Aluminium – Carbon – Silicon

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Literature Data

Phase diagram of the Al-C-Si system is of interest e.g. in the development of carbothermic reduction process for producing aluminium from alumina and also for understanding interfacial reaction between aluminium and silicon carbide in the of Al-based metal matrix composites containing SiC.
A ternary phase with the stoichiometry Al_4SiC_4 was first reported by [1961Bar]. Its presence was later ascertained by [1978Sch, 1979Sch, 1980Ino1, 1980Ino2, 1984Beh, 1984Bey, 1984Kid, 1987Ode1, 1987Yok, 1990Ode, 1990Via]. [1961Bar] additionally proposed a polymorphic transition of Al_4SiC_4 phase, but could not index the X-ray diffraction pattern. Other investigators could not confirm the transformation of Al_4SiC_4, though [1978Sch, 1979Sch] described the presence of a low temperature phase between Al_4SiC_4 and Al_5C_3N that formed a continuous series of solid solutions at high temperatures. Another ternary phase, $Al_4Si_2C_5$ was established by [1980Ino1, 1980Ino2] to be stable only at temperatures between 1900 and 1970°C. This phase could be retained at room temperature by rapid or moderately rapid cooling. Other researchers [1984Kid, 1987Ode1] could not verify this phase, despite several attempts to prepare it. [1984Kid] reported the existence of another phase Al_8SiC_7 that formed sluggishly between 2000 and 2100°C by a peritectic reaction. Existence of this phase was later confirmed by [1990Via].
[1987Ode1] determined the section Al_4C_3-SiC between 1900 and 2300°C by thermal analysis and X-ray diffraction of hot pressed samples. The same authors determined the solubility of carbon in the liquid phase at 2000 and 2150°C by chemical analysis of samples equilibrated in graphite crucibles and then rapidly cooled. The carbide phases in equilibrium with melt were identified by X-ray diffraction. By careful micrography, the authors verified that the parts of the samples analyzed corresponded to a homogeneous liquid at the equilibration temperature. Complete isothermal sections at 2150 and 2000°C, as well as a reaction scheme, were reported.
[1990Via] studied the Al-C-Si system under atmospheric pressure and at temperatures up to 1627°C, using X-ray diffraction, optical microscopy, scanning electron microscopy and electron microprobe analysis. Metastable isothermal sections at 567 and 997°C (i.e. without ternary carbides), stable isothermal section at 1497°C, and stable and metastable liquidus projections near the Al-corner were elucidated. From the results obtained, a thermodynamic model based on stable and metastable phase equilibria in the Al-C-Si ternary system was set up in order to provide a general description of the chemical interaction between aluminium and SiC. [2001Aks] also determined the metastable state of the phase diagram in Al-C-Si system between 700 to 900°C, employing essentially same techniques as [1990Via]. Using their own experimental data and data from literature they constructed metastable phase diagrams and their non-equilibrium variants to explain specific features of crystallization of Al-SiC composite materials.
[1966Rom] investigated microstructure and mechanical properties of an Al-SiC composite material. [1982Lil, 1985Lil] measured the compositions of the gaseous species in equilibrium with an Al-SiC mixture and analyzed them thermodynamically. [1984Bey] determined the heat capacity of Al_4SiC_4 between 5.26 and 1047 K (774°C). [1984Beh] measured the partial pressure of Al(g) above Al_4SiC_4+SiC+C using Knudsen Cell with mass spectrometry and evaluated thermodynamic functions of Al_4SiC_4. Referring to the formation of Al_4SiC_4 from Al_4C_3 and SiC, the values are smaller than the uncertainties. [1987Ode2] measured the molar heat capacity in the temperature range 174-1174°C and the enthalpy of peritectic decomposition of Al_4SiC_4 and Al_8SiC_7 by DSC.
[1982Doe, 1987Yok, 1993Wen, 1996Gro] calculated the ternary phase diagram based on data from the binary subsystems and the ternary phases. [1982Doe, 1987Yok] considered only the ternary carbides Al_4SiC_4 and $Al_4Si_2C_5$. [1993Wen, 1996Gro] included ternary phases Al_4SiC_4 and Al_8SiC_7, but ignored $Al_4Si_2C_5$ in their calculation of the phase diagram.
The present evaluation updates the work of [1990Luk] taking into account all literature published since then.

Binary Systems

Binary systems Al-Si [2003Luk] and Al-C [2003Per] are from the MSIT Binary Evaluation Program. The C-Si phase diagram is from [1996Gro].

Solid Phases

Table 1 gives crystallographic details of the solid phases of the system. All the three ternary carbides lie along Al_4C_3-SiC plane**.** Crystal structures of Al_4SiC_4 and $Al_4Si_2C_5$ proposed by [1980Ino2] were said to contain alternating layers of the Al_4C_3 and SiC structures. $Al_4Si_2C_5$ is treated as metastable, since other investigators could not establish its presence. For Al_8C_7Si, only the unit cell dimensions were given [1984Kid].

Pseudobinary Systems

There are no true pseudobinary sections known in the system, although the section Al_4C_3-SiC below solidus may be treated as pseudobinary (Fig. 5), since the amount of the phase C(gr.) is extremely low in this region.

Invariant Equilibria

The invariant equilibria associated with the liquid phase are given in Table 2. Figure 1 shows the reaction scheme after [1987Ode1, 1996Gro] assuming the phase $Al_4C_5Si_2$ to be metastable. All invariant reaction temperatures and compositions are calculated using the thermochemical data from [1996Gro]. They are in reasonable agreement with experimental data.

Liquidus Surface

The liquidus surface, calculated according to [1996Gro] is shown in Fig. 2. Isotherms above 2400°C are drawn with dotted lines to indicate that at these temperatures gas phase should be present. A schematic view of the Al corner is given in Fig. 2a. The calculated mole fractions of carbon for all the lines shown are below 10^{-8}.

Isothermal Sections

The calculated isothermal sections at 2150°C and 2000°C are shown in Fig. 3 and Fig. 4 respectively. They agree well with those reported by [1987Ode1].

Temperature – Composition Sections

Figure 5 is the calculated vertical section along the Al_4C_3-SiC plane according to [1996Gro]. The solubility of Si in Al_4C_3 is about 2 at.% at 2085°C. Note that the phase C(gr.) is not indicated in the sub-solidus region of the diagram, since its amount is very low ($< 6 \cdot 10^{-4}$ mole%).

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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) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	*a* = 404.96	at 25°C [Mas2]
(C) < 3827 (subl.)	*hP4* $P6_3/mmc$ C (graphite)	*a* = 246.12 *c* = 670.9	at 25°C [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ C (diamond)	*a* = 543.06	at 25°C [Mas2]
Al_4C_3 < 2156	*hR*7 $R\bar{3}m$ Al_4C_3	*a* = 330.75 *c* = 2490.6	[1991Sch]
SiC, βSiC < 2824	*cF*8 $Fd\bar{3}m$ ZnS (sphalerite)	*a* = 435.8	[V-C] only stable modification of SiC? [1984Ole]
* Al_8SiC_7 < 2085	*hP*16	*a* = 331.27(7) *c* = 1924.2(4)	[1984Kid]
* Al_4SiC_4 ≲ 1920	*hP*18 Al_5C_3N	*a* = 327.71 *c* = 2167.6	[1961Bar,1980Ino2]
* $Al_4Si_2C_5$ ~1970-1910	*hR11* $Al_6C_3N_2$	*a* = 325.12 *c* = 4010.8	[1980Ino2] metastable by [V-C] erroneously given as *hR*22

Table 2: Invariant Equilibria

Reactions	*T* [°C]	Type	Phase	Composition (at. %)		
				Al	C	Si
L + (C) + Al_4C_3 ⇌ Al_8SiC_7	2085	P_1	L	71.3	13.7	15
L + (C) ⇌ Al_8SiC_7 + Al_4SiC_4	2080	U_1	L	69.8	13	17.2
L + (C) ⇌ Al_4SiC_4 + SiC	2075	U_2	L	65.6	11.6	22.8
L + Al_4C_3 ⇌ (Al) + Al_8SiC_7	655	U_3	L	99.07	$< 10^{-8}$	0.93
L + SiC ⇌ (Si) + Al_4SiC_4	612	U_4	L	85.8	$< 10^{-8}$	14.2
L + Al_8SiC_7 ⇌ (Al) + Al_4SiC_4	605	U_5	L	91.57	$< 10^{-8}$	8.43
L ⇌ (Al) + (Si), Al_4SiC_4	577	D_1	L	87.9	~0.0	12.1

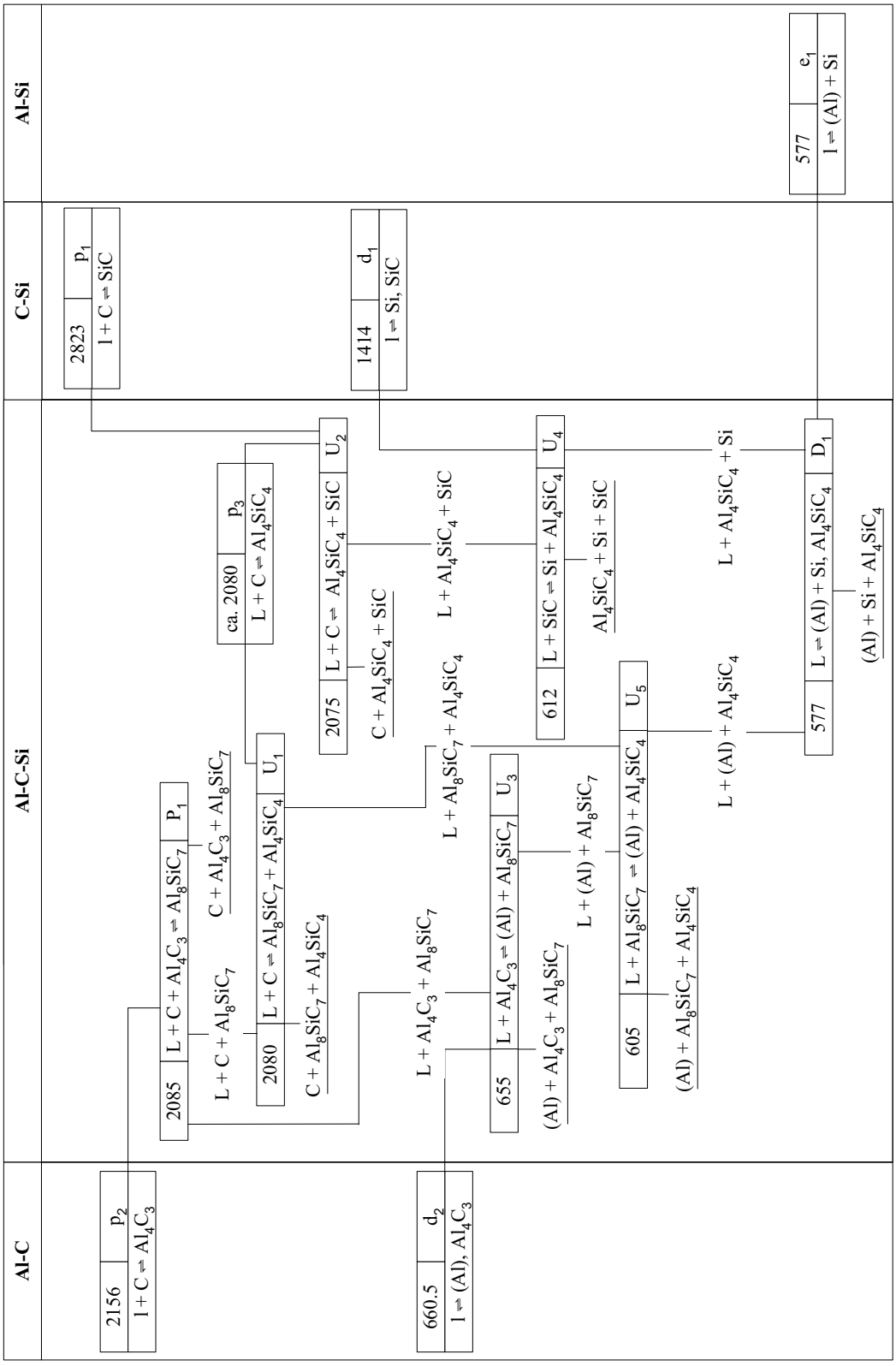

Fig. 1: Al-C-Si. Reaction scheme

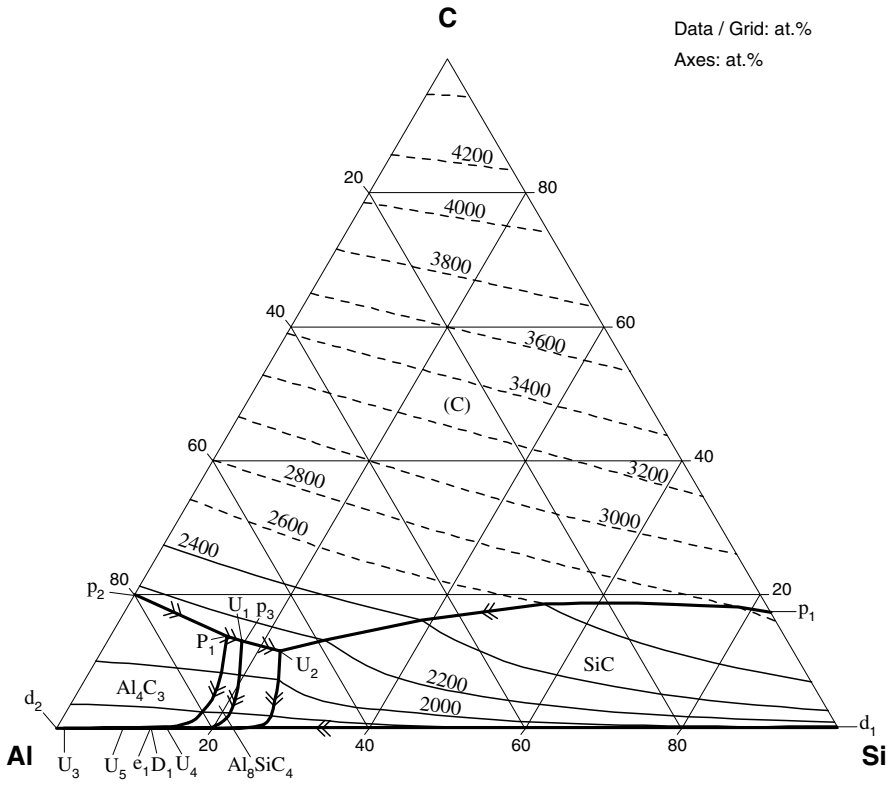

Fig. 2: Al-C-Si.
Liquidus surface

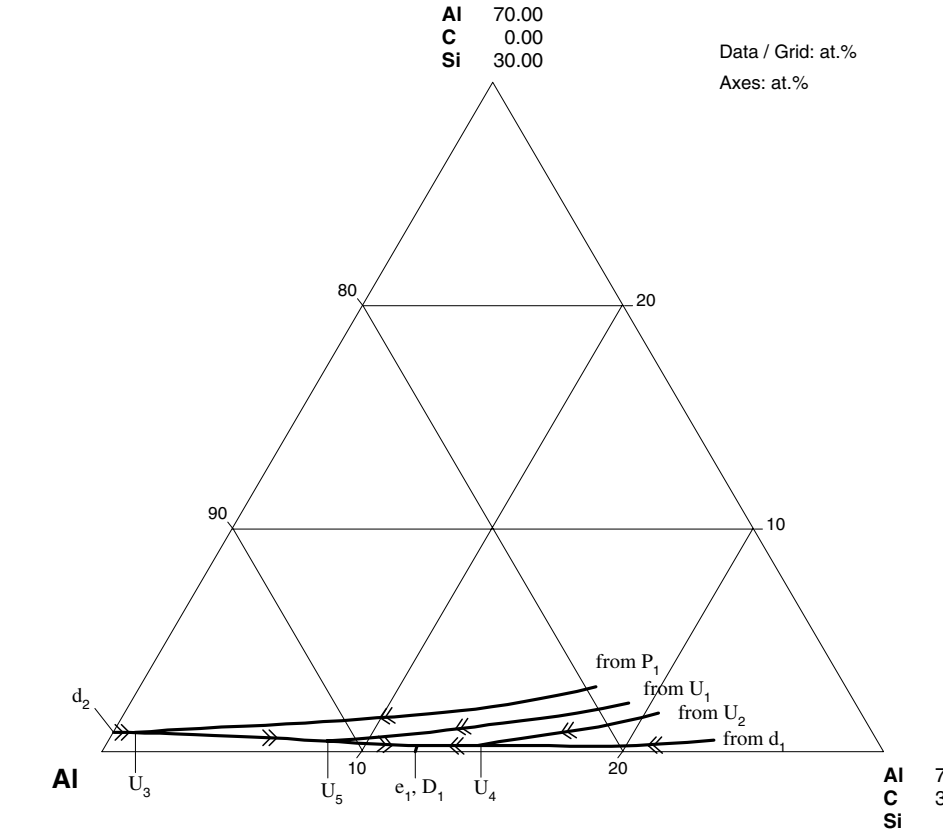

Fig. 2a: Al-C-Si.
Schematic liquidus surface near the Al-corner

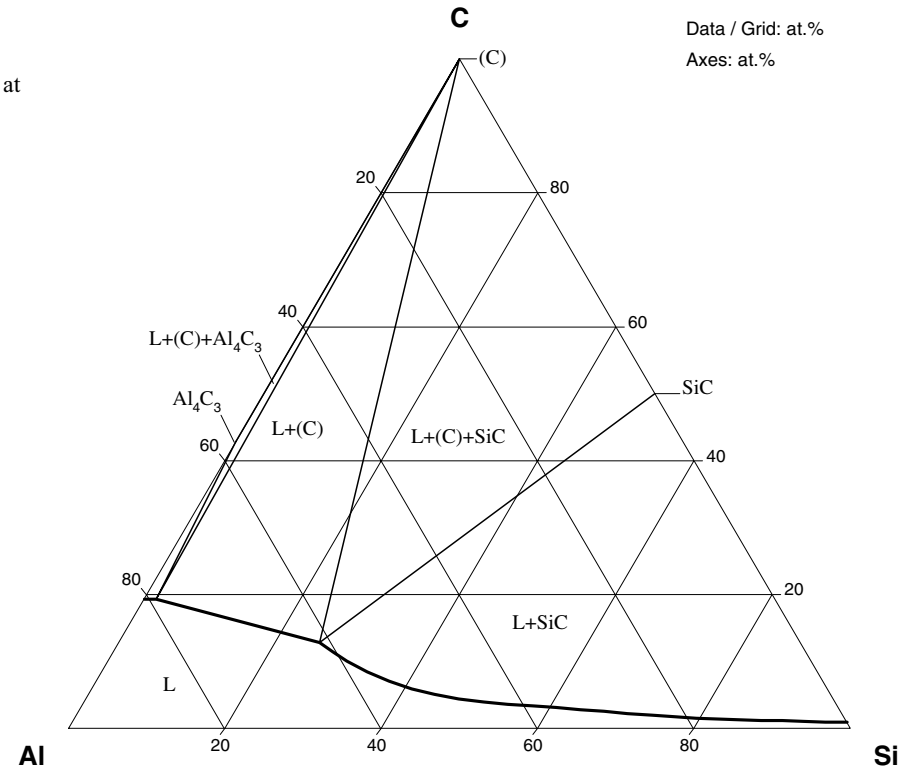

Fig. 3: Al-C-Si.
Isothermal section at 2150°C

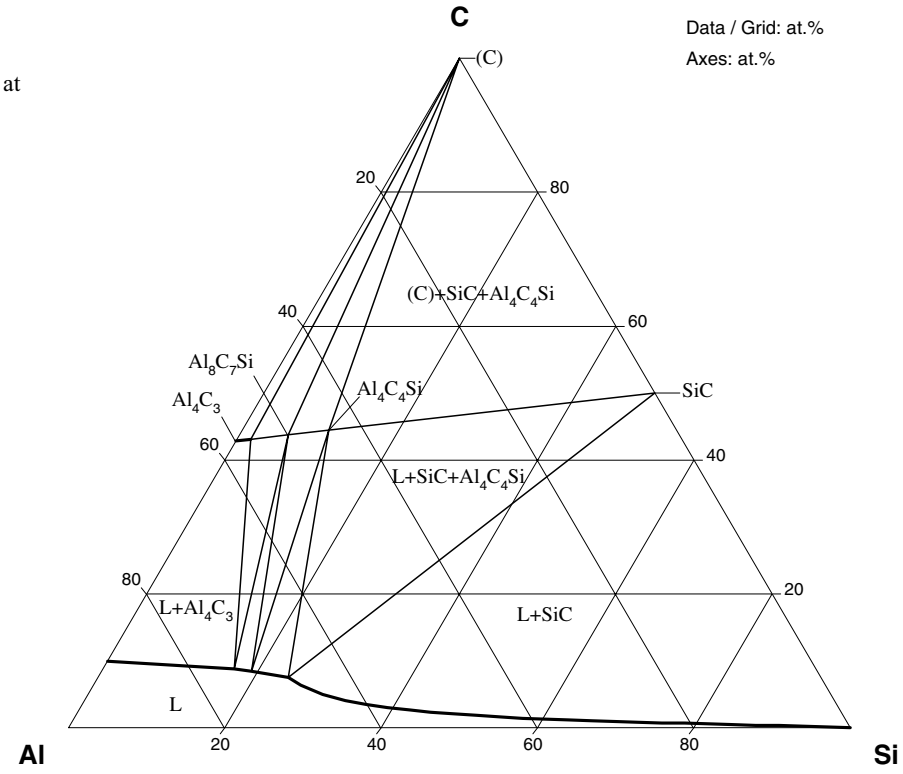

Fig. 4: Al-C-Si.
Isothermal section at 2000°C