

The Ge-Se (Germanium-Selenium) System

By A.B. Gokhale and R. Abbaschian
University of Florida

Equilibrium Diagram

The assessed Ge-Se equilibrium diagram is given in Fig. 1, and the selected monovariant and invariant equilibria are summarized in Table 1. Although in general, excellent agreement was found among the data of various investigators, the assessed diagram is based primarily on the work of [82Ips], which is considered to be the most reliable because of thoroughness of investigation and the wide range of compositions investigated.

The known features of the system include: (1) a monotectic at 904 °C and ~11.5 at.% Se, with the limit of liquid immiscibility extending to 40 at.% Se; (2) the nearly stoichiometric intermediate phase GeSe, which forms peritectically at 675 °C and transforms polymorphically from cubic to a low-temperature, orthorhombic structure between 666 and 647 °C; (3) the stoichiometric intermediate phase GeSe₂, with a monoclinic structure and congruent melting point at 742 °C; and (4) eutectics between α GeSe and GeSe₂ at 583 °C and 56 at.% Se and between GeSe₂ and (Se) at 212 °C and 92 at.% Se.

The most common method of investigation of the system appears to be differential thermal analysis (DTA), supplemented by microstructural and X-ray diffraction (XRD) analyses. As discussed below, alloys with Se contents greater than 70 at.% have a marked tendency toward glass formation and therefore require long annealing times (on the order of 200 to 1500 h). Also, as noted by [68Kar], [69Ros], and [82Ips], the alloys show a tendency to supercool by "large" amounts. Consequently, the invariant arrests observed during heating are judged to be more reliable.

[62Chu1] carried out the first extensive investigation of phase equilibria, using DTA and XRD. Their data show serious disagreement with those of later investigators, both in terms of liquidus temperatures and the nature of invariant reactions. Specifically, [62Chu1] indicated a eutectic between (Ge) and GeSe, the formation of GeSe through a

peritectic reaction involving GeSe₂ and a degenerate eutectic near (Se). None of these features agree with those discovered in subsequent investigations. Also, [62Chu1] failed to detect a monotectic on the Ge side of the diagram. For these reasons, the data of [62Chu1] are not considered in this evaluation. [68Kar] first established the currently accepted features of the system, using DTA, XRD, and microhardness measurements in the range 0 to 66.67 at.% Se. Their data show excellent agreement with the more recent work of [82Ips].

The most reliable work appears to be that of [82Ips], who employed DTA to investigate the equilibria over the entire composition range using 30 alloys. [82Ips] constructed an equilibrium diagram based on 73 thermal arrests, with a claimed compositional accuracy of ± 0.1 at.%.

Various other investigations [68Vin, 69Ros, 72Que, 75Bur, 77Nov, 84Gla1, 85Odi] have been reported in limited composition ranges. The data of these investigators, along with those of [68Kar] and [82Ips], are summarized in Table 2.

The assessed diagram of Fig. 1, based primarily on the work of [82Ips], incorporates the work of other investigators as follows:

- The composition of the monotectic—11.5 at.% Se—is based on the work of [69Ros]; [82Ips] did not determine this composition, but incorporated the data of [69Ros] in constructing their diagram.
- The eutectic between GeSe₂ and (Se) is indicated at 92 at.% Se, based on the data of [65Dem] and [68Vin], instead of the 94.5 at.% Se composition of [82Ips] for the following reasons: [82Ips] noted that because of its steepness, the GeSe₂ liquidus on the Se-rich side could not be determined accurately. Consequently, the extrapolation of their liquidus to the eutectic isotherm may be somewhat inaccurate. Furthermore, the data of [65Dem] and [68Vin] are supported by the observation that the 92 at.% Se composition exhibits a very

Table 1 Special Points of the Assessed Ge-Se Phase Diagram

Reaction	Composition of the respective phases, at.% Se			Temperature, °C	Reaction type	Reference
L \leftrightarrow Ge		0		938.3	Melting point	[Melt]
L ₁ \leftrightarrow L ₂ + (Ge)	~11.5	~0	~40	904 \pm 2	Monotectic	[69Ros, 82Ips]
L + (Ge) \leftrightarrow β GeSe	~50.5	~0	50	675 \pm 2	Peritectic	[82Ips]
β GeSe \leftrightarrow α GeSe		49.75		666 \pm 2	Polymorphic	[82Ips]
		~50.25		647 \pm 4	Polymorphic	[82Ips]
L \leftrightarrow α GeSe + GeSe ₂	56	~50.25	66.67	586 \pm 2	Eutectic	[82Ips]
L \leftrightarrow GeSe ₂		66.67		742 \pm 2	Congruent	[82Ips]
L \leftrightarrow GeSe ₂ + (γ Se)	92	66.67	100	212 \pm 1	Eutectic	[65Dem, 68Vin]
L \leftrightarrow γ Se		100		221	Melting point	[Melt]

Ge-Se

strong tendency toward glass formation [76Pol, 78Esq].

Liquid, L

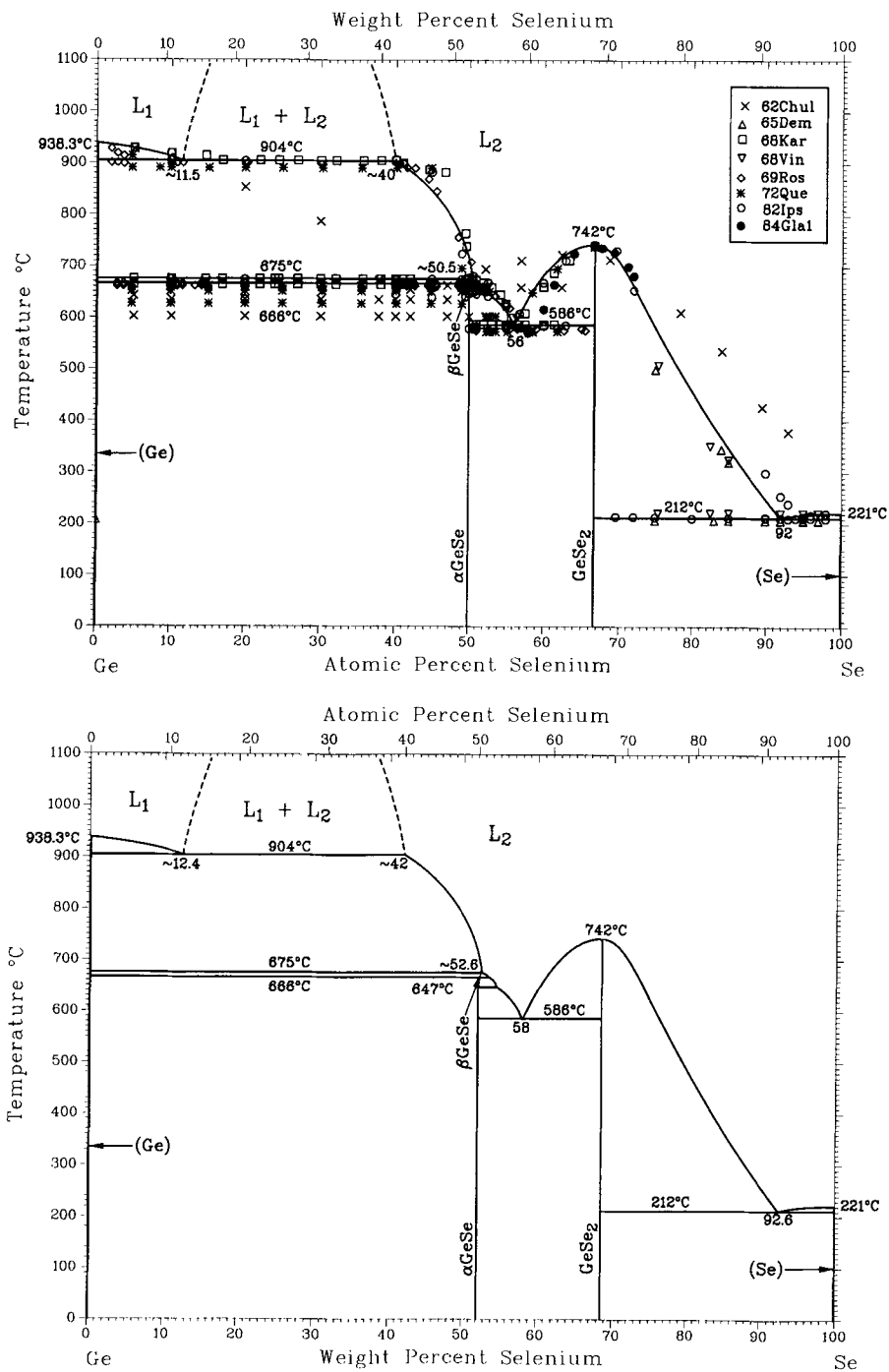
The liquidus is established reliably, except for the boundaries of the miscibility gap. According to [69Ros], the miscibility gap boundaries could not be determined, due to

very weak thermal effects associated with liquid separation.

Terminal Solid Solutions, (Ge) and (Se)

Based on Hall coefficient measurements as a function of temperature, [59Tyl] indicated the solubility of Se in (Ge) to be retrograde and on the order of 1.13×10^{-8} at.%. The sol-

Fig. 1 Assessed Ge-Se Phase Diagram



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ubility of Ge in (Se) has not been measured, but is likely to be very small.

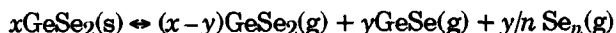
GeSe

GeSe transforms polymorphically from cubic to a low-temperature, orthorhombic modification. [68Vin], [77Nov], and [85Odi] indicated transformation temperatures of 630, 661 ± 9 , and 664°C , respectively. [68Kar] noted a first-order transformation of GeSe at 646°C and a second-order transformation at 644°C , whereas [72Que] indicated transformation temperatures of 627 and 603°C on the Ge-rich and Se-rich sides, respectively. [82Ips], judged to be the most reliable, indicated the polymorphic transformations at 666 ± 4 and $647 \pm 4^\circ\text{C}$ on the Ge-rich and Se-rich sides respectively. The latter, however, speculatively included a small (0.5 at.% Se) compositional

difference between the α and β forms, with a decomposition of βGeSe through a catatctic (inverse peritectic) reaction. In this evaluation, a homogeneity range of 0.5 at.% is indicated for GeSe, following [68Kar]. An alternate construction for the allotropic transformation is shown in Fig. 2, similar to that suggested by [72Que]. GeSe is semiconducting [59Oka] and has a density of 5.49 g/cm^3 [65Dut].

GeSe₂

GeSe₂ is nearly stoichiometric, with a monoclinic lattice and a density of 4.359 g/cm^3 [75Bur]. According to [62Chu2], based on X-ray analysis of sublimate layers, GeSe₂ sublimes with considerable decomposition according to the reaction:



Metastable and Amorphous Phases

Glass Formation

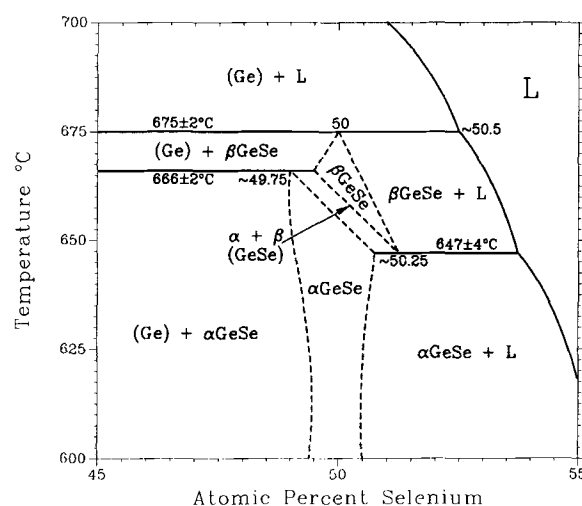
Se-rich Ge-Se alloys show a strong tendency toward glass formation. The most common methods of preparing amorphous alloys appear to be thermal sputtering on unheated substrates and quenching liquid alloys in an ice-water mixture. Substrates heated to 300°C have been reported to lead to a crystalline matrix [70Gos].

The glass transition temperature (T_g) of the amorphous alloys increases monotonically from approximately 40 to 400°C with increasing Ge content in the range 0 to 33 at.% Ge [65Dem, 76Ber, 77Bor, 78Esq]. [77Bor] also measured

Table 2 Reported Ge-Se Equilibria Involving the Liquid Phase

Reference	Temperature, °C	Composition of the respective phases, at.% Se			
Monotectic $L_1 \leftrightarrow L_2 + (\text{Ge})$					
[68Kar].....	905 ± 3	17 ± 2	40 ± 2	~0	
[69Ros].....	900	11 to 12	40 to 41	~0	
[72Que].....	890	8.4	44.8	~0	
[82Ips].....	904	...	40	~0	
[85Odi].....	905	
Peritectic $L + (\text{Ge}) \leftrightarrow \beta\text{GeSe}$					
[68Kar].....	675 ± 3	50.5	~0	50	
[68Vin].....	670	~50	~0	50	
[69Ros].....	666	50.5	~0	50	
[72Kar].....	...	50.7 ± 0.3	~0	50	
[72Que].....	651	52.8	~0	50	
[77Nov].....	678 ± 6	
[82Ips].....	675	50.6	~0	50	
[85Odi].....	675	
Eutectic $L \leftrightarrow \alpha\text{GeSe} + \text{GeSe}_2$					
[68Kar].....	587	56.5 ± 0.5	50	66.67	
[68Vin].....	580	62	50	66.67	
[69Ros].....	578	57 to 58	50	66.67	
[72Que].....	573	55.2	50	66.67	
[82Ips].....	583	56	50	66.67	
[85Odi].....	590	
Congruent melting					
[65Dem]....	740		66.67		
[68Kar].....	740		66.67		
[68Vin].....	740		66.67		
[69Ros].....	740		66.67		
[72Que].....	738		66.67		
[75Bur].....	740 ± 3		66.67		
[77Nov].....	734 ± 3		66.67		
[82Ips].....	742		66.67		
[84Gla2]....	742		66.67		
Eutectic $L \leftrightarrow \text{GeSe}_2 + (\text{Se})$					
[65Dem]....	207	92	66.67	~100	
[68Vin].....	221	92	66.67	~100	
[82Ips].....	212	94.5	66.67	~100	
[85Odi].....	213	

Fig. 2 Alternate Suggested Schematic Construction for the Polymorphic Transformation of GeSe



Reactions included: $L + (\text{Ge}) \rightleftharpoons \beta\text{GeSe}$ (peritectic at $675 \pm 2^\circ\text{C}$ and ~ 50.5 at.% Se); $(\text{Ge}) + \beta\text{GeSe} \rightleftharpoons \alpha\text{GeSe}$ (speculative peritectoid at $666 \pm 2^\circ\text{C}$ and ~ 49.75 at.% Se); and $\beta\text{GeSe} \rightleftharpoons \alpha\text{GeSe} + L$ (speculative catatctic or inverse peritectic at $647 \pm 4^\circ\text{C}$ and ~ 50.25 at.% Se).

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Table 3 Ge-Se Crystal Structure Data

Phase	Composition, at.% Se	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Ge	0	<i>cF8</i>	<i>Fd3m</i>	A4	C (diamond)	[King2]
α GeSe	50	<i>oC8</i>	<i>Cmca</i>	...	P (black)	[65Dut]
β GeSe	50	<i>cF8</i>	<i>Fm3m</i>	B1	NaCl	[75Wie]
GeSe ₂	66.67	(a)	GeS ₂ (HT)	[76Dit]
γ Se	100	<i>hP3</i>	<i>P3₁21</i>	A8	γ Se	[King2]

(a) Monoclinic.

Table 4 Ge-Se Lattice Parameter Data at Room Temperature

Phase	Composition, at.% Se	Lattice parameters, nm			Comment	References	
		<i>a</i>	<i>b</i>	<i>c</i>		Primary	Supplementary
Ge	0	0.56574	[King2]	...
α GeSe	50	0.4403(5)	0.3852(5)	1.082(1)	...	[65Dut]	[60Kan, 62Chu3, 69Ros, 72Kar, 75Wie]
β GeSe	50	0.5730(3)	At 651 \pm 5 °C	[75Wie]	...
GeSe ₂	66.67	0.7016(5)	1.6796(8)	1.1831(5)	$\beta = 90.65(5)^\circ$	[76Dit]	[75Bur]
γ Se	100	0.43655	...	0.49576	...	[King2]	...

the crystallization temperatures (T_c) of amorphous Ge-Se alloys. Their data indicated a monotonic increase in T_c from 86 to 490 °C in the range 0 to 33 at.% Ge. [77Bor] did not detect a T_c for the Ge-90 at.% Se alloy; this composition, close to the eutectic at 92 at.% Se, apparently transforms from the amorphous state directly into liquid without intermediate crystallization. It is interesting to note that according to [76Pol], the short-range order in amorphous Ge_{0.09}Se_{0.91} is essentially the same as that of its liquid. According to [65Dem] and [78Esq], the eutectic composition (92 at.% Se) is the most stable glass former. On crystallization, the conductivity of amorphous GeSe was reported to increase irreversibly by a factor of two to three [72Zak].

The short-range order in amorphous Ge-Se alloys has been deduced from radial distribution functions derived by Fourier transformation of diffraction data [72Faw, 73Pol, 74Mol, 74Uem, 76Pol]. The results indicated a monotonic increase in the coordination number (CN) from 2.4 (Se) to 4.0 (Ge). [72Faw] explained the results on the basis of a random covalent bond model, assuming that the local valence requirements are satisfied in the whole composition range. [74Uem] additionally found a singularity in CN at 33 at.% Ge, indicating a similarity in the short-range order of amorphous and crystalline GeSe₂. By contrast, the amorphous structure of GeSe is distorted considerably with respect to its crystalline counterpart [73Pol, 74Uem]. Raman spectra measurements of [80Kaw] indicated a monotonic increase in the band gap of amorphous alloys in the range 0 to 33 at.% Ge, with a maximum of ~5 eV at GeSe₂; the band gap decreases sharply between 40 and 50 at.% Se. [81Dem] noted the presence of a metastable phase (designated as ϕ) in the composition range 15 to 30 at.% Ge, without specifying either its stoichiometry or crystal structure.

Crystal Structures and Lattice Parameters

The selected Ge-Se crystal structure and lattice parameter data are summarized in Tables 3 and 4, respectively. The lattice parameter data are from references listed under "primary reference," chosen on the basis of thoroughness of investigation, listing of diffraction data, and agreement with other investigations. Other relevant references are listed under "supplementary references." In general, good agreement exists among the lattice parameter data of various investigations. However, the data of [40Iva] for GeSe and GeSe₂ and those of [62Chu2] for GeSe₂ differ considerably from those accepted in this evaluation.

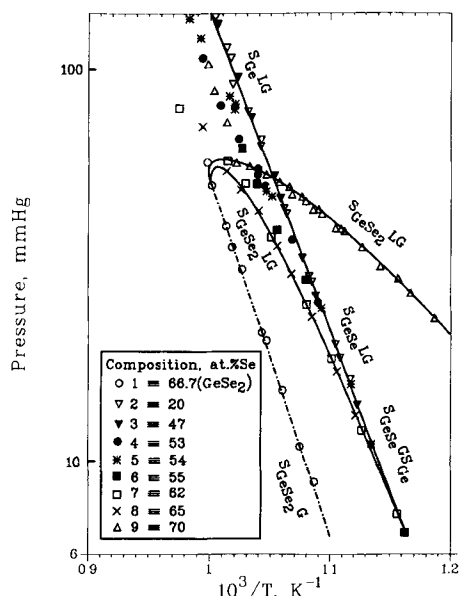
Thermodynamics

The enthalpies of mixing in the liquid solution were calculated by [84Gla] in the range 50 to 100 at.% Se. In their calculation, [84Gla] assumed an associated ideal-solution model and used the curvature of the liquidus near the melting temperature of GeSe₂ and its latent heat of fusion. The present evaluators are unaware of any other investigation pertaining to the thermodynamic properties of the liquid solution.

In this evaluation, the thermodynamic properties of the system were calculated under the assumptions that: (1) the enthalpies and excess entropies of mixing are independent of temperature; (2) the mutual solid solubilities of the pure components are nil; and (3) GeSe and GeSe₂ are line compounds.

A third-degree polynomial was fitted to the graphically transcribed enthalpy of mixing data of [84Gla1]. The polynomial expression was then used, together with the exper-

Fig. 3 Partial P - T Diagram of the Ge-Se System [70Kar]



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imental liquidus data of [68Kar], [69Ros], [82Ips], and [84Gla], and the Gibbs energies of fusion for the pure components and GeSe to calculate the excess entropies of mixing in the liquid as a function of composition.

The equilibrium diagram predicted on the basis of these calculations reproduced all the known features of the system. The only discrepancy found was in the predicted composition of the monotectic (very close to pure Ge), compared with that determined experimentally (11.5 at.% Se). This discrepancy may be possibly due to the lack of enthalpy of mixing data in this composition range.

The enthalpies and excess entropies of mixing used in generating the equilibrium diagram are as follows:

$$\Delta_{\text{mix}}H = X_{\text{Se}}(1 - X_{\text{Se}})(48.39 - 506.3X_{\text{Se}} + 294.65X_{\text{Se}}^2) \text{ kJ/mol of Se}$$

and

$$S^{\text{ex}} = -11.409X_{\text{Se}}(1 - X_{\text{Se}}) \text{ J/K} \cdot \text{mol of Se}$$

The calculations predicted the enthalpy and entropy of fusion of GeSe₂ to be 26.9 kJ/mol and 26.7 J/K·mol, respectively. The predicted latent heat of fusion is in good agreement with the experimentally determined values of 24.2 [75Bur] and 26.3 kJ/mol [77Nov].

The Gibbs energy of fusion for the pure components and GeSe may be represented as a function of temperature as:

$$\Delta_{\text{fus}}G(\text{Ge}) = 3.294 \times 10^4 + 23.45T + 36.78 \times 10^{-4}T^2 - 7.761 \times 10^{-2}T \ln T \text{ J/mol of Ge}$$

$$\Delta_{\text{fus}}G(\text{Se}) = 3.968 \times 10^2 + 100T + 1.255 \times 10^{-4}T^2 - 17.25T \ln T \text{ J/mol of Se}$$

$$\Delta_{\text{fus}}G(\text{GeSe}) = 1.455 \times 10^4 + 103.4T + 82.01 \times 10^{-4}T^2 - 18.49T \ln T \text{ J/mol of GeSe}$$

The heats of fusion and heat capacities for the pure components and GeSe used in the calculation are from [77Bar].

Pressure

The P - T - X equilibria in Ge-Se were determined by [70Kar] using the quartz null-manometer diaphragm method. [70Kar] determined the total pressure, with a claimed accuracy of ± 1 mmHg as a function of temperature for the s-L-g three-phase equilibria in the range 20 to 70 at.% Se. The P - T diagram of [70Kar] is reproduced in Fig. 3. Point B in Fig. 3 refers to the position of the invariant four-phase equilibrium between GeSe(s)-GeSe₂(s)-L-g. According to [70Kar], the maximum pressure, P_{max} , and maximum temperature, T_{max} , for the three-phase equilibrium GeSe(s)-L-g coincide with coordinates of 945 ± 10 K and 49 ± 5 mmHg, whereas for the GeSe₂(s)-L-g equilibrium, P_{max} and T_{max} had coordinates of 1012 ± 10 K and 60 ± 5 mmHg and 985 ± 10 K and 67 ± 1 mmHg, respectively.

The points that fall outside the line in Fig. 3 do not correspond to the three-phase equilibria, but indicate saturated vapor pressure over the melt. Using an associated ideal-solution model, the P - T - X equilibria in Ge-Se were calculated by [79Zlo] and [84Gla2], with comparable results.

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*Indicates key paper.

#Indicates presence of a phase diagram.

Ge-Se evaluation contributed by A.B. Gokhale and R. Abbaschian, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This program was supported by ASM INTERNATIONAL under grant No. FG 101-1. Literature searched through 1985. Professor Abbaschian is the ASM/NIST Data Program Category Editor for binary germanium alloys.

The Ag-Cr (Silver-Chromium) System

By M. Venkatraman* and J.P. Neumann
University of Wisconsin-Milwaukee

Equilibrium Diagram

The assessed Cr-Ag phase diagram (Fig. 1) is based on the studies of [08Hin], [54Gri], and [67All]. It is characterized by essential immiscibility of Cr and Ag in the liquid and the solid states and by the absence of intermediate phases. The assessed diagram is similar to that given by [Hansen], which was based on [54Gri].

The boundaries of the liquid miscibility gap above the monotectic temperature have not been established. The assessed monotectic temperature, $1450 \pm 50^\circ\text{C}$, is based on thermal analysis measurements by [54Gri]. It is in good agreement with the value of $\sim 1460^\circ\text{C}$ reported earlier by [08Hin]. The purity and the melting points of the Cr metal used by [08Hin] and [54Gri] were $\sim 98\text{ wt.}\%$ and 1550°C and $\sim 99.9\text{ wt.}\%$ and 1800°C , respectively.

The solubility of solid Cr in liquid Ag was measured by [67All] by chemical analysis in the temperature range 960 to 1445°C . The solubility data, which are shown in Fig. 1 and in more detail in Fig. 2, can be represented by:

$$\log(\text{at.}\% \text{Cr}) = 4.27 - 6560 \text{ K}/T \quad (\text{Eq 1})$$

where T is in K. Extrapolation of Eq 1 to the monotectic temperature of 1450°C (1723 K) yields a solubility value of $\sim 3\text{ at.}\% \text{Cr}$ at that temperature. This value is adopted for the phase diagram in Fig. 1. A considerably higher solubility—approximately $15\text{ at.}\% \text{Cr}$ —had been reported by [54Gri]. This high solubility is probably due to the low purity of the Cr used by [54Gri].

Based on diffusion measurements of the radioactive isotope ^{51}Cr in Ag single crystals, [81Neu] determined the solubility of solid Cr in solid (Ag) in the temperature range 700 to 960°C . The data, shown in Fig. 2, can be expressed by:

$$\log(\text{at.}\% \text{Cr}) = 5.24 - 8930 \text{ K}/T \quad (\text{Eq 2})$$

The data point at 976 K (703°C) was excluded in the derivation of Eq 2. Extrapolation of Eq 2 to the eutectic temperature of $\sim 961^\circ\text{C}$ yields for the solubility of Cr(s) in Ag(s) a value of $0.01\text{ at.}\% \text{Cr}$.

The composition ($0.09\text{ at.}\% \text{Cr}$) and the temperature (960.9°C) of the eutectic reaction, shown in Fig. 2, are obtained from the intersection of the liquidus curves for Cr and Ag. The liquidus curve for Cr is given by Eq 1; the liquidus curve for Ag is given by:

$$\log(\text{at.}\% \text{Ag}) = 2.4779 - 590.245 \text{ K}/T \quad (\text{Eq 3})$$

In deriving Eq 3, it is assumed that the liquid exhibits ideal behavior; the enthalpy of melting and the melting temperature of pure Ag are taken as 11.3 kJ/mol [Hultgren,E] and 961.93°C (1235.08 K) [Melt], respectively.

The absence of intermediate phases in the Cr-Ag system was confirmed by the thin-film studies of [78Sim].

Metastable Phases

The formation of a metastable solid solution of Cr in (Ag) beyond the equilibrium concentration was observed by [83Nin], who quenched liquid Ag-rich alloys at cooling rates of 10^5 to 10^6 K/s . The lattice parameter of the metastable solid solution decreases from $a = 0.40861\text{ nm}$ for pure Ag to 0.40853 nm for a solution containing $3\text{ at.}\% \text{Cr}$. The observed metastable solid solubility limit corresponds to the solubility of Cr in liquid Ag at the monotectic temperature.

*Present address: Naval Chemical and Metallurgical Laboratory, Naval Dockyard, Tiger Gate, Bombay, 400023, India.

Table 1 Cr-Ag Crystal Structure and Lattice Parameter Data at 25°C

Phase	Composition, at.% Ag	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameter, nm	Reference
(Cr)	~ 0	$cI2$	$Im\bar{3}m$	A2	W	0.28848	[Massalski]
(Ag)	99.99 to 100	$cF4$	$Fm\bar{3}m$	A1	Cu	0.40861	[King1]