The Al-S (Aluminum-Sulfur) System

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Equilibrium Diagram

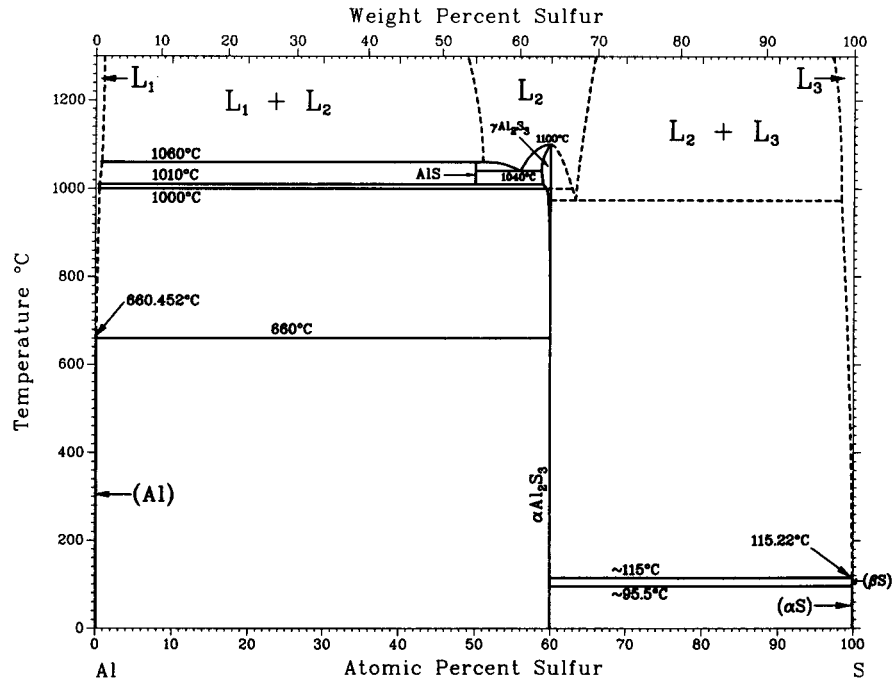
Two intermediate phases, AlS and Al_2S_3, exist in the Al-S system. The suggested Al-S phase diagram, shown in Fig. 1, is based essentially on the work of [74For].

Pure Al melts at 660.452 °C. Pure S, in the solid state, exists in two allotropic forms: (αS), stable up to 95.5 °C, and (βS), stable from 95.5 °C to its melting point of 115.22 °C. There was no systematic work on the determination of the Al-S phase diagram prior to the work of [74For]. [40Mur] studied the action of S on Al and Al alloys and suggested a tentative phase diagram (Fig. 2a) to explain their results. The main features of the diagram suggested by [40Mur] are: (1) AlS melts congruently at ~2100 °C, (2) a liquid miscibility gap exists in the Al-AlS region, resulting in a monotectic reaction at ~1800 °C and a eutectic reaction close to pure Al, and (3) Al_2S_3 is formed by a peritectic reaction between liquid and AlS at 1100 °C. [42Vog] studied the Al-Fe-S system and reported a misci-

Table 1 Special Points of the Assessed Al-S Phase Diagram

Reaction	Compositions of the respective phases, at.% S			Temperature, °C	Reaction type	Reference
Al ⇄ L		0		660.452	Melting point	[Melt]
L_1 ⇄ (Al) + αAl_2S_3	···	0	60	~660	Eutectic	[74For]
γAl_2S_3 ⇄ L		60			Congruent point	[51Fla1, 51Fla2, 52Fla]
L_1 + L_2 ⇄ AlS	···	~51	50	1060	Syntectic	[74For]
L_2 ⇄ AlS + γAl_2S_3	56	50	~59	1040	Eutectic	[74For]
AlS ⇄ L_1 + γAl_2S_3	50	···	≤60	1010	Catatectic	[74For]
L_2 ⇄ Al_2S_3 + L_3(?)	···	···	···	···	Monotectic	Suggested
L_3 ⇄ αAl_2S_3 + (βS)	~100	60	~100	~115	Eutectic	Suggested
(βS) ⇄ αAl_2S_3 + (αS)	~100	60	~100	~95.5	Eutectoid	Suggested
(βS) ⇄ L		100		115.22	Melting point	[Melt]

Fig. 1 Assessed Al-S Phase Diagram



Suggested; based on [74For].

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bility gap in the Al-S liquid extending from pure Al to ~57 at.% S and gave the melting point of Al_2S_3 as 1200 °C. [50Koh] suggested a different Al-S phase diagram, shown in Fig. 2b. They reported the melting points of AlS and Al_2S_3 as 1200 and 1100 °C, respectively, a liquid miscibility gap in the Al-AlS region, and the decomposition of AlS to liquid Al and Al_2S_3 below 950 °C. [Hansen] suggested a hypothetical Al-S phase diagram, shown in Fig. 2c, based on the diagram of [50Koh].

[74For] determined the Al-S phase diagram between Al and Al_2S_3 by DTA and X-ray diffraction methods. They found AlS to be stable between 1010 and 1060 °C. At 1010 °C, AlS decomposed to liquid Al and Al_2S_3, and at 1060 °C it melted to two liquids, L_1 and L_2 (Fig. 1). A eutectic reaction was found at $x_S = 0.56$ and 1040 °C where the liquid L_2 decomposed to AlS and Al_2S_3. The phase equilibria concerning the transformation of Al_2S_3 from the α form to the γ form were not studied in detail. In view of the narrow homogeneous range of αAl_2S_3, the transformation is taken to occur at a single temperature of 1000 °C. This represents a limiting case. More likely, the transformation takes place as $\gamma \rightleftarrows L_1 + \alpha$ (Al-rich) at 1000 °C and $\gamma + L_3 \rightleftarrows \alpha$ (S-rich) at (1000 + δ) °C; γ and α are separated by a two-phase field between these two temperatures.

Al_2S_3 is found in two allotropic forms: αAl_2S_3, stable up to 1000 °C, and γAl_2S_3, stable from 1000 °C to its melting point at 1100 °C [51Fla1, 51Fla2, 52Fla]. [74For] found that Al_2S_3 can dissolve excess Al and reported the composition of Al_2S_3 at the eutectic point (1040 °C) to be ~59 at.% S.

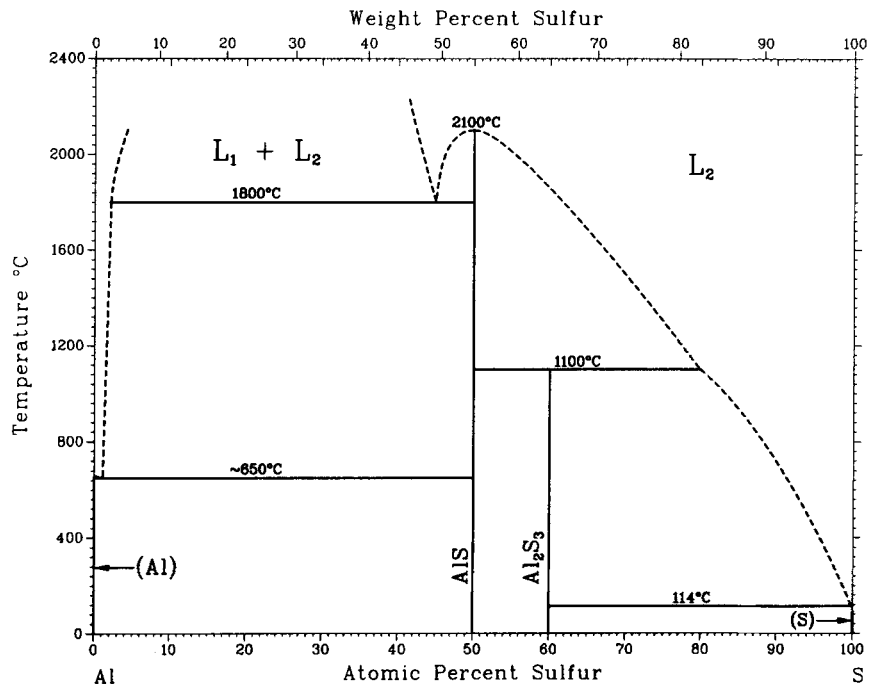
The suggested phase diagram (Fig. 1) is based essentially on the work of [74For] between 0 to 60 at.% S, but between

Table 2 Al-S Crystal Structure and Lattice Parameter Data

Phase	Composition, at.% S	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm a	b	c	Comment	Reference
(Al)	0	*cF*4	*Fm*3*m*	*A*1	Cu	0.40496	...	...	...	[Pearson2]
αAl_2S_3	60	*hP*30	...	...	...	0.6423	...	1.783	...	[51Fla1], [52Fla]
βAl_2S_3(a)	60	(b)	$P6_3mc$	*B*4	...	0.3579	...	0.5829	...	[Pearson2]
γAl_2S_3	60	*hR*10	*R*3*C*	$D5_1$	αAl_2O_3	0.686	...	...	α = 56°16′	[52Fla]
Al_2S_3(c)	60	(d)	$I4_1/amd$	...	...	0.7026	...	2.9819	...	[70Don]
Al_2S_3(e)	60	(f)	*Fd*3*m*	...	...	0.994	...	...	...	[73Ran]
(αS)	100	*oF*128	*Fddd*	*A*16	αS	1.0465	1.2866	2.4486	...	[Pearson2]
(βS)	100	*mP*48	$P2_1/a$	...	...	1.092	1.098	1.104	β = 83°16′	[Pearson2]

(a) Stable in the presence of Al_4C_3 between 1000 to 1100 °C. (b) Hexagonal. (c) High pressure, formed at 2 to 65 kbar and 1000 to 1200 °C. (d) Tetragonal. (e) High pressure, formed at 40 kbar and 400 °C. (f) Cubic.

Fig. 2 Earlier Versions of the Al-S Phase Diagram



(a)

(a) [40Mur]. (b) [50Koh]. (c) [Hansen].

(continued)

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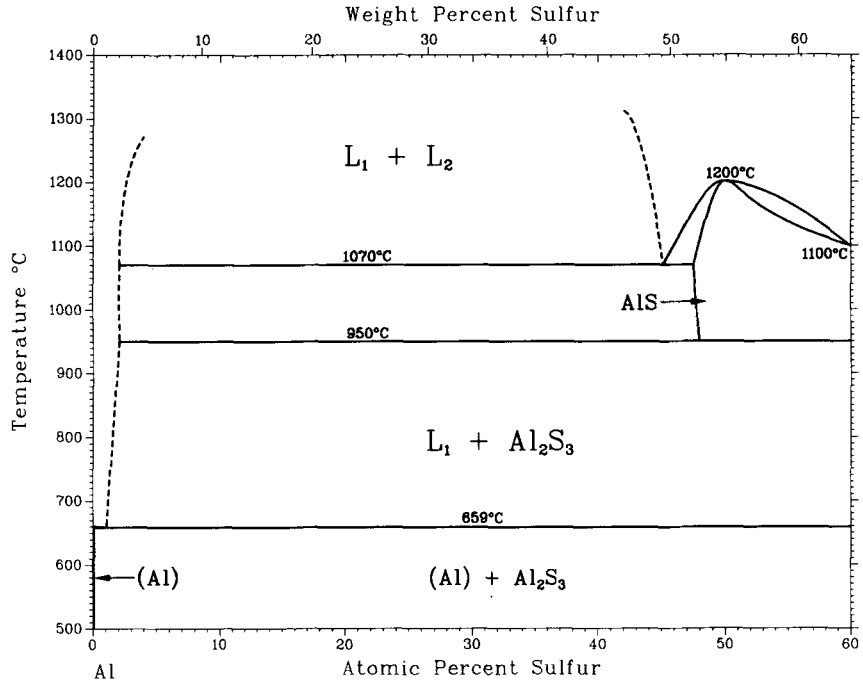
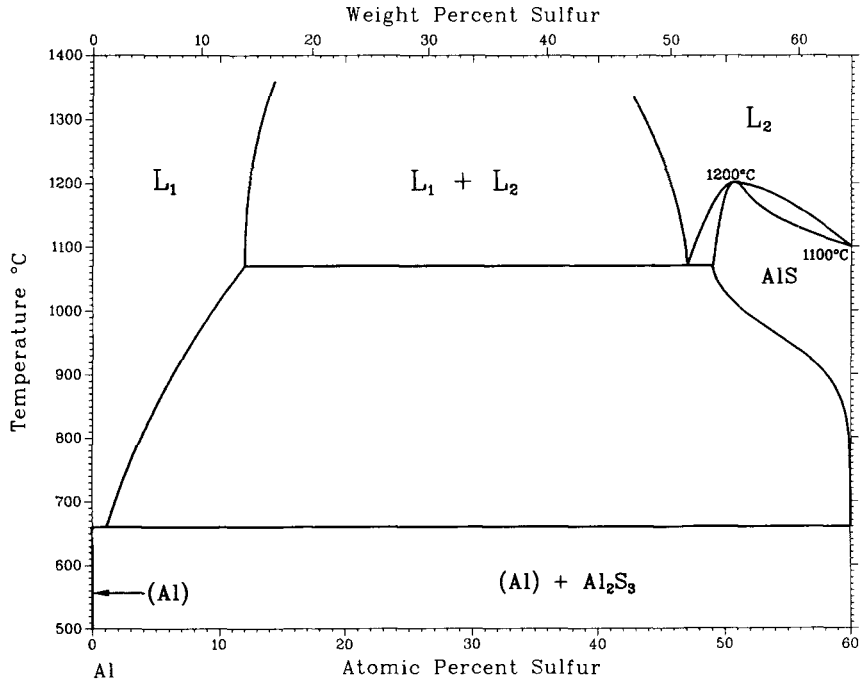
Fig. 2 Earlier Versions of the Al-S Phase Diagram (continued)

(b)



(c)



(a) [40Mur]. **(b)** [50Koh]. **(c)** [Hansen]. R.C. Sharma and Y.A. Chang, 1987.

60 to 100 at.% S it is hypothetical (suggested by the authors based on the knowledge of other metal-sulfur phase diagrams). Table 1 lists the invariant equilibria in the suggested Al-S phase diagram.

High-Pressure Phases. Two additional high-pressure modifications of Al_2S_3 are reported in the literature. [70Don] reported a tetragonal modification with a structure similar to that of βIn_2S_3 when Al_2S_3 was subjected to pressures of 2 to 65 kbar at 1000 to 1200 °C. [73Ran] reported a cubic modification of Al_2S_3 at 40 kbar and 400 °C.

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data for the different phases present in the Al-S system are given in Table 2. The crystal structure of AlS is not known. [52Fla] reported a form of Al_2S_3 (referred to as βAl_2S_3 in Table 2) stable between 1000 and 1100 °C in the presence of Al_4C_3.

Thermodynamics

No thermodynamic data for the liquid phase were found in the literature. [74Mil] critically assessed the thermodynamic data for the AlS and Al_2S_3 phases and his suggested values are summarized in Table 3.

Vapor Phase. $Al_2S(g)$, AlS(g), and $Al_2S_2(g)$ species have been identified in the vapor phase [48Kle, 68Fic, 71Uy]. [61Pap], [66Mal], [68Fic], [69Kro], and [71Uy] determined the thermodynamic properties of these species. [74Mil] critically assessed these data and selected values are given in Table 4. [79Hel] discussed methods for the preparation of αAl_2S_3.

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*Indicates key paper.
#Indicates presence of a phase diagram.

Table 3 Thermodynamic Data for AlS and Al_2S_3

Phase	Enthalpy (ΔH^0_{298}), kJ/mol	Entropy (S^0_{298}), J/mol·K	Heat capacity, (C_p), J/mol·K
AlS	−265 ± 40	42 ± 10	...
Al_2S_3	−723	113 ± 20	102.2 + 36.67 × $10^{-3}T$(a)

(a) 298 to 1300 K. From [74Mil].

Table 4 Thermodynamic Data for Al_2S, AlS, and Al_2S_2

Species	Enthalpy of dissociation (D^0_0), kJ/mol	Enthalpy of dissociation (D^0_{298}), kJ/mol	Entropy (S^0_{298}), J/mol · K	Enthalpy of formation ($\Delta_f H^0_{298}$), kJ/mol
$Al_2S(g)$	709	717	275	230.5
AlS(g)	370	374	230.5	239
$Al_2S_2(g)$	1127	1140	286	66

From [74Mil]. The symbols D^0_0 and D^0_{298} denote the energies of dissociation of the gaseous phase at 0 and 298 K, respectively.

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