{17–19} ¹⁾	Al ₉ Fe ₂ Si ₂	<i>mC</i> 52	<i>C</i> 2 / <i>m</i>	[186]
Al ₃ Fe ₂ Si ₃ (τ_7) Al _{39.2–48.7} Fe _{23.5–24.5} Si _{27.8–36.3} ¹⁾	Al ₃ Fe ₂ Si ₃	<i>mP</i> 64	<i>P</i> 2 ₁ / <i>n</i>	[187]
Al ₂ Fe ₃ Si ₄ (τ_8) Al _{24.1–28.6} Fe _{31.9–32.9} Si _{39.5–43} ¹⁾	Al ₂ Fe ₃ Si ₄	<i>oC</i> 48	<i>Cmcm</i>	[149]
τ_{10} Al _{57–59} Fe _{24–25} Si _{17–18} ¹⁾	—	hexagonal ?	*	[46]
Al ₄ Fe _{1.7} Si (τ_{11}) Al _{64–66.5} Fe _{24–25} Si _{9.5–11} ¹⁾	Co ₂ Al ₅	<i>hP</i> 28	<i>P</i> 6 ₃ / <i>mmc</i>	[188]

¹⁾ Composition ranges of ternary phases according to [46]

Appendix-Table 2. Experimental phase compositions and cell parameters of selected samples in the partial isothermal sections at 800 °C and 900 °C.

Sample No.	Nominal sample composition (at.%)	Annealing (°C)	Phases (XRD)	Cell parameters (Å)			Phase composition determined by EPMA		
							Al(at.%)	Fe(at.%)	Si(at%)
1	Al ₆₂ Fe ₂₇ Si ₁₁	800	Al ₁₃ Fe ₄	$a = 15.4980(2)$	$b = 7.9627(2)$	$c = 12.5567(1)$	70.7(1)	24.9(2)	4.4(2)
				$\beta = 107.96$					
			τ_1	$a = 4.6335(1)$	$b = 6.3467(2)$	$c = 7.5355(2)$	36.4(2)	37.5(1)	26.1(2)
				$\alpha = 102.14$	$\beta = 106.04$	$\gamma = 101.30$			
			τ_{11}	$a = 7.5355(1)$		$c = 7.5805(2)$	64.7(2)	26.1(2)	9.2(1)
2	Al ₅₅ Fe ₂₇ Si ₁₈	800	τ_1	$a = 4.6483(1)$	$b = 6.3225(3)$	$c = 7.5063(3)$	28.6(3)	38.0(2)	33.4(4)
				$\alpha = 101.35$	$\beta = 105.92$	$\gamma = 101.21$			
			τ_3	$a = 7.9755(1)$	$b = 15.2067(1)$	$c = 15.2378(1)$	54.5(1)	26.6(1)	18.9(2)
			τ_{11}	$a = 7.5253(1)$		$c = 7.5605(2)$	62.3(2)	25.9(1)	11.8(3)
3	Al ₄₆ Fe ₂₇ Si ₂₇	800	τ_1	$a = 4.6840(2)$	$b = 6.3370(2)$	$c = 7.4952(3)$	27.1(2)	37.8(1)	35.1(3)
				$\alpha = 101.40$	$\beta = 105.75$	$\gamma = 101.60$			
			τ_3	$a = 7.9557(1)$	$b = 15.1789(5)$	$c = 15.2259(6)$	51.8(2)	25.2(1)	23.0 (2)
			τ_7	$a = 7.3257(1)$	$b = 8.2792(1)$	$c = 14.6096(3)$	46.6(3)	26.1(2)	27.3(2)
				$\beta = 93.71$					

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4	$\text{Al}_{27}\text{Fe}_{27}\text{Si}_{46}$	800	Si	$a = 5.4229(2)$			0.3(3)	0.5(1)	99.2(3)
			τ_7	$a = 7.1829(3)$	$b = 8.3569(3)$	$c = 14.4564(6)$	41.3(2)	23.8(1)	34.9(1)
			τ_8	$a = 3.6665(5)$	$b = 12.3419(1)$	$c = 10.1365(1)$	25.5(1)	33.4(1)	41.0(3)
5	$\text{Al}_{14}\text{Fe}_{27}\text{Si}_{59}$	800	HT-FeSi ₂	$a = 2.7067(1)$		$c = 5.1797(2)$	4.5(5)	31.0(2)	64.5(5)
			Si	$a = 5.4293(1)$			0.0(1)	0.6(1)	99.4(1)
			τ_8	$a = 3.6679(5)$	$b = 12.3430(2)$	$c = 10.1413(2)$	24.0(1)	33.7(1)	42.3(1)
6	$\text{Al}_{51}\text{Fe}_{35}\text{Si}_{14}$	800	AlFe	$a = 2.8508(6)$			37.0(1)	47.5(1)	15.5(1)
			Al_5Fe_2	$a = 7.6381(5)$	$b = 6.3876(4)$	$c = 4.2302(3)$	68.8(1)	29.0(5)	2.2(4)
			τ_{12}	$a = 10.8011(2)$			48.3(2)	36.3(2)	15.4(1)
7	$\text{Al}_{48}\text{Fe}_{35}\text{Si}_{17}$	800	Al_5Fe_2	$a = 7.6461(2)$	$b = 6.3879(2)$	$c = 4.2427(1)$	70.1(2)	27.4(2)	2.5(2)
			τ_1	$a = 4.7385(2)$	$b = 6.3217(3)$	$c = 7.4828(3)$	40.0(1)	37.7(2)	22.3(3)
			τ_{12}	$\alpha = 100.17$	$\beta = 104.97$	$\gamma = 102.39$	49.5(3)	34.9(2)	15.6(2)
8	$\text{Al}_{29}\text{Fe}_{35}\text{Si}_{36}$	800	τ_1	$a = 4.6134(3)$	$b = 6.3304(4)$	$c = 7.5082(4)$	25.4(2)	38.0(2)	36.6(1)
			τ_7	$\alpha = 101.76$	$\beta = 106.29$	$\gamma = 100.75$			
			τ_8	$a = 7.2656(3)$	$b = 8.3165(3)$	$c = 14.5216(7)$	44.9(2)	25.7(1)	29.3(2)
9	$\text{Al}_{19}\text{Fe}_{35}\text{Si}_{46}$	800		$\beta = 93.83$					
			HT-FeSi ₂	$a = 3.6599(4)$	$b = 12.4729(5)$	$c = 10.1568(2)$	28.6(1)	34.1(1)	37.3(1)
			τ_1	$a = 2.7171(1)$		$c = 5.2131(1)$	7.8(2)	33.5(2)	58.4(2)
			τ_1	$a = 4.5889(1)$	$b = 6.3373(2)$	$c = 7.5251(2)$	21.1(1)	38.2(2)	40.6(2)
				$\alpha = 101.93$	$\beta = 106.45$	$\gamma = 100.70$			
			τ_8	$a = 3.6689(1)$	$b = 12.3245(2)$	$c = 10.1407(1)$	23.2(1)	34.5(2)	42.3(2)

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10	Al ₁ Fe ₃₅ Si ₆₄	800	FeSi	a = 4.4909(1)			0.9(1)	50.6(1)	48.5(1)				
			HT-FeSi ₂	a = 2.6792(5)		c = 5.1676(6)	2.5(5)	32.4(1)	64.4(2)				
			LT-FeSi ₂	a = 9.8886(1)	b = 7.8073(1)	c = 7.8487(1)	0.7(1)	34.3(1)	65.0(1)				
11	Al ₅₅ Fe ₄₀ Si ₅	900	AlFe	a = 2.8790(1)			44.3(1)	47.5(1)	8.2(1)				
			Al ₅ Fe ₂	a = 7.6464(4)		b = 6.4002(3)				c = 4.2223(2)			
			Al ₂ Fe	a = 4.8811(6)		b = 6.4472(7)				c = 8.7706(1)			
				α = 91.65		β = 73.21				γ = 96.61			
12	Al ₄₈ Fe ₃₇ Si ₁₅	900	AlFe	a = 2.8544(2)			36.5(1)	46.7(1)	16.8(0)				
			Al ₅ Fe ₂	a = 7.6446(1)		b = 6.3938(1)	c = 4.2340(1)	69.6(1)	28.6(1)	1.8(2)			
			τ ₁₂	a = 10.8039(1)			47.6(1)	36.4(2)	16.0(1)				
13	Al ₄₅ Fe ₄₀ Si ₁₅	900	AlFe	a = 2.8514(1)			37.1(1)	46.6(0)	16.3(1)				
			Al ₅ Fe ₂	a = 7.6378(7)		b = 6.3878(5)	c = 4.2328(4)	69.2(2)	28.4(1)	2.4(2)			
			τ ₁₂	a = 10.7980(1)			48.1(0)	36.4(1)	15.5(1)				
14	Al ₄₀ Fe ₄₀ Si ₂₀	900	AlFe	a = 2.8471(1)			35.0(2)	46.8(2)	18.2(1)				
			τ ₁	a = 4.7553(1)		b = 6.3208(2)				c = 7.4757(2)			
			τ ₁₂	α = 99.92		β = 104.72				γ = 102.55	41.7(1)	37.5(1)	20.8(1)
				a = 10.8008(5)						47.7(1)	36.4(0)	15.9(2)	
15	Al ₃₅ Fe ₄₀ Si ₂₅	900	AlFe	a = 2.8400(1)			32.0(0)	47.3(1)	20.7(1)				
			FeSi	a = 4.5329(2)		c = 7.4866(2)							
			τ ₁	a = 4.7238(1)						b = 6.3224(2)			
				α = 100.45						β = 105.10	γ = 102.21		

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16	$\text{Al}_{15}\text{Fe}_{40}\text{Si}_{45}$	900	FeSi HT-FeSi ₂ τ_1	$a = 4.4925(1)$ $a = 2.7174(1)$ $a = 4.5855(1)$ $\alpha = 101.96$	$b = 6.3357(1)$ $\beta = 106.45$	$c = 5.2150(4)$ $c = 7.5259(2)$ $\gamma = 100.70$	1.8(0) 8.5(0) 21.2(0)	49.4(0) 32.9(0) 37.6(0)	48.8(1) 58.6(0) 41.2(1)
17	$\text{Al}_3\text{Fe}_{33}\text{Si}_{64}$	900	FeSi LT-FeSi ₂ HT-FeSi ₂	$a = 4.4885(1)$ $a = 9.8978(3)$ $a = 2.7067(1)$	$b = 7.8015(2)$	$c = 7.8300(2)$ $c = 5.1708(1)$	0.5(0) 0.8(2) 2.9(4)	49.2(2) 33.9(3) 31.8(2)	50.3(2) 65.3(2) 65.3(5)
18	$\text{Al}_5\text{Fe}_{10}\text{Si}_{85}$	900	HT-FeSi ₂ Si L	$a = 2.7107(1)$ $a = 5.1990(3)$ ————		$c = 5.4303(1)$	8.4(1) 0.3(4) 49.6(2)	31.5(0) 0.2(0) 16.7(1)	60.3(0) 99.5(4) 33.7(1)

Appendix-Table 3. Supplementary Material-DTA results in the Al–Fe–Si system.

Nominal sample composition	Annealing (°C, d)	Invariant effects	Temperature (°C)		
			Other effects	Liquidus on heating	Liquidus on cooling
Al ₁₄ Fe ₂₇ Si ₅₉	800, 14	885.7		1135.0	1133.0
Al ₂₇ Fe ₂₇ Si ₄₆	800, 14	889.3		1008.0	986.4
Al _{33.7} Fe ₂₇ Si _{39.3}	800, 14	886.1	913.0	1012.9	1005.5
Al ₃₇ Fe ₂₇ Si ₃₆	800, 14	929.0	894.9 / 917.8 / 999.6	1017.5	1007.3
Al ₃₉ Fe ₂₇ Si ₃₄	800, 14	927.8	969.5	1011.4	1007.7
Al ₄₃ Fe ₂₇ Si ₃₀	800, 14	933.9		1006.6	1002.3
Al ₄₆ Fe ₂₇ Si ₂₇	800, 14	936.0		1007.9	996.5
Al ₄₉ Fe ₂₇ Si ₂₄	800, 14	932.9		986.1	967.5
Al ₅₂ Fe ₂₇ Si ₂₁	800, 14	943.6		1003.3	980.3
Al ₅₅ Fe ₂₇ Si ₁₈	800, 14	942.7	997.2	1018.5	1012.3
Al ₅₈ Fe ₂₇ Si ₁₅	800, 14	942.5	1000.7	1047.1	1034.7
Al ₆₂ Fe ₂₇ Si ₁₁	800, 14		1002.1	1067.5	1060.4

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$\text{Al}_{65}\text{Fe}_{27}\text{Si}_8$	800, 14	1054.8		1100.1	1091.4
$\text{Al}_{69}\text{Fe}_{27}\text{Si}_4$	800, 14	1051.4		1131.3	1112.2
$\text{Al}_{0.2}\text{Fe}_{35}\text{Si}_{64.8}$	800, 14	1209.0		1268.0	1266.5
$\text{Al}_1\text{Fe}_{35}\text{Si}_{64}$	800, 14	1203.0		1271.0	1261.3
$\text{Al}_{10}\text{Fe}_{35}\text{Si}_{55}$	800, 14	1007.0	1140.7	1269.0	1251.9
$\text{Al}_{19}\text{Fe}_{35}\text{Si}_{46}$	800, 14	1007.0		1251.0	1231.0
$\text{Al}_{25}\text{Fe}_{35}\text{Si}_{40}$	800, 14	987.0	1009.0 / 1034.6	1231.0	1200.4
$\text{Al}_{29}\text{Fe}_{35}\text{Si}_{36}$	800, 14	928.2	960.0 / 1048.8	1195.0	1171.7
$\text{Al}_{33}\text{Fe}_{35}\text{Si}_{32}$	800, 14	934.1 / 1048.7	1048.8	1148.0	1143.1
$\text{Al}_{37}\text{Fe}_{35}\text{Si}_{28}$	800, 14	1051.5	982.3	1120.0	1117.7
$\text{Al}_{38.2}\text{Fe}_{35}\text{Si}_{26.8}$	800, 14	1048.8	998.0	1125.1	1111.3
$\text{Al}_{41}\text{Fe}_{35}\text{Si}_{24}$	800, 14	995.4 / 1057.0		1133.4	1100.2
$\text{Al}_{45}\text{Fe}_{35}\text{Si}_{20}$	800, 14	1024.3 / 1040.3		1090.9	1085.0
$\text{Al}_{48}\text{Fe}_{35}\text{Si}_{17}$	800, 14	1034.9		1102.7	1097.9
$\text{Al}_{51}\text{Fe}_{35}\text{Si}_{14}$	800, 14		1036.5 / 1057.3		1101.2

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$\text{Al}_{56}\text{Fe}_{35}\text{Si}_9$	800, 14		1099.6	1134.4	1131.3
$\text{Al}_{59.5}\text{Fe}_{35}\text{Si}_{5.5}$	800, 14				
$\text{Al}_{62}\text{Fe}_{35}\text{Si}_3$	800, 14		1127.0	1142.1	1132.0
$\text{Al}_{64.5}\text{Fe}_{35}\text{Si}_{0.5}$	800, 14	1149.0	1161.0	1181.4	1178.8
$\text{Al}_5\text{Fe}_{10}\text{Si}_{85}$	900, 25		1160.5	1379.7	1367.0
$\text{Al}_5\text{Fe}_{20}\text{Si}_{75}$	900, 25		1189.0	1256.0	1245.0
$\text{Al}_5\text{Fe}_{30}\text{Si}_{60}$	900, 25			1200.0	1180.0
$\text{Al}_5\text{Fe}_{40}\text{Si}_{55}$	900, 25	1001.9	1168.8	1344.4	1335.7
$\text{Al}_5\text{Fe}_{50}\text{Si}_{45}$	900, 25		1351.0	1385.6	1374.0
$\text{Al}_{14}\text{Fe}_{55}\text{Si}_{40}$	900, 25	1191.8		1346.8	1336.3
$\text{Al}_5\text{Fe}_{60}\text{Si}_{35}$	900, 25	1192.0		1252.8	1243.1
$\text{Al}_5\text{Fe}_{65}\text{Si}_{30}$	900, 25	1187.8	1195.9	1219.8	1209.3
$\text{Al}_5\text{Fe}_{75}\text{Si}_{20}$	900, 25		1272.5	1302.7	1297.9
$\text{Al}_5\text{Fe}_{80}\text{Si}_{15}$	900, 25		1324.0	1389.0	1380.0
$\text{Al}_5\text{Fe}_{85}\text{Si}_{10}$	900, 25		1405.0	1421.3	1417.3

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$\text{Al}_{55}\text{Fe}_{40}\text{Si}_5$	900, 25	1118.1		1207.0	1200
$\text{Al}_{50}\text{Fe}_{40}\text{Si}_{10}$	900, 25		1098.0	1188.0	1185.4
$\text{Al}_{45}\text{Fe}_{40}\text{Si}_{15}$	900, 25	1036.6	1061.0	1175.0	1171.0
$\text{Al}_{40}\text{Fe}_{40}\text{Si}_{20}$	900, 25	1033.7	1058.2	1168.0	1160.4
$\text{Al}_{35}\text{Fe}_{40}\text{Si}_{25}$	900, 25	1049.1		1152.0	1147.5
$\text{Al}_{30}\text{Fe}_{40}\text{Si}_{30}$	900, 25	1153.4		1194.5	1189.9
$\text{Al}_{25}\text{Fe}_{40}\text{Si}_{35}$	900, 25	1047.6		1238.6	1232.9
$\text{Al}_{20}\text{Fe}_{40}\text{Si}_{40}$	900, 25		1050.0	1275.3	1267.7
$\text{Al}_{15}\text{Fe}_{40}\text{Si}_{45}$	900, 25	999.0	1023.7	1308.0	1304.0
$\text{Al}_{10}\text{Fe}_{40}\text{Si}_{50}$	900, 25	1006.7	1090.8	1320.7	1317.5
$\text{Al}_5\text{Fe}_{40}\text{Si}_{55}$	900, 25	1001.9	1173.9	1344.2	1335.7
$\text{Al}_{45}\text{Fe}_{50}\text{Si}_5$	900, 25		1248.5	1291.0	1288.0
$\text{Al}_{35}\text{Fe}_{50}\text{Si}_{15}$	900, 25		1225.4	1252.9	1248.3
$\text{Al}_{25}\text{Fe}_{50}\text{Si}_{25}$	900, 25		1201.3	1217.0	1211.0

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$\text{Al}_{15}\text{Fe}_{50}\text{Si}_{35}$	900, 25	1203.0		1300.0	1290.0
$\text{Al}_5\text{Fe}_{50}\text{Si}_{45}$	900, 25		1351.0	1385.6	1374.0
$\text{Fe}_{50}\text{Si}_{50}$	900, 25	1421.0			
$\text{Al}_{35}\text{Fe}_{60}\text{Si}_5$	900, 25		1319.3	1362.4	1358.0
$\text{Al}_{25}\text{Fe}_{60}\text{Si}_{15}$	900, 25		1265.8	1287.4	1283.8
$\text{Al}_{15}\text{Fe}_{60}\text{Si}_{25}$	900, 25		1216.8	1238.2	1230.8
$\text{Al}_5\text{Fe}_{60}\text{Si}_{35}$	900, 25	1191.8		1252.1	1243.7

Appendix-Table 4. Experimental phase compositions and cell parameters of selected samples in the Al-Fe-Si-Ti system at 900 °C in the sections of 50, 60 and 70 at.% Fe.

Sample No.	Nominal sample composition (at. %)	Annealing Temperature/Time (°C) / h	Phase (XRD)	Cell parameter (Å)			Phase composition determined by EPMA			
							Al(at. %)	Fe(at. %)	Si(at%)	Ti(at%)
01	Al ₅ Fe ₅₀ Si ₅ Ti ₄₀	Quartz 900; 400	Fe ₂ Ti	$a = 4.832(1)$	$c = 7.846(1)$		5.4(1)	50.7(1)	8.3(1)	35.6(1)
			FeTi	$a = 2.976(1)$			4.8(2)	47.1(1)	0.6(1)	47.5(2)
02	Al ₅ Fe ₅₀ Si ₁₀ Ti ₃₅	Quartz 900; 400	Fe ₂ Ti	$a = 4.804(1)$	$c = 7.774(1)$		4.0(2)	49.4(1)	11.4(x)	35.2(1)
03	Al ₅ Fe ₅₀ Si ₁₅ Ti ₃₀	Quartz 900; 400	Fe ₂ Ti	$a = 4.806(1)$	$c = 7.777(1)$		2.3(1)	48.5(1)	17.2(1)	32.0(1)
			D0 ₃	$a = 5.953(1)$			26.0(1)	55.2(1)	1.6(1)	17.2(2)
04	Al ₅ Fe ₅₀ Si ₂₀ Ti ₂₅	Quartz 900; 400	Fe ₂ Ti	$a = 4.795(1)$	$c = 7.711(1)$		2.4(1)	46.6(3)	21.7(1)	29.3(2)
			D0 ₃	$a = 5.770(1)$			23.6(4)	66.9(7)	5.5(3)	4.0(8)
05	Al ₅ Fe ₅₀ Si ₂₅ Ti ₂₀	Quartz 900; 400	Fe ₂ Ti	$a = 4.794(1)$	$c = 7.676(2)$		2.2(3)	46.2(5)	25.0(2)	26.6(5)
			D0 ₃	$a = 5.705(2)$			11.0(1)	66.2(1)	17.3(1)	5.5(1)
			FeSiTi	$a = 6.994(2)$	$b = 10.813(3)$	$c = 6.275(2)$	0.0(1)	34.2(1)	33.2(1)	32.6(1)
06	Al ₅ Fe ₅₀ Si ₃₀ Ti ₁₅	Quartz 900; 400	B2	$a = 2.827(1)$			8.9(1)	61.7(1)	26.4(1)	2.9(1)
			Fe ₄ Si ₃ Ti	$a = 17.218(6)$	$c = 7.991(5)$		0.7(1)	47.7(1)	35.8(1)	15.7(1)
			FeSiTi	$a = 6.987(1)$	$b = 10.811(1)$	$c = 6.271(1)$	0.2(1)	35.5(2)	32.8(1)	31.5(1)

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07	$\text{Al}_5\text{Fe}_{50}\text{Si}_{35}\text{Ti}_{10}$	Quartz 900; 400	B2 FeSi $\text{Fe}_4\text{Si}_3\text{Ti}$ FeSiTi	$a = 2.829(1)$ $a = 4.518(1)$ $a = 17.230(1)$ $a = 6.971(2)$	$c = 7.980(1)$ $b = 10.810(4)$ $c = 6.264(2)$	9.9(4) 6.8(1) 0.8(1) 1.4(4)	57.2(7) 50.1(1) 48.1(3) 38.9(9)	27.8(6) 42.7(3) 35.8(3) 33.1(9)	5.0(5) 0.4(1) 15.3(6) 26.7(3)
08	$\text{Al}_5\text{Fe}_{50}\text{Si}_{40}\text{Ti}_5$	Quartz 900; 400	B2 FeSi $\text{Fe}_4\text{Si}_3\text{Ti}$ FeSiTi	$a = 2.828(1)$ $a = 4.515(1)$ $a = 17.229(3)$ $a = 7.055(7)$	$c = 7.983(2)$ $b = 10.693(1)$ $c = 6.388(1)$	10.3(2) 6.1(1) 0.8(1) Trace	60.6(3) 50.3(1) 48.1(3)	26.6(1) 43.4(1) 36.0(1)	2.5(3) 0.2(1) 15.2(4)
09	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_5\text{Ti}_{25}$	Quartz 900; 400	Fe_2Ti D0_3	$a = 4.823(1)$ $a = 5.865(1)$	$c = 7.815(1)$	11.0(1) 25.7(2)	48.6(1) 51.0(1)	10.4(1) 1.0(1)	30.0(1) 22.3(1)
10	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_{10}\text{Ti}_{20}$	Quartz 900; 400	Fe_2Ti D0_3	$a = 4.809(2)$ $a = 5.827(3)$	$c = 7.753(4)$	8.2(3) 32.7(4)	46.5(3) 53.5(2)	16.9(1) 1.8(2)	28.4(3) 12.0(4)
11	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_{15}\text{Ti}_{15}$	Quartz 900; 400	Fe_2Ti B2 FeSiTi	$a = 4.808(1)$ $a = 2.890(1)$ $a = 7.011(5)$	$c = 7.697(3)$ $b = 10.802(8)$ $c = 6.285(5)$	6.9(1) 33.6(7) 0.4(5)	44.7(1) 56.0(1) 34.1(5)	22.6(1) 6.1(5) 32.4(4)	25.7(2) 4.4(4) 33.0(5)
12	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_{20}\text{Ti}_{10}$	Quartz 900; 400	B2 FeSiTi	$a = 2.860(2)$ $a = 6.992(5)$	$b = 10.810(8)$ $c = 6.279(5)$	27.0(3) –	55.8(2) –	14.9(2) –	2.4(1) –
13	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_{25}\text{Ti}_5$	Quartz 900; 400	FeSi B2 FeSiTi	$a = 4.535(2)$ $a = 2.843(2)$ $a = 6.995(4)$	$b = 10.829(1)$ $c = 6.271(5)$	11.0(1) 23.5(2) –	50.0(1) 52.8(4) –	38.5(1) 21.9(2) –	0.5(1) 1.9(1) –

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14	$\text{Al}_{35}\text{Fe}_{50}\text{Si}_5\text{Ti}_{10}$	Quartz 900; 600	Fe_2Ti B2	$a = 4.821(1)$ $a = 2.913(1)$	$c = 7.730(1)$	10.6(1) 38.9(1)	44.5(2) 52.2(2)	19.1(1) 2.0(1)	25.8(3) 6.9(1)
15	$\text{Al}_{35}\text{Fe}_{50}\text{Si}_{10}\text{Ti}_5$	Quartz 900; 400	B2 FeSiTi	$a = 2.889(3)$ $a = 7.004(1)$	$b = 10.818(1)$ $c = 6.285(1)$	38.5(2) 5.8(1)	52.2(1) 35.9(1)	7.3(2) 29.5(1)	1.9(1) 28.8(1)
16	$\text{Al}_{27.5}\text{Fe}_{50}\text{Si}_5\text{Ti}_{17.5}$	Quartz 900; 430	Fe_2Ti B2	$a = 4.834(1)$ $a = 2.926(4)$	$c = 7.785(9)$	13.3(3) 33.1(1)	44.4(1) 51.4(2)	14.4(2) 1.2(1)	27.9(1) 14.4(1)
17	$\text{Al}_{30}\text{Fe}_{50}\text{Si}_5\text{Ti}_{15}$	Quartz 900; 430	Fe_2Ti B2	$a = 4.826(4)$ $a = 2.923(3)$	$c = 7.766(7)$	12.7(5) 35.5(4)	46.1(2) 52.0(3)	15.1(2) 1.3(2)	26.0(4) 11.3(4)
18	$\text{Al}_{32.5}\text{Fe}_{50}\text{Si}_5\text{Ti}_{12.5}$	Quartz 900; 430	Fe_2Ti B2	$a = 4.825(1)$ $a = 2.920(4)$	$c = 7.748(1)$	10.9(1) 37.8(1)	46.6(1) 51.8(1)	16.8(2) 1.4(1)	25.6(1) 9.0(1)
19	$\text{Al}_{35}\text{Fe}_{50}\text{Si}_5\text{Ti}_{10}$	Quartz 900; 430	Fe_2Ti B2	$a = 4.823(1)$ $a = 2.917(5)$	$c = 7.725(1)$	12.8(9) 39.7(1)	44.5(3) 51.8(1)	18.4(5) 1.8(1)	24.4(7) 6.7(1)
20	$\text{Al}_{37.5}\text{Fe}_{50}\text{Si}_5\text{Ti}_{7.5}$	Quartz 900; 430	B2 FeSiTi Fe_2Ti	$a = 2.913(6)$ $a = 6.991(1)$ –	$b = 10.825(1)$ $c = 6.282(1)$ –	40.3(2) 5.6(1) 10.2(1)	51.9(4) 36.9(1) 43.8(1)	2.0(3) 29.0(1) 20.3(1)	5.7(3) 28.5(1) 25.9(1)
21	$\text{Al}_{40}\text{Fe}_{50}\text{Si}_5\text{Ti}_5$	Quartz 900; 430	B2 FeSiTi	$a = 2.907(1)$ $a = 7.000(4)$	$b = 10.821(1)$ $c = 6.281(7)$	42.4(2) 4.1(1)	51.6(2) 36.6(1)	2.9(1) 30.2(1)	3.2(1) 29.1(1)
22	$\text{Al}_{30}\text{Fe}_{50}\text{Si}_{15}\text{Ti}_5$	Quartz 900; 430	B2 FeSiTi	$a = 2.871(1)$ $a = 6.998(3)$	$b = 10.807(7)$ $c = 6.286(4)$	33.4(2) 8.1(1)	52.4(1) 40.1(1)	12.5(1) 28.2(1)	1.6(1) 23.7(1)

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23	$\text{Al}_{30}\text{Fe}_{50}\text{Si}_{19}\text{Ti}_1$	Quartz 900; 430	B2	$a = 2.850(1)$		30.3(1)	50.1(1)	18.9(1)	0.7(1)
24	$\text{Al}_{17.5}\text{Fe}_{50}\text{Si}_{17.5}\text{Ti}_{15}$	Quartz 900; 430	Fe_2Ti	$a = 4.798(2)$	$c = 7.684(4)$	6.4(2)	46.1(3)	22.5(1)	25.0(3)
			B2	$a = 2.883(1)$		30.6(1)	58.9(5)	6.8(1)	3.7(4)
			FeSiTi	$a = 6.998(4)$	$b = 10.799(6)$ $c = 6.276(3)$	0.1(1)	33.9(1)	32.8(1)	33.3(1)
25	$\text{Al}_{13.8}\text{Fe}_{50}\text{Si}_{20}\text{Ti}_{16.2}$	Quartz 900; 430	Fe_2Ti	$a = 4.796(1)$	$c = 7.687(1)$	5.7(3)	46.1(1)	23.3(1)	25.0(2)
			B2	$a = 2.869(1)$		24.7(2)	61.8(2)	10.2(2)	3.3(3)
			FeSiTi	$a = 7.007(1)$	$b = 10.814(1)$ $c = 6.275(1)$	0.1(1)	34.0(2)	32.7(1)	33.1(1)
26	$\text{Al}_{10}\text{Fe}_{50}\text{Si}_{22.5}\text{Ti}_{17.5}$	Quartz 900; 430	Fe_2Ti	$a = 4.799(3)$	$c = 7.6807(1)$	4.0(1)	46.3(6)	23.8(2)	25.9(5)
			B2	$a = 2.860(2)$		17.6(2)	65.0(1)	13.4(1)	3.9(1)
			FeSiTi	$a = 7.001(5)$	$b = 10.815(7)$ $c = 6.280(4)$	0.0(1)	34.6(3)	32.7(1)	32.7(2)
27	$\text{Al}_2\text{Fe}_{50}\text{Si}_{43}\text{Ti}_5$	Quartz 900; 600	FeSi	$a = 4.500(1)$		* —	* —	* —	* —
			$\text{Fe}_4\text{Si}_3\text{Ti}$	$a = 17.212(2)$	$c = 7.982(1)$	* —	* —	* —	* —
28	$\text{Al}_4\text{Fe}_{60}\text{Si}_4\text{Ti}_{32}$	Quartz 900; 480	Fe_2Ti	$a = 4.804(1)$	$c = 7.826(1)$	4.9(4)	60.5(2)	2.1(3)	32.6(2)
29	$\text{Al}_4\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{24}$	Quartz 900; 480	Fe_2Ti	$a = 4.784(2)$	$c = 7.764(2)$	2.3(2)	55.8(4)	13.5(3)	28.4(4)
			A2	$a = 2.893(1)$		7.2(6)	71.5(3)	7.6(5)	13.7(3)
30	$\text{Al}_4\text{Fe}_{60}\text{Si}_{20}\text{Ti}_{16}$	Quartz 900; 480	Fe_2Ti	$a = 4.781(2)$	$c = 7.693(4)$	1.2(1)	51.9(4)	22.0(2)	24.9(4)
			D0_3	$a = 5.712(3)$		6.8(2)	73.1(2)	15.9(2)	4.2(2)

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31	$\text{Al}_4\text{Fe}_{60}\text{Si}_{24}\text{Ti}_{12}$	Quartz 900; 480	Fe_2Ti	$a = 4.785(4)$	$c = 7.665(6)$	1.8(1)	49.1(3)	24.9(3)	24.1(1)
			D0_3	$a = 5.687(4)$		4.8(1)	67.4(3)	21.2(2)	6.6(2)
			FeSiTi	$a = 6.992(5)$	$b = 10.804(8)$ $c = 6.270(5)$	0.0(1)	34.7(4)	32.9(2)	32.3(2)
32	$\text{Al}_4\text{Fe}_{60}\text{Si}_{28}\text{Ti}_8$	Quartz 900; 480	D0_3	$a = 5.657(4)$		4.6(1)	65.0(2)	26.3(2)	4.2(1)
			$\text{Fe}_4\text{Si}_3\text{Ti}$	$a = 17.212(1)$	$c = 7.984(6)$	0.5(1)	48.0(1)	36.0(1)	15.6(1)
			FeSiTi	$a = 6.977(6)$	$b = 10.785(8)$ $c = 6.266(5)$	0.1(1)	35.8(4)	33.0(3)	31.1(2)
33	$\text{Al}_4\text{Fe}_{60}\text{Si}_{32}\text{Ti}_4$	Quartz 900; 480	B2	$a = 2.819(1)$		5.3(1)	64.2(2)	28.4(1)	2.2(1)
			FeSi	$a = 4.502(2)$		4.2(1)	50.3(2)	45.4(2)	0.1(1)
			$\text{Fe}_4\text{Si}_3\text{Ti}$	$a = 17.208(8)$	$c = 7.978(4)$	0.3(1)	53.6(3)	37.1(1)	9.0(2)
			Fe_5Si_3	$a = 6.851(4)$	$c = 4.718(4)$	—	—	—	—
34	$\text{Al}_8\text{Fe}_{60}\text{Si}_8\text{Ti}_{24}$	Quartz 900; 480	Fe_2Ti	$a = 4.797(1)$	$c = 7.792(2)$	4.9(3)	56.1(3)	9.5(3)	29.5(4)
			A2	$a = 2.904(1)$		19.1(2)	75.2(2)	0.3(1)	5.4(2)
35	$\text{Al}_8\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{20}$	Quartz 900; 480	Fe_2Ti	$a = 4.787(5)$	$c = 7.751(8)$	3.4(3)	52.5(4)	16.0(2)	28.1(5)
			A2	$a = 2.900(3)$		18.0(2)	77.8(3)	1.4(2)	2.8(3)
36	$\text{Al}_8\text{Fe}_{60}\text{Si}_{16}\text{Ti}_{16}$	Quartz 900; 480	Fe_2Ti	$a = 4.785(5)$	$c = 7.706(8)$	2.6(2)	50.6(4)	20.8(2)	26.0(4)
			D0_3	$a = 5.761(6)$		15.0(1)	73.3(3)	8.5(1)	3.2(2)
37	$\text{Al}_8\text{Fe}_{60}\text{Si}_{20}\text{Ti}_{12}$	Quartz 900; 480	Fe_2Ti	$a = 4.788(3)$	$c = 7.671(5)$	3.1(1)	48.9(2)	24.0(2)	24.1(2)
			D0_3	$a = 5.706(4)$		10.5(2)	67.1(3)	17.1(2)	5.3(3)
38	$\text{Al}_8\text{Fe}_{60}\text{Si}_{24}\text{Ti}_8$	Quartz 900; 480	D0_3	$a = 5.676(1)$		9.1(1)	65.1(3)	21.8(2)	4.1(3)
			FeSiTi	$a = 6.986(3)$	$b = 10.804(7)$ $c = 6.270(4)$	0.1(1)	35.7(4)	32.5(3)	31.7(3)

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39	$\text{Al}_8\text{Fe}_{60}\text{Si}_{28}\text{Ti}_4$	Quartz 900; 480	B2 $\text{Fe}_4\text{Si}_3\text{Ti}$	$a = 2.826(1)$ $a = 17.219(8)$	$c = 7.981(5)$	8.8(1) 0.7(1)	62.4(2) 48.3(2)	26.4(2) 35.9(2)	2.4(1) 15.2(2)
40	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_4\text{Ti}_{24}$	Quartz 900; 480	Fe_2Ti B2	$a = 4.794(1)$ $a = 2.914(1)$	$c = 7.803(1)$	7.7(4) 23.0(2)	59.3(2) 61.4(3)	5.0(2) 0.5(1)	28.0(4) 15.1(3)
41	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{16}$	Quartz 900; 480	Fe_2Ti D0_3	$a = 4.789(4)$ $a = 5.799(5)$	$c = 7.725(6)$	4.3(1) 21.0(2)	51.4(2) 71.8(4)	18.4(2) 3.9(2)	25.9(2) 3.2(4)
42	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_{20}\text{Ti}_8$	Quartz 900; 480	Fe_2Ti D0_3 FeSiTi	– $a = 5.698(3)$ $a = 6.987(5)$	– $b = 10.812(8)$ $c = 6.273(4)$	6.0(7) 13.6(2) 0.6(2)	48.3(8) 65.7(3) 36.3(3)	25.8(8) 16.9(2) 32.0(3)	20.0(9) 3.7(2) 31.1(4)
43	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_{24}\text{Ti}_4$	Quartz 900; 480	B2 FeSiTi	$a = 2.843(2)$ $a = 6.974(7)$	$b = 10.853(3)$ $c = 6.251(2)$	12.3(1) 1.0(1)	62.5(2) 38.4(1)	22.8(2) 32.0(1)	2.4(1) 28.5(1)
44	$\text{Al}_{16}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{12}$	Quartz 900; 480	Fe_2Ti D0_3	$a = 4.787(5)$ $a = 5.777(6)$	$c = 7.704(8)$	5.4(2) 23.2(3)	50.6(3) 67.7(3)	19.6(2) 5.7(2)	24.4(2) 3.4(3)
45	$\text{Al}_{20}\text{Fe}_{60}\text{Si}_4\text{Ti}_{16}$	Quartz 900; 480	Fe_2Ti D0_3	$a = 4.789(4)$ $a = 5.823(5)$	$c = 7.778(6)$	7.7(3) 24.2(4)	55.7(3) 61.8(3)	10.1(2) 1.4(2)	26.5(4) 12.7(3)
46	$\text{Al}_{20}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_8$	Quartz 900; 480	Fe_2Ti B2	$a = 4.795(6)$ $a = 2.875(7)$	$c = 7.689(7)$	7.4(5) 23.7(5)	50.8(1) 63.8(6)	20.3(6) 8.7(3)	21.5(2) 3.9(6)
47	$\text{Al}_{28}\text{Fe}_{60}\text{Si}_4\text{Ti}_8$	Quartz 900; 480	Fe_2Ti B2	$a = 4.798(5)$ $a = 2.902(3)$	$c = 7.742(7)$	15.7(5) 29.9(2)	54.7(39) 61.9(2)	11.5(3) 2.2(1)	18.1(3) 6.0(1)
48	$\text{Al}_{28}\text{Fe}_{60}\text{Si}_8\text{Ti}_4$	Quartz 900; 480	Fe_2Ti B2	$a = 4.797(1)$ $a = 2.881(1)$	$c = 7.695(2)$	* – 28.5(2)	* – 61.4(2)	* – 7.0(1)	* – 3.1(1)

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49	$\text{Al}_2\text{Fe}_{60}\text{Si}_{36}\text{Ti}_2$	Quartz 900; 618	D0 ₃ FeSi Fe ₅ Si ₃	$a = 5.645(1)$ $a = 4.500(1)$ $a = 6.786(1)$ $c = 4.727(1)$	3.5(3) 1.5(1) 1.8(2)	64.8(4) 52.9(1) 61.2(6)	30.1(5) 43.9(1) 34.6(6)	1.7(1) 1.7(1) 2.4(1)
50	$\text{Al}_{10.8}\text{Fe}_{60}\text{Si}_{27.2}\text{Ti}_2$	Quartz 900; 618	FeSi B2	$a = 4.515(1)$ $a = 2.825(1)$	* 10.6(3)	* 58.9(7)	* 28.3(3)	* 2.1(4)
51	$\text{Al}_{17}\text{Fe}_{60}\text{Si}_{21}\text{Ti}_2$	Quartz 900; 618	B2	$a = 2.840(1)$	16.8(2)	59.2(1)	22.0(3)	2.0(0)
52	$\text{Al}_{10.9}\text{Fe}_{60}\text{Si}_{25.9}\text{Ti}_{3.2}$	Quartz 900; 618	B2 FeSiTi	$a = 2.828(1)$ $a = 6.997(4)$ $b = 10.775(1)$ $c = 6.270(4)$	11.2(1) 0.2(4)	59.5(2) 36.0(5)	27.0(1) 34.5(1)	2.3(1) 29.3(8)
53	$\text{Al}_5\text{Fe}_{60}\text{Si}_{33}\text{Ti}_2$	Quartz 900; 1030	D0 ₃ FeSi Fe ₄ Si ₃ Ti Fe ₅ Si ₃	$a = 5.647(1)$ $a = 4.894(1)$ $a = 17.321(1)$ $a = 6.846(1)$ $c = 8.000(1)$ $c = 4.723(1)$	3.7(1) * * 0.2(2)	65.3(1) * * 56.1(2)	28.5(1) * * 37.6(1)	2.5(1) * * 6.1(1)
54	$\text{Al}_5\text{Fe}_{60}\text{Si}_{34}\text{Ti}_1$	Quartz 900; 1030	D0 ₃ FeSi Fe ₄ Si ₃ Ti Fe ₅ Si ₃	$a = 5.648(2)$ $a = 4.896(2)$ $a = 16.777(7)$ $a = 6.826(3)$ $c = 8.112(7)$ $c = 4.724(2)$	2.3(1) * 0.0(1) 0.3(2)	66.7(1) * 55.5(2) 56.4(2)	28.1(1) * 37.6(2) 37.6(2)	2.9(1) * 6.9(2) 5.7(1)
55	$\text{Al}_{1.8}\text{Fe}_{70}\text{Si}_{1.8}\text{Ti}_{26.4}$	Quartz 900; 360	Fe ₂ Ti A2	$a = 4.785(1)$ $a = 2.882(1)$ $c = 7.800(1)$	1.4(1) 4.2(1)	67.0(3) 90.4(2)	1.9(2) 0.1(1)	29.6(2) ..5.3(2)

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56	$\text{Al}_3\text{Fe}_{70}\text{Si}_6\text{Ti}_{21}$	Quartz 900; 360	Fe_2Ti A2	$a = 4.781(1)$ $a = 2.884(1)$	$c = 7.784(1)$	1.5(1) 6.1(1)	61.7(2) 88.9(3)	7.9(1) 0.6(1)	28.9(1) 4.3(1)
57	$\text{Al}_3\text{Fe}_{70}\text{Si}_{12}\text{Ti}_{15}$	Quartz 900; 360	Fe_2Ti A2	$a = 4.776(5)$ $a = 2.875(3)$	$c = 7.733(8)$	0.9(1) 5.4(1)	56.1(2) 87.4(3)	17.0(1) 4.9(1)	26.0(2) 2.3(2)
58	$\text{Al}_3\text{Fe}_{70}\text{Si}_{18}\text{Ti}_9$	Quartz 900; 360	Fe_2Ti D0 ₃	$a = 4.775(3)$ $a = 5.708(4)$	$c = 7.693(5)$	0.5(1) 3.9(1)	53.2(2) 77.2(2)	21.5(1) 15.7(1)	24.8(2) 3.2(2)
59	$\text{Al}_3\text{Fe}_{70}\text{Si}_{21}\text{Ti}_6$	Quartz 900; 360	Fe_2Ti D0 ₃	$a = 4.785(3)$ $a = 5.690(1)$	$c = 7.673(6)$	0.5(1) 3.0(1)	51.8(2) 71.5(2)	23.0(1) 20.3(2)	24.6(2) 5.3(1)
60	$\text{Al}_3\text{Fe}_{70}\text{Si}_{24}\text{Ti}_3$	Quartz 900; 360	D0 ₃	$a = 5.668(4)$		2.9(1)	70.8(2)	23.2(1)	3.1(2)
61	$\text{Al}_6\text{Fe}_{70}\text{Si}_3\text{Ti}_{21}$	Quartz 900; 360	Fe_2Ti A2	$a = 4.785(4)$ $a = 2.895(2)$	$c = 7.796(6)$	3.7(1) 11.0(1)	63.2(2) 84.0(2)	4.2(1) 0.2(1)	28.9(2) 4.8(2)
62	$\text{Al}_9\text{Fe}_{70}\text{Si}_6\text{Ti}_{15}$	Quartz 900; 360	Fe_2Ti A2	$a = 4.782(1)$ $a = 2.897(1)$	$c = 7.778(1)$	3.9(1) 14.3(1)	58.3(3) 81.8(2)	10.6(1) 0.6(1)	27.2(2) 3.3(2)
63	$\text{Al}_9\text{Fe}_{70}\text{Si}_{12}\text{Ti}_9$	Quartz 900; 360	Fe_2Ti A2	$a = 4.780(6)$ $a = 2.879(4)$	$c = 7.704(9)$	2.1(1) 12.2(2)	53.1(3) 78.2(2)	20.1(2) 7.6(1)	24.8(3) 2.0(1)
64	$\text{Al}_9\text{Fe}_{70}\text{Si}_{18}\text{Ti}_3$	Quartz 900; 360	D0 ₃	$a = 5.698(1)$		8.9(1)	70.6(2)	17.4(1)	3.1(1)
65	$\text{Al}_{15}\text{Fe}_{70}\text{Si}_3\text{Ti}_{12}$	Quartz 900; 360	Fe_2Ti A2	$a = 4.788(1)$ $a = 2.903(1)$	$c = 7.791(2)$	7.4(4) 19.4(1)	59.4(6) 76.1(2)	7.5(3) 0.2(1)	25.7(7) 5.3(1)

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66	$\text{Al}_{15}\text{Fe}_{70}\text{Si}_6\text{Ti}_9$	Quartz 900; 360	Fe_2Ti A2	$a = 4.786(1)$ $a = 2.901(5)$	$c = 7.748(1)$	4.4(2) 19.6(2)	53.5(2) 76.9(1)	16.0(1) 1.5(1)	26.1(3) 2.0(1)
67	$\text{Al}_{15}\text{Fe}_{70}\text{Si}_{12}\text{Ti}_3$	Quartz 900; 360	B2	$a = 2.867(5)$		14.9(1)	70.3(2)	11.7(1)	3.1(1)
68	$\text{Al}_{21}\text{Fe}_{70}\text{Si}_3\text{Ti}_6$	Quartz 900; 360	Fe_2Ti B2	$a = 4.785(2)$ $a = 2.910(1)$	$c = 7.768(6)$	6.0(5) 23.2(2)	54.0(3) 72.5(2)	14.3(4) 1.1(1)	25.7(5) 3.2(1)
69	$\text{Al}_{21}\text{Fe}_{70}\text{Si}_6\text{Ti}_3$	Quartz 900; 360	Fe_2Ti B2	$a = 4.787(8)$ $a = 2.893(5)$	$c = 7.7090(\text{x})$	8.2(4) 21.6(1)	56.2(3) 70.9(2)	16.4(3) 5.3(1)	19.2(3) 2.2(1)
70	$\text{Al}_{16.4}\text{Fe}_{70}\text{Si}_1\text{Ti}_{12.6}$	Quartz 900; 618	Fe_2Ti A2	$a = 4.800(7)$ $a = 2.905(4)$	$c = 7.817(1)$	8.5(3) 18.6(1)	61.6(2) 76.1(1)	3.0(1) 0.0(1)	26.9(2) 5.3(2)

– not measured due to the fine microstructure, –* additional sample

Appendix-Table 5. Thermal effects in the quaternary system Al–Fe–Si–Ti determined by DTA

Composition (at.%)		Temperature (°C)				
Sample No.	Nominal sample composition	Invariant effect	Non-invariant: Onset	Non-Invariant: Maximum or Step	Liquidus on heating	Liquidus on cooling
01	Al ₅ Fe ₅₀ Si ₅ Ti ₄₀		1322		≈ 1500	
02	Al ₅ Fe ₅₀ Si ₁₀ Ti ₃₅		1320 (c)		> 1480	
03	Al ₅ Fe ₅₀ Si ₁₅ Ti ₃₀		1222	1438	> 1480	
04	Al ₅ Fe ₅₀ Si ₂₀ Ti ₂₅		1286(c)	1292, 1438	> 1480	
05	Al ₅ Fe ₅₀ Si ₂₅ Ti ₂₀		1185, 1201(c)	1212, 1433	> 1480	
06	Al ₅ Fe ₅₀ Si ₃₀ Ti ₁₅		1164*, 1175(c)	1169, 1187, 1439	> 1480	
07	Al ₅ Fe ₅₀ Si ₃₅ Ti ₁₀	1157	1144(c), 1153, 1175, 1191(c)	1167, 1203	1354?	1313
08	Al ₅ Fe ₅₀ Si ₄₀ Ti ₅	1158	1145, 1149(c), 1189, 1213(c)	1164, 1209, 1228	1298	1294
09	Al ₂₀ Fe ₅₀ Si ₅ Ti ₂₅		1284, 1433, 1279(c)	1290	1455	1455
10	Al ₂₀ Fe ₅₀ Si ₁₀ Ti ₂₀		1276, 1286(c)	1439	1475	1474
11	Al ₂₀ Fe ₅₀ Si ₁₅ Ti ₁₅		1232, 1255*, 1259(c)	1268	1437	1433

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12	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_{20}\text{Ti}_{10}$	1203(c), 1204, 1220, 1221(c)	1236	1334	1331
13	$\text{Al}_{20}\text{Fe}_{50}\text{Si}_{25}\text{Ti}_5$	1165, 1177(c), 1182,1188(c)	1169, 1170	1199	1188
14	$\text{Al}_{35}\text{Fe}_{50}\text{Si}_5\text{Ti}_{10}$	1245	1253	1275	1271
15	$\text{Al}_{35}\text{Fe}_{50}\text{Si}_{10}\text{Ti}_5$	1221*, 1226(c)	1229, 1252	1259	1253
16	$\text{Al}_{27.5}\text{Fe}_{60}\text{Si}_5\text{Ti}_{17.5}$	1252		1273	1264
17	$\text{Al}_{30}\text{Fe}_{50}\text{Si}_5\text{Ti}_{15}$	1247, 1264(c)	1253, 1294	1351	1343
18	$\text{Al}_{32.5}\text{Fe}_{50}\text{Si}_5\text{Ti}_{12.5}$	1237, 1257*, 1261(c)	1245, 1266	1303	1299
19	$\text{Al}_{35}\text{Fe}_{50}\text{Si}_5\text{Ti}_{10}$	1226	1250	1261	1252
20	$\text{Al}_{37.5}\text{Fe}_{50}\text{Si}_5\text{Ti}_{7.5}$	1220, 1234(c), 1239*		1269	1267
21	$\text{Al}_{40}\text{Fe}_{50}\text{Si}_5\text{Ti}_5$	1209, 1214(c)	1232	1271	1268
22	$\text{Al}_{30}\text{Fe}_{50}\text{Si}_{15}\text{Ti}_5$	1205, 1207(c), 1217*		1234	1224
23	$\text{Al}_{30}\text{Fe}_{50}\text{Si}_{19}\text{Ti}_1$	1172(c), 1187, 1211*		1223	1215
24	$\text{Al}_{17.5}\text{Fe}_{50}\text{Si}_{17.5}\text{Ti}_{15}$	1221, 1227(c)	1236	1451	1448
25	$\text{Al}_{13.8}\text{Fe}_{50}\text{Si}_{20}\text{Ti}_{16.2}$	1227(c), 1233	1254	1403	1388
26	$\text{Al}_{10}\text{Fe}_{50}\text{Si}_{22.5}\text{Ti}_{17.5}$	1221, 1227(c)	1233	1480	1475

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28	$\text{Al}_4\text{Fe}_{60}\text{Si}_4\text{Ti}_{32}$		1431, 1404(c)		> 1490	
29	$\text{Al}_4\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{24}$		1327(c), 1329		> 1490	
30	$\text{Al}_4\text{Fe}_{60}\text{Si}_{20}\text{Ti}_{16}$		1231, 1234(c), 1244(c)	1252	> 1490	
31	$\text{Al}_4\text{Fe}_{60}\text{Si}_{24}\text{Ti}_{12}$		1194	1208	1392	1391
32	$\text{Al}_4\text{Fe}_{60}\text{Si}_{28}\text{Ti}_8$	1150	1154(c), 1166, 1166(c)	1175	1242	
33	$\text{Al}_4\text{Fe}_{60}\text{Si}_{32}\text{Ti}_4$	1150	1140(c), 1141	1158	1161	1156
34	$\text{Al}_8\text{Fe}_{60}\text{Si}_8\text{Ti}_{24}$		1320(c), 1323		> 1490	
35	$\text{Al}_8\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{20}$		1320, 1322(c)		> 1490	
36	$\text{Al}_8\text{Fe}_{60}\text{Si}_{16}\text{Ti}_{16}$		1269, 1282(c)	1279	1480	1470
37	$\text{Al}_8\text{Fe}_{60}\text{Si}_{20}\text{Ti}_{12}$		1216, 1227(c)	1238	1406	1398
38	$\text{Al}_8\text{Fe}_{60}\text{Si}_{24}\text{Ti}_8$		1173, 1189(c)	1198	1262	1260
39	$\text{Al}_8\text{Fe}_{60}\text{Si}_{28}\text{Ti}_4$		1152, 1150(c)	1168	1186	1181
40	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_4\text{Ti}_{24}$		1307, 1302(c)		1455	1450
41	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{16}$		1294, 1302(c)		1441	1434

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42	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_{20}\text{Ti}_8$	1202, 1219(c)	1226	1280	1276
43	$\text{Al}_{12}\text{Fe}_{60}\text{Si}_{24}\text{Ti}_4$	1172, 1173(c)		1211	1207
44	$\text{Al}_{16}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_{12}$	1274, 1287(c)	1293	1375	1378
45	$\text{Al}_{20}\text{Fe}_{60}\text{Si}_4\text{Ti}_{16}$	1305, 1309(c)		1365	1360
46	$\text{Al}_{20}\text{Fe}_{60}\text{Si}_{12}\text{Ti}_8$	1254, 1264(c), 1272(c)	1266	1274	1272
47	$\text{Al}_{28}\text{Fe}_{60}\text{Si}_4\text{Ti}_8$	1282, 1284(c)		1338	1334
48	$\text{Al}_{28}\text{Fe}_{60}\text{Si}_8\text{Ti}_4$	1253(c), 1256		1318	1313
55	$\text{Al}_{1.8}\text{Fe}_{70}\text{Si}_{1.8}\text{Ti}_{26.4}$	1296, 1296(c)		1437	1431
56	$\text{Al}_3\text{Fe}_{70}\text{Si}_6\text{Ti}_{21}$	1317, 1317(c)		1463	1459
57	$\text{Al}_3\text{Fe}_{70}\text{Si}_{12}\text{Ti}_{15}$	1308, 1312(c)		1435	1430
58	$\text{Al}_3\text{Fe}_{70}\text{Si}_{18}\text{Ti}_9$	1167(c), 1226, 1243(c)	1257	1299	1291
59	$\text{Al}_3\text{Fe}_{70}\text{Si}_{21}\text{Ti}_6$	1209		1223	1211
60	$\text{Al}_3\text{Fe}_{70}\text{Si}_{24}\text{Ti}_3$	1205		1234	1225
61	$\text{Al}_6\text{Fe}_{70}\text{Si}_3\text{Ti}_{21}$	1310(c), 1312		1430	1421

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62	$\text{Al}_9\text{Fe}_{70}\text{Si}_6\text{Ti}_{15}$	1328, 1328(c)		1384	1380
63	$\text{Al}_9\text{Fe}_{70}\text{Si}_{12}\text{Ti}_9$	1278	1284	1304	1297
64	$\text{Al}_9\text{Fe}_{70}\text{Si}_{18}\text{Ti}_3$	1210, 1211(c)		1281	1274
65	$\text{Al}_{15}\text{Fe}_{70}\text{Si}_3\text{Ti}_{12}$	1324(c), 1325		1351	1347
66	$\text{Al}_{15}\text{Fe}_{70}\text{Si}_6\text{Ti}_9$	1317, 1320(c)	1038, 1110	1363	1358
67	$\text{Al}_{15}\text{Fe}_{70}\text{Si}_{12}\text{Ti}_3$	1241(c), 1247, 1295(c), 1296		1348	1344
68	$\text{Al}_{21}\text{Fe}_{70}\text{Si}_3\text{Ti}_6$	1313(c), 1315		1418	1415
69	$\text{Al}_{21}\text{Fe}_{70}\text{Si}_6\text{Ti}_3$	1268(c), 1288		1410	1406

* Could be invariant, based on shape of effect

(c) = on cooling

Appendix-Table 6. Experimental primary phase compositions of selected as-cast samples in the sections of 50, 60 and 70 at.% Fe.

Sample No.	Nominal sample composition (at.%)	Primary phase	Phase composition determined by EPMA			
			Al(at.%)	Fe(at.%)	Si(at%)	Ti(at%)
01	Al ₅ Fe ₅₀ Si ₅ Ti ₄₀	Fe ₂ Ti	3.4	52.2	7.9	36.5
02	Al ₅ Fe ₅₀ Si ₁₀ Ti ₃₅	Fe ₂ Ti	4.6	51.2	10.3	33.8
03	Al ₅ Fe ₅₀ Si ₁₅ Ti ₃₀	Fe ₂ Ti	2.7	48.2	16.7	32.4
04	Al ₅ Fe ₅₀ Si ₂₀ Ti ₂₅	Fe ₂ Ti	1.7	46.0	21.5	30.7
05	Al ₅ Fe ₅₀ Si ₂₅ Ti ₂₀	Fe ₂ Ti	2.3	46.1	25.0	26.6
06	Al ₅ Fe ₅₀ Si ₃₀ Ti ₁₅	FeSiTi (τ_2)	0.2	35.5	32.8	31.6
07	Al ₅ Fe ₅₀ Si ₃₅ Ti ₁₀	FeSi	5.4	49.8	43.5	1.4
08	Al ₅ Fe ₅₀ Si ₄₀ Ti ₅	FeSi	3.6	50.3	45.8	0.4
09	Al ₂₀ Fe ₅₀ Si ₅ Ti ₂₅	Fe ₂ Ti	15.7	49.6	6.4	28.2
10	Al ₂₀ Fe ₅₀ Si ₁₀ Ti ₂₀	Fe ₂ Ti	9.1	46.0	16.2	28.7
11	Al ₂₀ Fe ₅₀ Si ₁₅ Ti ₁₅	Fe ₂ Ti	8.4	44.4	21.1	26.2
12	Al ₂₀ Fe ₅₀ Si ₂₀ Ti ₁₀	A2/B2	27.0	55.8	14.9	2.4
13	Al ₂₀ Fe ₅₀ Si ₂₅ Ti ₅	A2/B2	21.5	52.4	23.9	2.2
14	Al ₃₅ Fe ₅₀ Si ₅ Ti ₁₀	A2/B2	38.1	52.1	2.7	7.1
15	Al ₃₅ Fe ₅₀ Si ₁₀ Ti ₅	A2/B2	36.9	51.8	8.2	3.2
40	Al ₁₂ Fe ₆₀ Si ₄ Ti ₂₄	Fe ₂ Ti	6.6	55.4	7.7	30.3
41	Al ₁₂ Fe ₆₀ Si ₁₂ Ti ₁₆	Fe ₂ Ti	5.4	51.7	17.3	25.7
42	Al ₁₂ Fe ₆₀ Si ₂₀ Ti ₈	A2/B2	12.2	58.9	19.2	9.7
43	Al ₁₂ Fe ₆₀ Si ₂₄ Ti ₄	A2/B2	15.3	62.0	20.7	2.0

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44	Al ₁₆ Fe ₆₀ Si ₁₂ Ti ₁₂	Fe ₂ Ti	6.7	50.8	17.9	24.6
45	Al ₂₀ Fe ₆₀ Si ₄ Ti ₁₆	Fe ₂ Ti	11.8	54.0	8.7	25.4
46	Al ₂₀ Fe ₆₀ Si ₁₂ Ti ₈	A2/B2	20.1	59.7	12.0	8.2
47	Al ₂₈ Fe ₆₀ Si ₄ Ti ₈	A2/B2	29.9	61.3	2.5	6.3
48	Al ₂₈ Fe ₆₀ Si ₈ Ti ₄	A2/B2	29.5	60.6	6.7	3.2
55	Al _{1.8} Fe ₇₀ Si _{1.8} Ti _{26.4}	Fe ₂ Ti	1.1	63.9	3.5	31.5
56	Al ₃ Fe ₇₀ Si ₆ Ti ₂₁	Fe ₂ Ti	1.4	60.1	9.5	29.1
57	Al ₃ Fe ₇₀ Si ₁₂ Ti ₁₅	Fe ₂ Ti	1.2	57.6	15.4	25.8
58	Al ₃ Fe ₇₀ Si ₁₈ Ti ₉	Fe ₂ Ti	1.2	55.7	20.4	22.7
59	Al ₃ Fe ₇₀ Si ₂₁ Ti ₆	A2/B2	3.7	73.2	19.3	3.9
60	Al ₃ Fe ₇₀ Si ₂₄ Ti ₃	A2/B2	3.1	70.6	23.3	3.0
61	Al ₆ Fe ₇₀ Si ₃ Ti ₂₁	Fe ₂ Ti	3.3	61.9	5.9	29.0
62	Al ₉ Fe ₇₀ Si ₆ Ti ₁₅	Fe ₂ Ti	4.6	60.5	10.3	24.6
63	Al ₉ Fe ₇₀ Si ₁₂ Ti ₉	A2/B2	11.4	77.8	8.2	2.5
64	Al ₉ Fe ₇₀ Si ₁₈ Ti ₃	A2/B2	9.4	71.0	17.1	2.4
65	Al ₁₅ Fe ₇₀ Si ₃ Ti ₁₂	A2/B2	16.9	73.5	1.3	8.3
66	Al ₁₅ Fe ₇₀ Si ₆ Ti ₉	A2/B2	18.4	75.5	2.5	3.6
67	Al ₁₅ Fe ₇₀ Si ₁₂ Ti ₃	A2/B2	16.2	71.2	10.4	2.2
68	Al ₂₁ Fe ₇₀ Si ₃ Ti ₆	A2/B2	21.7	71.2	2.1	5.0
69	Al ₂₁ Fe ₇₀ Si ₆ Ti ₃	A2/B2	20.9	70.2	5.9	2.9

(-) single data point

7.4. Appendix IV: Curriculum Vitae

Last name, first names,	MARKER Martin Christian Johannes
Graduate degree:	Magister (rer.nat.)
Date of Birth/Place :	18 th August 1972, Vienna
Nationality :	Austria
City :	Pillersdorfsgasse 8/8, 1020, Vienna

Education and professional experience:

September 2010	Further education „Starting with teaching at the University – Basic qualification for beginners“ at the University of Vienna
February 2010	Scientific assistant (prae-doc) at the University of Vienna
February – March 2010	Visiting research, EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining and Interface Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
March 2008	Research associate at the Department of Inorganic Chemistry / Materials Chemistry of the University of Vienna
March 2008	PhD student at the Department of Inorganic Chemistry / Materials Chemistry of the University of Vienna „ <i>Phase equilibria, structural and physical characterization of the ternary system Al–Fe–Si and the quaternary system Al–Fe–Si–Ti</i> “
March 2008	Graduation from University with distinction
2007	Tutor at the Faculty of Chemistry, Co-worker “Kinderuni” and “Kinderuni on Tour”
December 2006	Diploma Thesis " <i>Phase equilibria and structural investigations in the ternary system Ge–V–Zr</i> " at the Department of Inorganic Chemistry / Materials Chemistry of the University of Vienna (Diploma Thesis awarded with the prize of the Austrian Chemical Society)

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August 2004	Scientific co-worker at the Department of Inorganic Chemistry / Materials Chemistry: „ <i>Phase equilibria in the ternary system Al–Co–Si</i> “
February 2004	Further education „ <i>mass spectrometry - a practical introduction</i> “
October 2002	University of Vienna, course of study: Chemistry (with specialization in Inorganic Chemistry, Physical Chemistry and Food Chemistry)
2001-2002	Certificate of access to higher education (SBP)
1997-2002	Exertion of the vocation: Domiciliary care; Disabled- and stationary nursing service
1995-1996	Alternative civilian service „Am Himmel“ (severely disabled domain) – Vienna
July 1993	Degree at the College of health and nursing – Oberwart, Burgenland
1987-1991	Grammar School (with emphasis on musical education) – Oberschützen
1986-1987	Higher technical school for civil engineering (HTL) – Pinkafeld, Burgenland
1982-1986	Secondary Grammar School – Oberschützen, Burgenland
1978-1982	Primary School – St.Michael/Olbendorf, Burgenland

Additional qualification

Workshop: Patent Research, Basic of patent law and independent patent research.

Educations

Fire warden (incl. education for companies with increased fire hazard)

First-Aid Education

7.5. Appendix V: Contributions to scientific & academic fields

Publications

Martin C.J. Marker and Klaus W. Richter, *Partial liquidus projection and isothermal sections in the system Al–Fe–Si–Ti*, Intermetallics, D-13-00320R1 (2013) revised.

Martin C.J. Marker, Liliana I. Duarte, Christian Leinenbach and Klaus W. Richter, *Characterization of the Fe-rich corner of Al–Fe–Si–Ti*, Intermetallics, 39, 38-49 (2013).

Clemens Schmetterer, Herta S. Effenberger, Martin C.J Marker, Hans Flandorfer, *Ni₅Sn₄Zn from single-crystal data.*, Acta Crystallographica, C68, (3), i9-i11 (2012).

L.I. Duarte, C. Leinenbach, U.E Klotz, M.C.J. Marker, K.W. Richter and J.F. Löffler, *Experimental study of the FeAl–NiAl–TiAl section*, Intermetallics, 23, 80-90 (2012).

Martin C.J. Marker, Barbara Skolyszewska-Kühberger, Herta S. Effenberger, Clemens Schmetterer and Klaus W. Richter, *Phase equilibria and structural investigations in the system Al–Fe–Si*, Intermetallics, 19(12), 1919-1929 (2011).

Martin C. J Marker, Herta S. Effenberger, Klaus W Richter, *Crystal structures, site occupations and phase equilibria in the system V–Zr–Ge*, Solid State Sciences , 11(8), 1475-1483 (2009)

Contributions to conferences

Martin C.J. Marker, Liliana I. Duarte, Christian Leinenbach and Klaus W. Richter, *A Characterization of the Multicomponent System Al–Fe–Si–Ti*; 14. Österreichische Chemietage, Linz; 26 – 29. Sept. 2011

(Oral presentation)

Martin C.J. Marker, Liliana I. Duarte, Christian Leinenbach and Klaus W. Richter, *Phase-Equilibria and Structural Investigations in the Quaternary System Al–Fe–Si–Ti*; EUROMAT 2011 - European Congress and Exhibition on Advanced Materials and Processes; 12 – 15. Sept. 2011

(Oral presentation)

Martin C.J. Marker, K.W. Richter, *Phase equilibria and structural investigations in the system Al-Fe-Si*; TOFA Discussion meeting on thermodynamics alloys, Porto, Portugal; 12 – 16. Sept. 2010

(Oral presentation)

Martin C.J. Marker, K.W. Richter, *Phase equilibria and structural investigation in the system Al-Fe-Si*; WACÖ – 6. Workshop Anorganische Chemie in Österreich, Johannes Kepler Universität Linz; 29 – 30. March. 2010

(Oral presentation)

Martin C.J. Marker, K.W. Richter, *Phase-Equilibria and Structural Investigations in the Ternary System Al-Fe-Si and the Quaternary System Al-Fe-Si-Ti*; EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining and Interface Technology, Dübendorf, Switzerland. March 2010

(Oral presentation)

Martin C.J. Marker, K.W. Richter, *Phase-Equilibria and Structural Investigations in the System Al-Fe-Si*; EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining and Interface Technology, Dübendorf, Switzerland. February 2010

(Oral presentation)

K.W. Richter, Piotr Warczok, Norbert Ponweiser and Martin C.J. Marker, *Site occupations in metal rich arsenides, germanides and gallides: experiments and modeling*; TOFA - Discussion Meeting on Thermodynamics of Alloys, Krakow, Poland. 2008

(Co-author)

Martin C.J. Marker, K.W. Richter, *Phase equilibria and structural investigation in the system Al-Fe-Si*; 13. Österreichische Chemietage, Wien; 24 – 27. August 2009

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Martin C.J. Marker, K.W. Richter, *Phase equilibria and structure investigation in the system Ge-V-Zr*; 12. Österreichische Chemietage Klagenfurt, 10 – 13. September 2007

(Poster)

Lectures

- 2008 – 2013 Chemie II (BA12) (PI) - Erdwissenschaften
- 2008 – 2013 Chem. Grundpraktikum I - einführende Laborübungen
- 2008 – 2013 Chemisches Grundpraktikum I – Proseminar
- 2009 – 2011 Festkörperchemie
- 2009 Chemische Übungen für Molekularbiologen