The S-Se (Sulfur-Selenium) System

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Equilibrium Diagram

Solid S exists in two allotropic forms; low-temperature αS transforms to βS at 95.5 °C. The melting points of pure S and pure Se are 115.22 and 221 °C, respectively [Massalski2]. The S-Se phase diagram was determined by [02Rin] over the whole composition range by thermal and dilatometric methods, and [73Nak] investigated the liquidus in the Se-rich region from ~75 to 100 at.% Se. The assessed S-Se phase diagram (Fig. 1) is essentially from [Hansen] (based on the work of [02Rin]) and was corrected for the currently accepted melting points of pure S and pure Se. In addition to the primary solid solutions, (αS), (βS), and (Se), and intermediate phase, γ, with wide stability range (from ~48.7 to 83 at.% Se) is formed.

Invariant Equilibria

The assessed data for the invariant equilibria in the S-Se system are given in Table 1.

Metastable Phases

Several metastable phases, mostly based on the known structures of S and Se may be obtained in the S-Se system over the whole composition range [60Deh, 62Fer, 78Cal, 78Lai, 79Lai,

Table 1 Special Points in the S-Se System

Reaction	Composition, at.% Se		Temperature, °C	Reaction type	Reference
L ↔ βS	0		115.22	Melting	[Massalski2]
βS ↔ αS	0		95.5	Allotropic	[Massalski2]
(βS) ↔ (αS) + γ	16.5	12	~50	75	Eutectoid	[Hansen]
L ↔ (βS) + γ	40	29	48.7	105	Eutectic	[Hansen]
L + (Se) ↔ γ	73.5	87	83	160	Peritectic	[Hansen]
L ↔ Se	100		221	Melting	[Massalski2]

Table 2 S-Se Crystal Structure Data

Phase	Composition, at.% Se	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(αS)(a)	0 to 12	*oF*128	*Fddd*	*A*16	αS	[Massalski2]
(βS)(b)	0 to 29	*mP*48	$P2_1/a$	...	...	[Massalski2]
γ	48.7 to 83	(c)	...	...	...	[31Hal]
(Se)	87 to 100	*hP*3	$P3_121$	*A*8	Se	[Massalski2]
High-pressure phase						
$S_{0.555}Se_{0.445}$	44.5	(d)	$P3_1$ or $P3_2$	...	...	[67Gel]

(a) At <95.5 °C. **(b)** From 95.5 to 115.22 °C. **(c)** Monoclinic. **(d)** Trigonal.

Table 3 S-Se Lattice Parameter Data

Phase	Composition, at.% Se	Lattice parameters, nm			Comment	Reference
		a	*b*	*c*		
(αS)	0 to 12	1.0464	1.28660	2.44860	...	[Massalski2]
(βS)	0 to 29	1.092	1.098	1.104	β=83°16′	[Pearson2]
γ	48.7 to 83	...	...	...	...	...
(Se)	87 to 100	0.43659	...	0.49537	...	[Massalski2]
High-pressure phase						
$S_{0.555}Se_{0.445}$	44.5	0.785	...	0.462	...	[67Gel]

81Bou]. The exact composition range and structure of these phases depends on the preparation method. S-Se melts may be solidified easily into vitreous (or amorphous) structures, and metastable crystalline phases may also be obtained on annealing the amorphous alloys at higher temperatures. The crystallization kinetics of amorphous S-Se alloys and the structure of the resulting phases has been studied by [67Elm], [68Nak], [77Elm1], [77Elm2], [77Elm3], [77Elm4], and [78Elm].

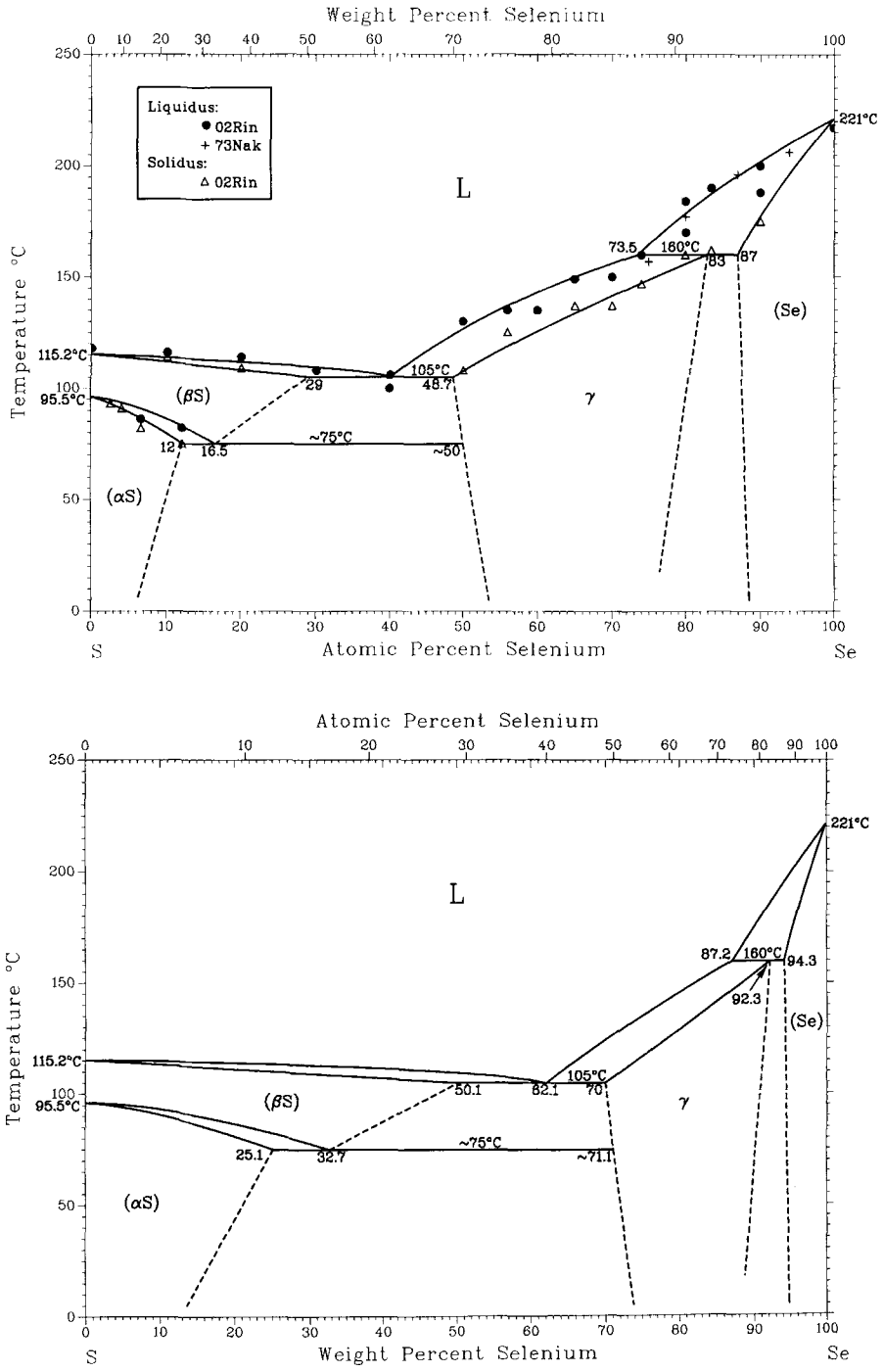

Fig. 1 Assessed S-Se phase diagram.

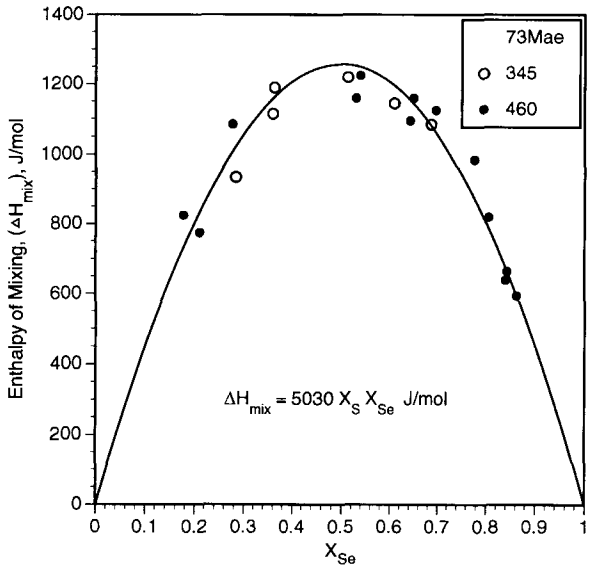

Fig. 2 Enthalpy of mixing of S-Se liquid alloys.

Crystal Structures and Lattice Parameters

Tables 2 and 3 summarize S-Se crystal structure and lattice parameter data. [30Hal] determined the lattice parameters of (αS) as a function of composition.

Thermodynamics

Liquid

[73Mae] measured the enthalpies of mixing of liquid S-Se alloys at 345 and 460 °C. They are essentially independent of temperature and can be expressed as:

$$\Delta_{mix}H = 5030X_SX_{Se} \quad \text{J/mol} \qquad \text{(Eq 1)}$$

where $\Delta_{mix}H$ is the enthalpy of mixing of liquid alloy, and X_S and X_{Se} are atomic fractions of S and Se, respectively.

Pressure

[67Gel] obtained a trigonal phase of $S_{0.555}Se_{0.445}$ composition when a mixture of equiatomic composition was subjected to 20 kbar pressure at 280 °C.

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

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