Aluminium – Carbon – Iron

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Literature Data

After preliminary investigations [1930Kei, 1931Soe] the first detailed studies of the iron corner of the system were reported by [1934Mor, 1936Vog] and [1938Loe]. The system was reinvestigated later by [1968Nis, 1969Loe, 1980Gor1] and [1980Gor2]. For studying the Fe-rich side [1968Nis] prepared 24 ternary alloys using electrolytic Fe, graphite (99.8% C) and Al (99.99%) in an argon atmosphere. As C does not dissolve in liquid Al-Fe alloys [1936Vog, 1938Loe] and [1968Nis], the ternary alloys were always prepared by adding Al to liquid C-Fe alloys. They were isothermally annealed between 1000 and 1250°C over a period of 1.5 to 6h in an argon atmosphere. Then the samples were quenched in iced brine and examined by means of X-ray diffraction, metallography and hardness measurements. Using thermodynamic data from [1987Yok] liquidus curves were calculated which agree fairly well with the values measured at 1600°C [1955Chi, 1963Mor]. [1986Sch] investigated the iron rich part of the liquidus surface by isothermal saturation of melts and by thermal analysis. [1987Sch] calculated the surfaces of primary crystallization of αFe, γFe and graphite.
[1989Ode] investigated the ternary system in the temperature range of 1500 to 2300°C. He reported isothermal sections of the entire system and also the solubility of C in two Al-Fe liquid alloys. Using 99.99 mass% Fe, [1989Ode] prepared several binary Al-Fe alloys, which were equilibrated in graphite crucibles, heated in a graphite resistance furnace above atmospheric pressure of high purity Ar. Isothermal sections were constructed from the chemical analyses and metallographic observations.
These results were assessed by [1987Rag], [1990Gho] and [1993Rag].
Recently, [1995Pal] reinvestigated the phase equilibria of the Fe-corner and reported the liquidus surface, three isothermal sections and three temperature-composition sections. [1995Pal] used 99.99% Al, 99.97% Fe and graphite. They prepared 50 ternary alloys by arc melting. The alloys were equilibrated at 1200 (24 or 2 h), 1000 (50h) and 800°C (240h) and water quenched. The microstructure and phases were characterized by EPMA, SEM and XRD.
The effect of pressure on the phase equilibria has been studied by [1978Kam, 1992Put]. [1996Koc] presented a review of the effect of pressure on the Al-C-Fe phase equilibria. [1978Kam] determined the liquid/solid equilibria of Fe-rich alloys up to 10 GPa. [1992Put] quenched ternary alloys from 1527 to 25°C at a pressure of 6 GPa. They determined the solid-state phase equilibria using metallography, microprobe and XRD techniques.
All these results have been reviewed by [1987Rag, 1993Rag, 2002Rag]. Raghvan [2002Rag] has provided an update summerizing these results.

Binary Systems

The Al-C binary is accepted from [2003Per]. Both liquid and solid solubilities of C in Al are very limited and the only reported compound in this system is Al_4C_3. The Al-Fe binary is accepted from [2003Pis]. The C-Fe binary is adopted from [1982Kub]. Since Al is a graphite stabilizer the stable form (graphite) of the C-Fe diagram is accepted here.

Solid Phases

The known solid phases are listed in Table 1. So far only one ternary phase Fe_3AlC_x(κ) has been reported [1934Mor, 1938Loe, 1958Hue, 1961Hen, 1962Mas, 1964Bae, 1964Pal, 1968Nis, 1971Kuc, 1973Nud, 1975Ver, 1976Pog]. Structurally, Fe and Al form an $AuCu_3$-type superlattice in which C atoms occupy interstitial positions. The x in the formula Fe_3AlC_x can vary from 0.5 to 1.0. [1985Cho] reported the variation of lattice parameter as a function of x: $a = 366.26 \pm 0.33 + 0.59x$, in pm. However, to account for the atom distributions and deviation from stoichiometry the formula $Fe_{4-y}Al_yC_x$ has been suggested [1985And]

for the κ phase. [1985And] did not report the ranges for *x* and *y*. Adopting this formula, [1995Pal] reported the composition dependence of lattice parameter of κ as: a = 362.5+0.14 (at.% Al)+0.72 (at.% C), in pm. This empirical relationship is valid in the composition range between $Fe_{3.2}Al_{0.8}C_{0.71}$ and $Fe_{2.8}Al_{1.2}C_{0.42}$. The data of [1983Lys] also confirm the increase in lattice with Al content in κ phase.

Invariant Equilibria

Figure 1 shows the partial reaction scheme based on the experimental results for the Fe-rich alloys [1995Pal]. However, [1993Rag] presented a complete reaction scheme based on the thermodynamic calculations of [1991Kum].
The invariant temperatures for U_1, U_2 and U_3 reactions differ by less than 20°C compared with earlier results [1938Loe, 1969Loe, 1985Gor, 1986Sch]. Within the composition range studied by [1969Loe], the solidification was not complete, and the complete path starting from the U_2 reaction is not known. The temperature of the U_4 reaction is 825°C [1995Pal] which higher than 780°C reported by [1980Gor2]. The temperature of the three-phase peritectic reaction p_2 is 1410°C [1995Pal], and the temperature of the three-phase eutectic reaction e_1 is 1335°C [1995Pal] which is much lower than 1410°C suggested by [1986Sch]. The compositions of the phases [1995Pal] participating in the invariant reactions are listed in Table 2. The predicted invariant temperatures [1991Kum], based on thermodynamic modeling, for U_1, U_2, U_3 and U_4 reactions agree within 5°C of the experimental values reported by [1995Pal].

Liquidus Surface

Figure 2 shows the liquidus surface and the extent of the fields of primary crystallization of the phases α, γ, κ and graphite [1995Pal]. They observed significant differences in compositions of phases participating in the invariant equilibria, particularly α, γ, and κ, compared with earlier results [1938Loe, 1969Loe, 1980Gor1]. The liquidus surfaces of both [1936Vog, 1980Gor1] were rejected. [1936Vog] assumed that the double carbide reported by [1934Mor] was a ternary solid solution of the high temperature ε phase of the Al-Fe system. [1980Gor1] presented the liquidus surface as Al-C-Fe containing both graphite and cementite. However, here we accept the stable form of the C-Fe diagram. With the addition of Al to the binary C-Fe alloys, the temperature of the graphite eutectic reaction increases [1930Kei, 1931Soe, 1938Loe, 1977Car, 1988Mag] and the eutectic carbon content decreases up to the addition of about 10 mass% Al.

Isothermal Sections

Figures 3, 4, 5 show isothermal sections of the Al-C-Fe system at 2000°C, 1850°C and 1700°C respectively after [1989Ode]. Isothermal sections of the Fe-rich corner have been investigated several times [1934Mor, 1936Vog, 1938Loe, 1959Vyk, 1968Nis] and [1995Pal]. Three isotherms at 1200, 1000, and 800°C reported by [1995Pal] are shown in Figs. 6, 7 and 8, respectively. [1968Nis] reported isothermal sections at 1250, 1200, 1100 and 1000°C. The results of [1968Nis] and [1995Pal] essentially agree very well in terms of the topology of the phase fields. However, the main differences between these two sets of results are that [1995Pal] reported higher Al solubility in γ, higher C solubility in α, and larger homogeneity range of the κ phase. The isothermal section determined by [1934Mor] is essentially the same as [1968Nis] except for the extents of the (α+κ), (α+κ+graphite) and (α+γ+κ) regions. As aluminum is a graphitizing element, the fraction of graphite formation increases with the addition of aluminum, giving a maximum at about 4 mass% Al and then decreases to about zero at 10 mass% Al. The double carbide Fe_3AlC_x appears in the composition range of about 10-17 mass% Al. Beyond 17 mass% Al, graphite again dominates the phase equilibria. As shown in Figs. 6, 7 and 8 with increasing temperature the homogeneity range of κ increases.

Temperature – Composition Sections

[1936Vog] determined several isopleths at 2, 7, 10, 13 and 20 mass% Al and at 0.5, 1.0, 1.4, 2.0 and 2.7 mass% C. [1938Loe] reported the vertical sections at 0.5, 7, 10 and 15 mass% Al and 0.4, 0.7, 1.1 and 2.2 mass% C. [1967Ken] determined a vertical section at 0.3 mass% C.

[1995Pal] reported three vertical sections at 5, 10.5 and 23 at.% C. These are shown in Figs. 9, 10 and 11, respectively.

Thermodynamics

Thermodynamics of ternary Al-C-Fe alloys have been reported by [1955Chi, 1963Mor, 1973Rim, 1974Sig, 1977Cho, 1983Jan, 1983Vre, 1987Yok] and [1991Kum]. Among these, the thermodynamic modeling of [1991Kum] is the most comprehensive. Aluminum increases the activity of C in liquid iron. [1978Zhu, 1979Zhu] provided the thermodynamic explanations of the composition dependence of the graphitizing power of Al in ternary alloys.
[1987Yok] calculated isothermal sections at 2027 and 1600°C. On the other hand, [1991Kum] calculated eight isothermal sections at 2000, 1850, 1700, 1300, 1200, 1100 and 800°C, and also presented a complete reaction scheme.

Notes on Materials Properties and Applications

The atomic and magnetic structures of the κ phase have been discussed by several authors [1985And, 1994Mor, 1994Oda, 1995Fuj, 1998Iva]. The latter authors found that the stoichiometric Fe_3AlC is paramagnetic while non-stoichiometric $Fe_3AlC_{0.64}$ is ferromagnetic with T_c = 210°C. The magnetic moment of Fe is determined primarily by the nearest neighbour C atoms. Quantum-mechanical calculations show that the transition from para to ferromagnetic state, with increasing Al content, is caused by the charge transfer and *p-d* hybridization [1994Mor].
[1989Jun] and [1997San] investigated the strength, ductility and creep of Fe_3AlC_x alloys. These were either single phase, duplex and three-phase microstructures containing (αFe) and/or graphite phase. The strength and ductility were sensitive to microstructure. [1989Jun] found that the creep exponent is 4.4 ± 1.1, and activation energy is 355 kJ·mol^{-1} for single phase κ, 365 kJ·mol^{-1} for κ+graphite microstructure, 244 kJ·mol^{-1} for κ+(αFe) microstructure, and 365 kJ·mol^{-1} for κ+(αFe)+graphite microstructure. On the other hand, [1997San] reported that in Fe_3AlC_x ($0.3 \le x \le 0.8$) alloys the stress exponent for creep is 3 and activation energy lies between 250 to 320 kJ·mol^{-1}.
The hardening, softening, tensile and compressive properties of B2 alloys [2001Mun, 2001Oca, 2001Rad, 2002Bal]. The hardening and softening of the B2 phase have been attributed to the precipitation of $Fe_3AlC_{0.5}$ and graphite, respectively.
[1991Jia] investigated the shape memory behavior in an Fe-7Al-2C (at.%) alloy. They found that the shape memory effect is restricted by the alloy brittleness and precipitation of carbide. The precipitation of κ phase during aging of martensite has also been reported by [1982Suy] and [1983Lys].

Miscellaneous

[1989Ode] reported the solubility of C in liquid Fe-12.5Al (at.%) and Fe-25.0Al (at.%) alloys over an extended temperature range. The C solubility can be expressed as:
In Fe-12.5 at.% Al:
$C = - 0.55067+0.01112 \cdot T$ (in °C)
In Fe-25.0 at.% Al:
$C = - 8.46728+0.01373 \cdot T$ (in °C)
The solid solubility of C in Al-Fe ferrite has been measured by [1966Jae]. Whose results, in the temperature range of 548 to 723°C and up to 2.1 mass% Al, can be described by the empirical equation:
log (mass% C) = - 2200/T+0.0675 (mass% Al)+0.52,
where T is in K.
Using single crystals, [1995Pal] investigated the effect of C on the order-disorder transition temperature involving (αFe) and B2 phases. Their results are shown in Fig. 12. It is obvious that at a constant Al content, C increases the order-disorder temperature. This was attributed to the fact that in B2 structure six Fe atoms create favorable sites for the C atoms.

[1978Kam] reported that under high pressure, cementite is stabilized despite the presence of significant quantity of graphitizing elements. Also, under high pressure the primary crystallization products of liquid Fe-rich ternary alloys were reported to be austenite, graphite, cementite and diamond.
Figure 13 shows the 25°C isothermal section at pressure of 6 GPa. An important feature to be noted that in addition to the binary phases at ambient pressure, high pressure phases $FeAl_6$, Fe_7C_3 and diamond.
[1991Sar] investigated the microstructure of Fe-(8 to 10) wt.% Al-(1.8 to 2.4) wt.% C alloys by melt spinning and levitation melting. They found the melt spun alloys yielded $\gamma+\gamma'(L1_2)$ microstructure while levitation melting always yielded $\alpha+\gamma+Fe_3C$ microstructure.
Fe-rich alloys containing Al and C undergoes martensitic transformation [1986And]. One particular feature of Al-C-Fe martensite that has receive numerous attention is the abnormally high tetragonality [1972Lys, 1980Dra, 1980Lys, 1981Koz, 1981Lys, 1986Lys, 1986Pro1, 1986Pro2, 1992Ueh]. The abnormal tetragonality has been attributed to the presence of short-range order, nanoscale fcc ordered ($L1_2$) domains and the elastic strain fields around them.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al)	*cF*4 $Fm\bar{3}m$ Cu	a = 404.88	Pure Al at 24°C [V-C]
(C)	*hP*4 $P6_3/mmc$ C (graphite)	a = 246.4 c = 671.1	[V-C]
δ, (δFe)(h_2)	*cI*2 $Im\bar{3}m$ W	a = 293.78	pure Fe at 1480°C [V-C]
γ, (γFe)(h_1)	*cF*4 $Fm\bar{3}m$ Cu	a = 366.60	pure Fe at 1167°C [V-C]
α, (αFe)(r)	*cI*2 $Im\bar{3}m$ W	a = 286.65	pure Fe at 20°C [V-C]
Al_4C_3	*hR*7 $R\bar{3}m$ Al_4C_3	a = 855.0 α = 22.28°	[V-C]
α_1, Fe_3Al ≤ 552	*cF*16 $Fm\bar{3}m$ BiF_3	a = 579.23	[V-C] Solid solubility ranges from 22.5 to 36.5 at.% Al
α_2, FeAl ≤ 1310	*cP*2 $Im\bar{3}m$ CsCl	a = 290.9	[V-C] Solid solubility ranges from 22 to 54.5 at.% Al

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ε, Fe_2Al_3 1215-1092	*cI*16		[1982Kub]; Solid solubility ranges from 54.5 to 62.5 at.% Al
ζ, $FeAl_2$ ≤ 1154	*aP*18 *P1* $FeAl_2$	*a* = 487.8 *b* = 646.1 *c* = 880.0 α = 91.75° β = 73.27° γ = 96.89°	[V-C] Solid solubility ranges from 65.5 to 67 at.% Al
η, Fe_2Al_5 ≤ 1171	*oC*56 *Cmcm*	*a* = 767.5 *b* = 640.3 *c* = 420.3	Solid solubility ranges from 71 to 72.5 at.% Al
θ, Fe_4Al_{13} ≤ 1160	*mC*102 *C2/m* Fe_4Al_{13}	*a* = 1548.9 *b* = 808.3 *c* = 1247.6 β = 107.72°	[V-C] Solid solubility ranges from 74.5 to 75.5 at.% Al sometimes called $FeAl_3$ in the literature
κ, Fe_3AlC_x	*cP*5 $Pm\bar{3}m$ $CaTiO_3$	*a* = 366.6 to 366.8 *a* = 375.8	0.5 ≤ *x* ≤ 1.0 Solid solubility is up to 14 at.% C and 21 at.% Al [V-C]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Al	C	Fe
L + α ⇌ γ + κ	1315	U_1	L	20.2	7.9	71.9
			α	27.0	0.7	72.3
			γ	24.5	4.0	71.5
			6	24.0	8.5	67.7
L + κ ⇌ α + C	1295	U_2	L	34.2	5.4	60.4
			κ	27.3	8.7	64.0
			α	33.7	0.7	65.6
			C	0.0	100.0	0.0
L + κ ⇌ γ + C	1282	U_3	L	13.4	12.4	74.2
			κ	19.0	13.0	68.0
			γ	16.5	4.5	79.0
			C	0.0	100.0	0.0
γ + κ ⇌ α + C	825	U_4	γ	8.5	4.7	86.7
			κ	17.6	14.6	67.8
			α	8.5	0.7	90.0
			C	0.0	100.0	0.0

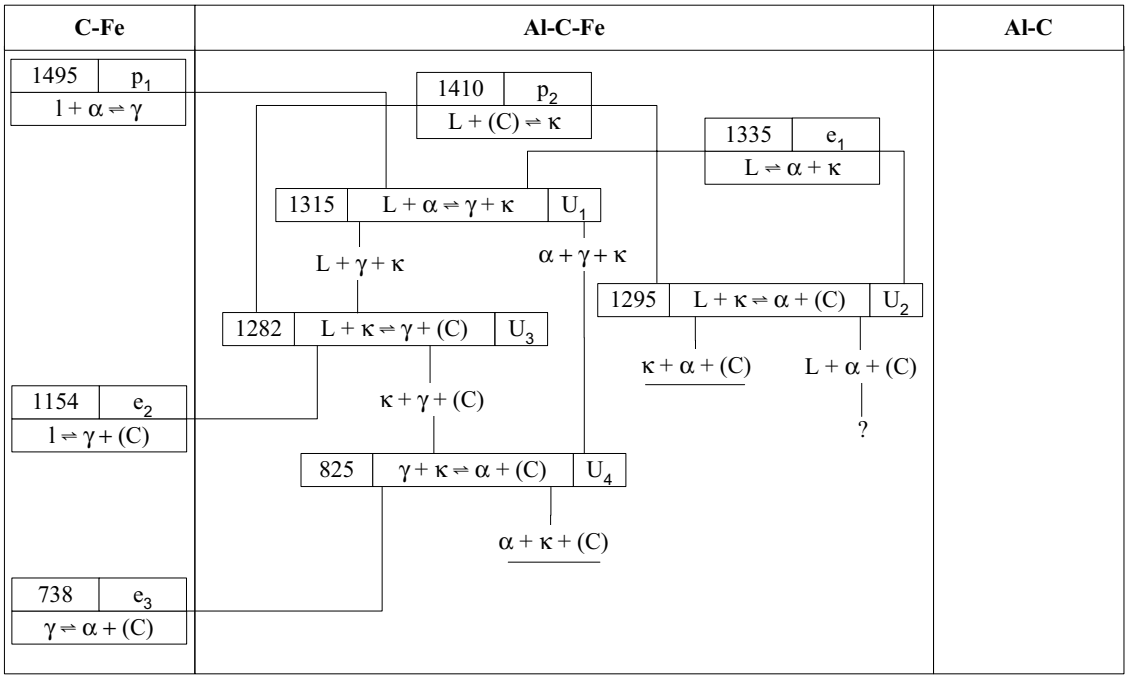

Fig. 1: Al-C-Fe. Reaction scheme

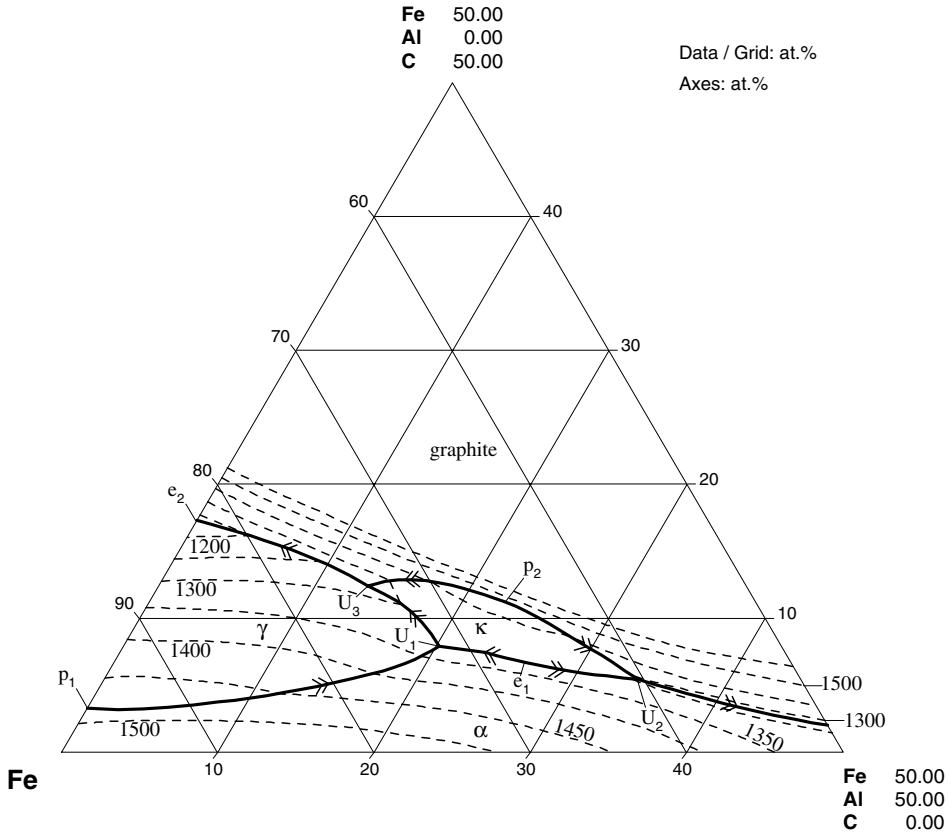

Fig. 2: Al-C-Fe. Liquidus surface

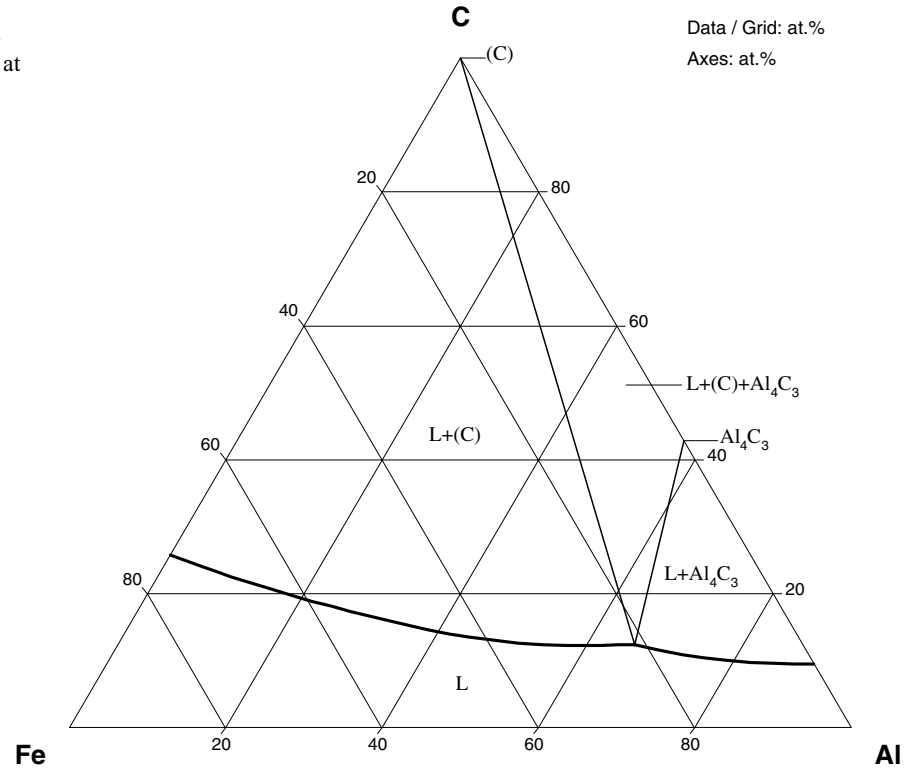

Fig. 3: Al-C-Fe. Isothermal section at 2000° C

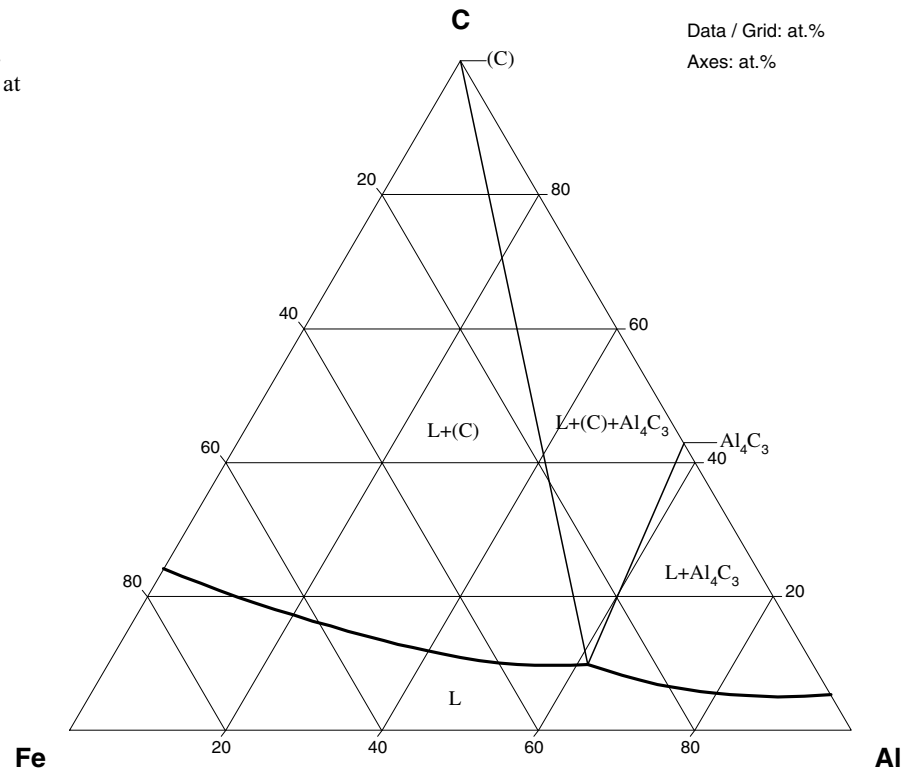

Fig. 4: Al-C-Fe. Isothermal section at 1850°C

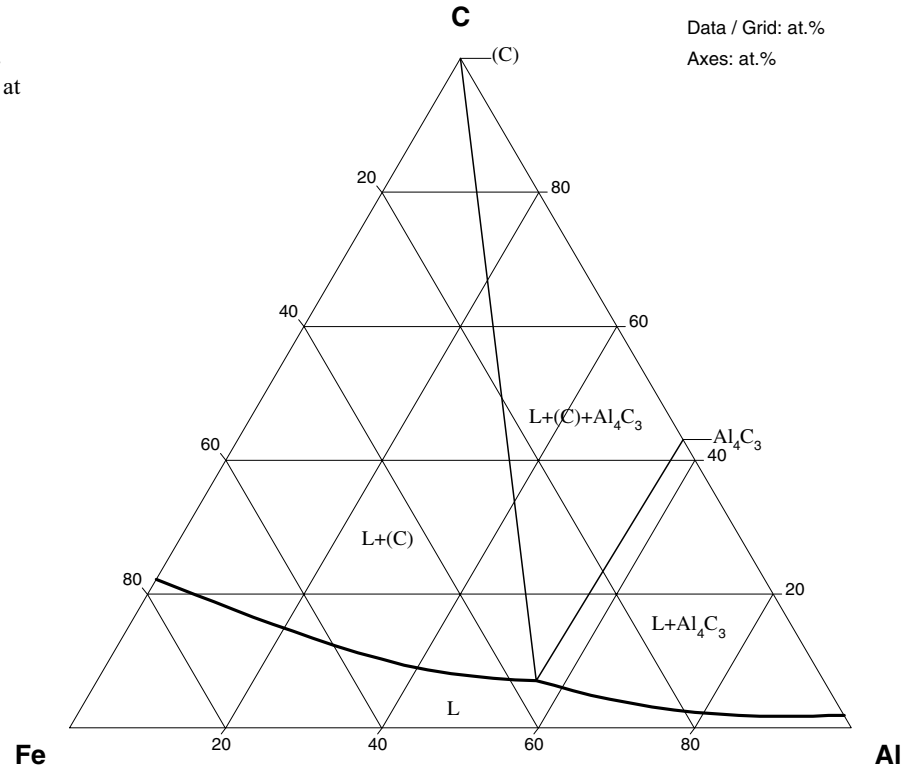

Fig. 5: Al-C-Fe. Isothermal section at 1700°C

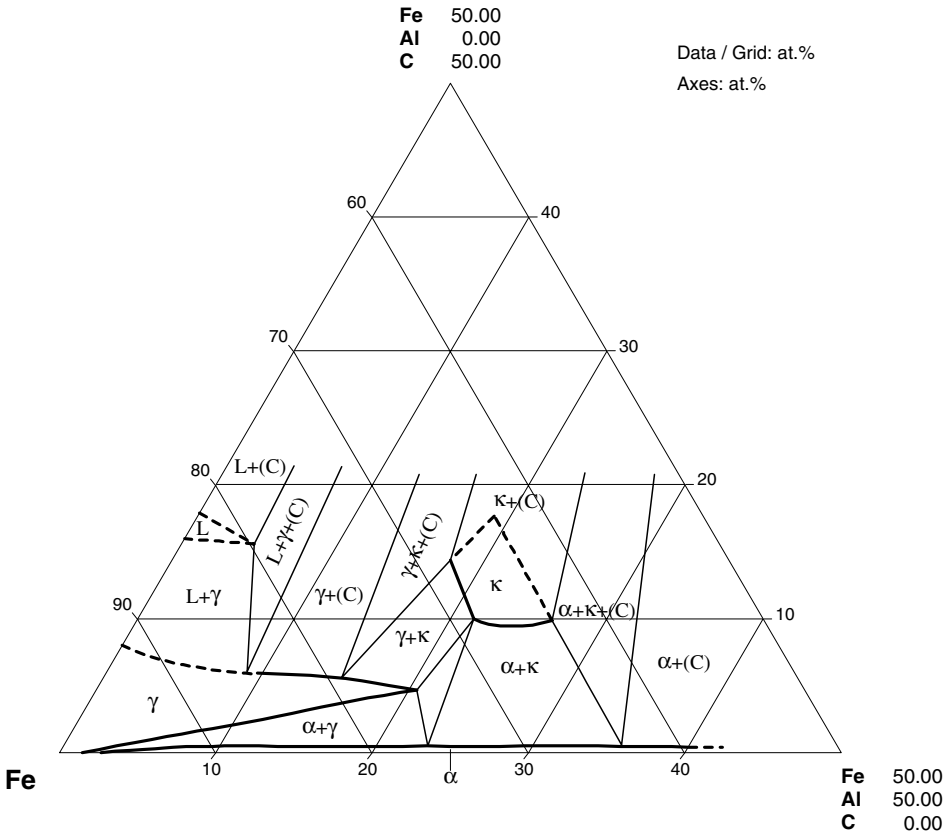

Fig. 6: Al-C-Fe. The isothermal section at 1200°C

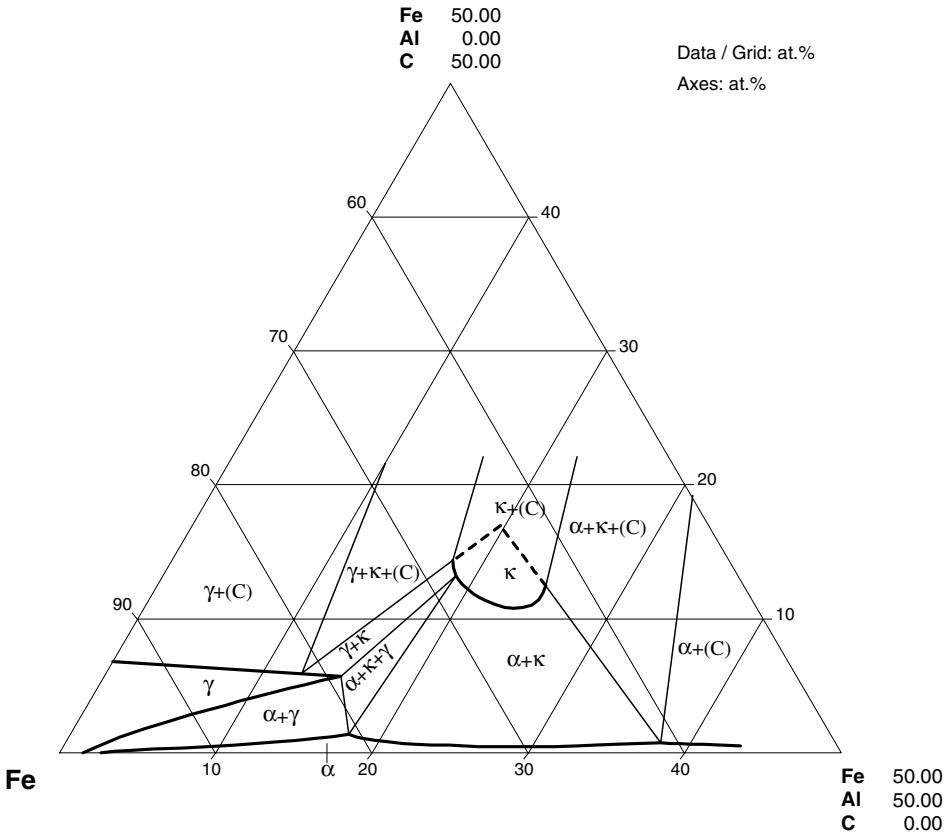

Fig. 7: Al-C-Fe. The isothermal section at 1000°C

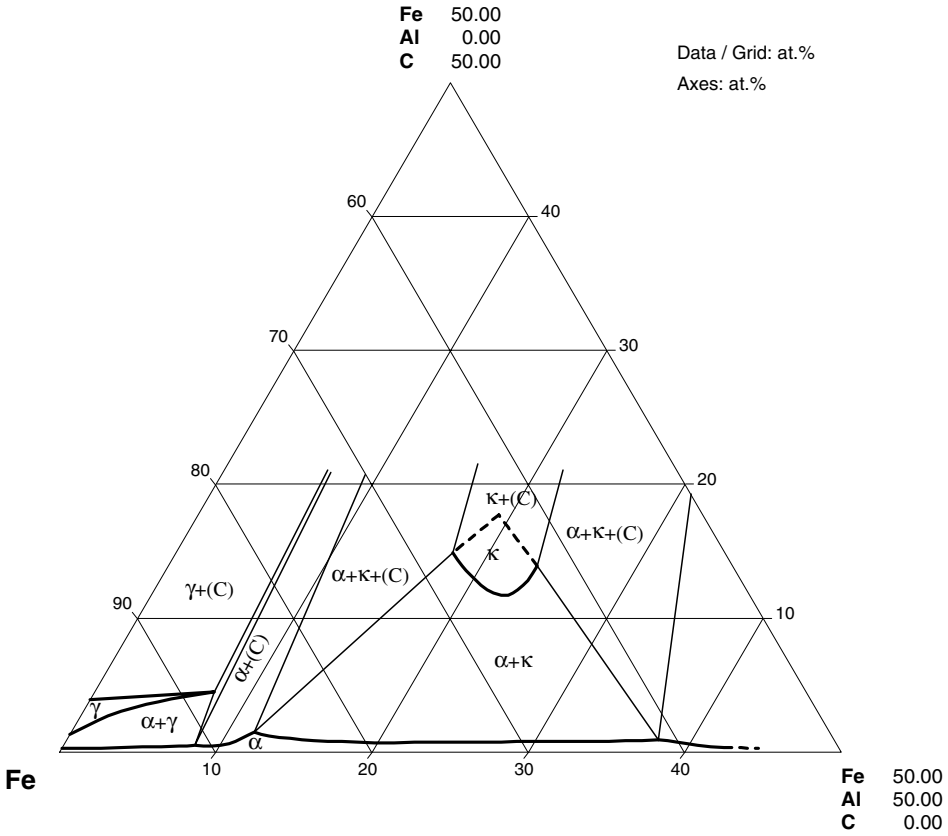

Fig. 8: Al-C-Fe. The isothermal section at 800°C

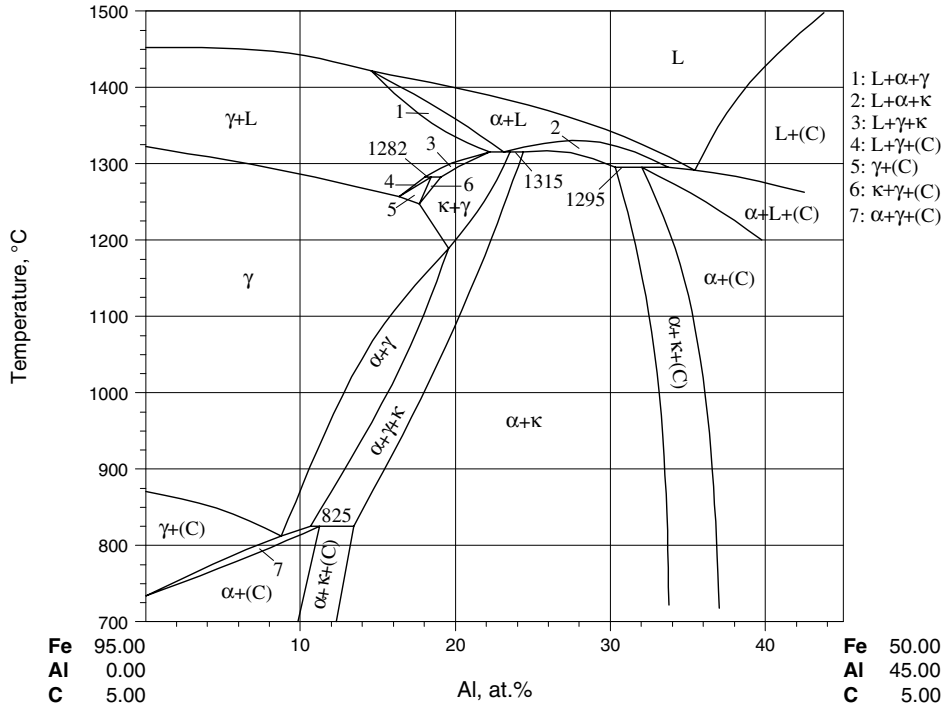

Fig. 9: Al-C-Fe. The vertical section at a constant C content of 5.0 at.%

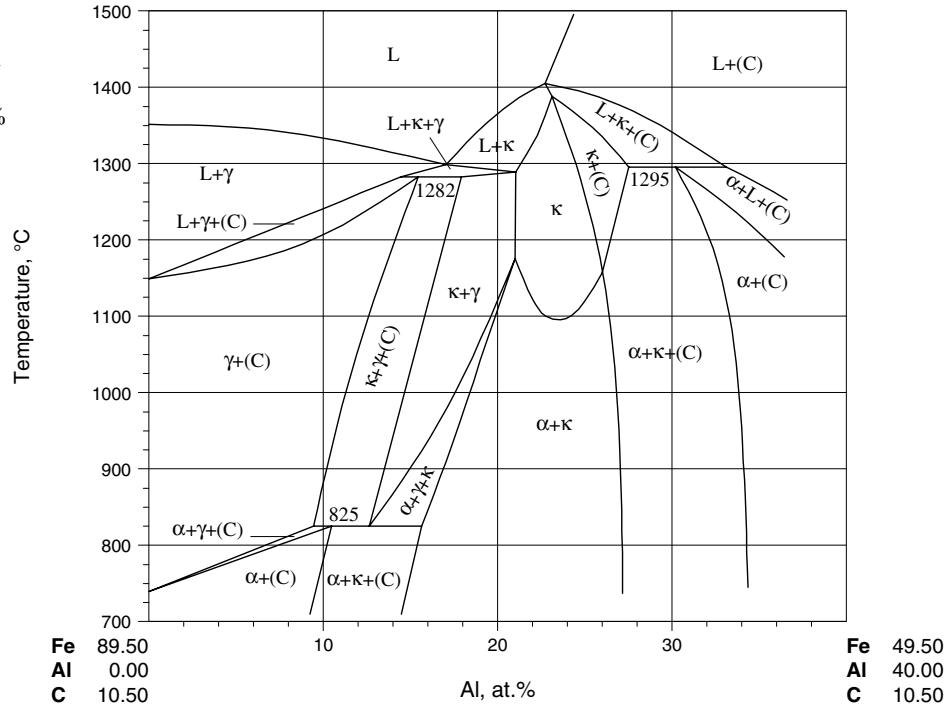

Fig. 10: Al-C-Fe. The vertical section at a constant C content of 10.5 at.%

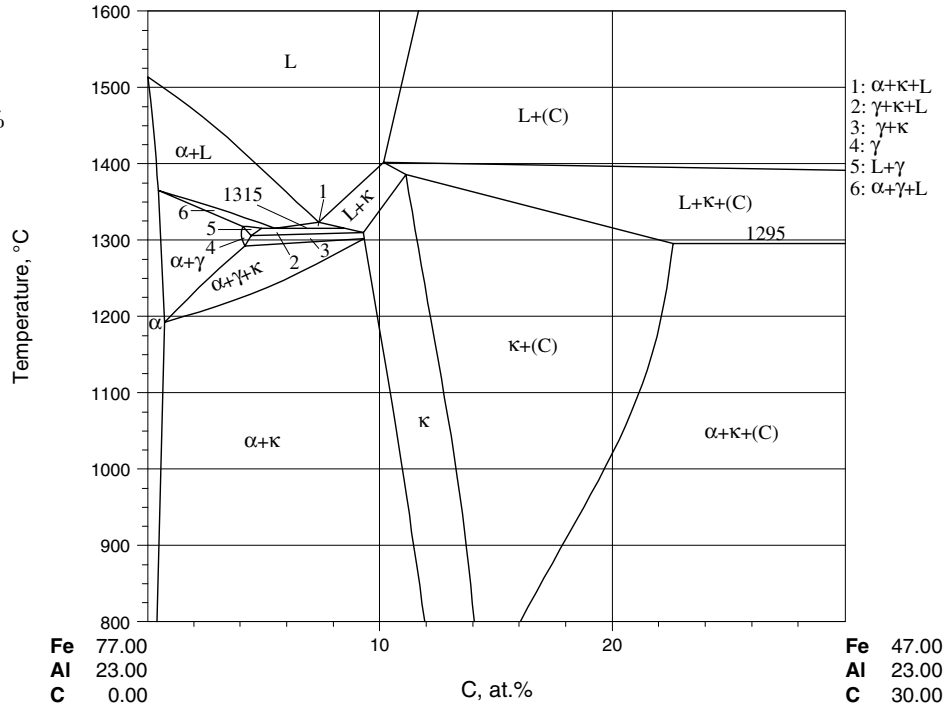

Fig. 11: Al-C-Fe. The vertical section at a constant Al content of 23.0 at.%

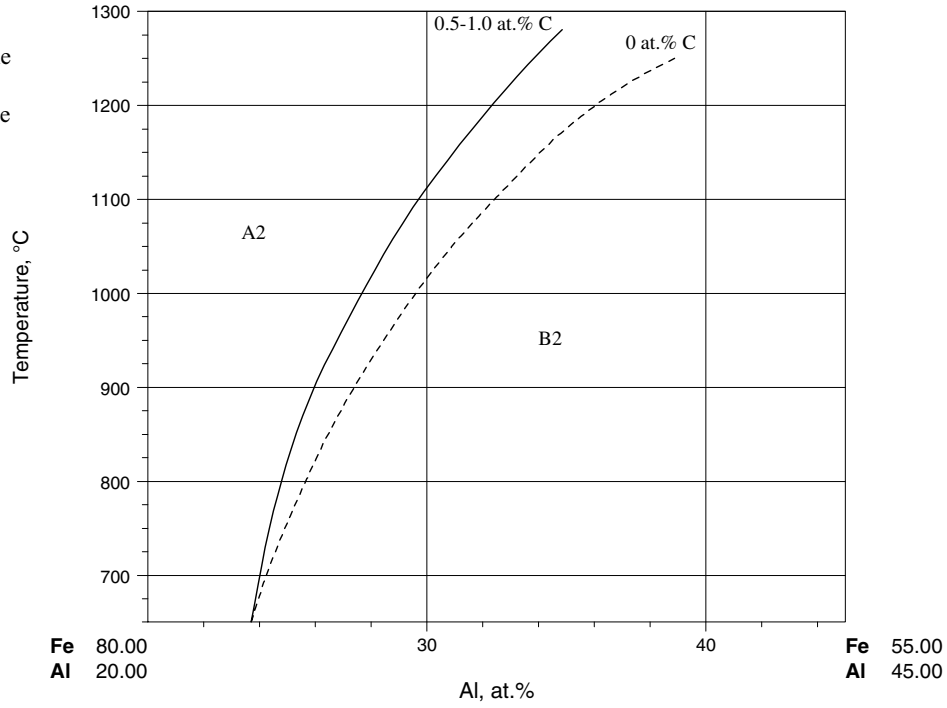

Fig. 12: Al-C-Fe. The effect of C on the order-disorder temperature of Al-Fe alloys

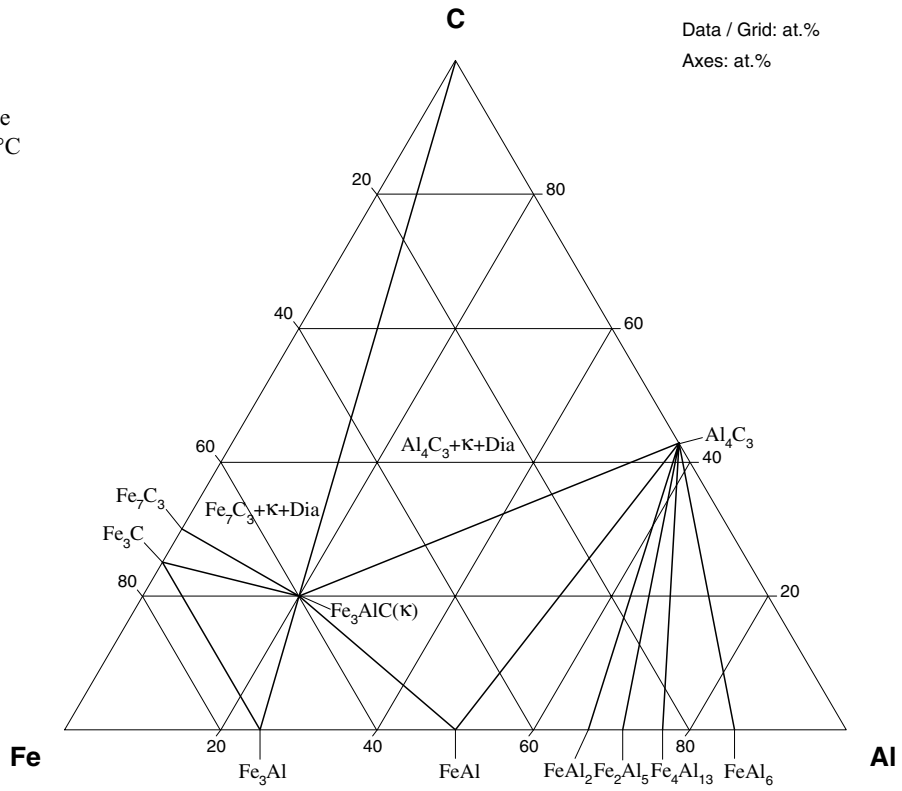

Fig. 13: Al-C-Fe. The isothermal section at a pressure of 6 GPa and at 25°C