The Ag-O (Silver-Oxygen) System

By I. Karakaya
Middle East Technical University
and
W.T. Thompson
Royal Military College of Canada

Equilibrium Diagram

The partial Ag-O phase diagram at atmospheric pressure (hydrostatic) is presented in Fig. 1. A thermodynamic treatment (discussed below) was used to construct the phase boundaries. The diagram is qualitatively similar to that shown in [Hansen], but the invariant point at 939 °C is 9 degrees higher than that reported by [67Cha]. The slightly higher O solubility in the solid Ag-rich phase reported in this evaluation is based on the work of [62Eic], [64Pod], and [72Ram], emphasizing the first of these.

The liquid phase solubility of O was studied by [09Sie], [10Don], [63Miz], [65Par1], [65Par2], [67Sha], [68Lup], and [70Bou] under atmospheric pressure. The absorption-desorption technique used by [09Sie] was adopted with minor changes by [10Don], [63Miz], [65Par1], [65Par2], [67Sha], and [68Lup]. Modifications were made to avoid the possible reaction of the liquid with silica [65Par1, 67Sha, 68Lup]. Both optical pyrometry [65Par1] and thermocouple techniques [67Sha, 68Lup] were used for temperature measurements. [65Dia] used an electrochemical technique. Figure 1 indicates that the results of [09Sie], [10Don], [65Dia], and [65Par1] show slightly higher O solubility in liquid Ag than do other measurements. The solubility shown in Fig. 1 emphasizes the work of [67Sha], who took special precautions against contamination and who made more precise temperature measurements.

The solubility of O in solid (Ag) was reported by [09Sie] and [62Eic] under standard atmospheric pressure; Fig. 2 shows a comparison. The data of [64Pod] were reported for 450 Torr, but were extrapolated to atmospheric pressure and are included for comparison. A lower solubility with a minimum near 400 °C was reported by [26Ste], but was not confirmed by [62Eic] or [64Pod]. Further, the solubility and diffusivity of O in (Ag), determined from measurements of internal oxidation band widths [64Ver], are in agreement with [62Eic]. Consequently, the assessed solubility is based primarily on the results of [62Eic]. Slightly higher solubilities were reported by electrochemical measurements [72Ram] and an AC impedance spectroscopy technique [86Mog].

The existence of Ag_2O and AgO has been established [58Gra]. The most extensively studied oxide, Ag_2O, dissociates to solid (Ag) and O_2 gas at temperatures above 190 °C under atmospheric pressure [Hansen]. A comprehensive review on the higher silver oxides can be found in [58Gra]. The uncertainties surrounding the existence and properties of these higher oxides has yet to be resolved.

The two-phase region labeled L + G in Fig. 1 applies to oxygen at standard atmospheric pressure. Figure 3 shows isobars corresponding to O_2 pressures of 0.21, 2, and 4 atm. These were calculated from a thermodynamic treatment discussed below. At pressures as high as 530 atm, the (Ag)-Ag_2O-L invariant point was reported at 530 °C, with a liquid phase

Table 1 Ag-O Crystal Structure Data

Phase	Composition, at.% O	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Ag	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu	[King1]
Ag_2O	33.3	*cP*6	$Pn\bar{3}m$	*C*3	Cu_2O	[62Swa]
αO(a)	100	*mC*4	*C*2*m*	...	αO	[King1]

(a) O form is the diatomic gas molecule. Crystal structure is for molecular unit O_2 at −250 °C.

Table 2 Ag-O Lattice Parameter Data

Phase	Composition, at.% O	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
Ag	0	0.40861	...	...	...	[King1]
Ag_2O	33.3	0.47156	...	...	...	[62Pal]
αO	100	0.5403	0.3429	0.5086	β = 132.53°(a)	[King1]

(a) At −250 °C.

composition of 22 at.% O [68Bak]. An earlier study of this system at 414 atm [32All] suggested 507 °C for this invariant temperature. Thermogravimetric measurement of bubble formation by [68Kna], however, suggested a much higher liquidus temperature at high pressures. The invariant point among the (Ag), L, and g phases under atmospheric pressure is at 2.09 at.% O and 939 °C.

Crystal Structures and Lattice Parameters

Crystal structures of Ag, O, and Ag_2O are given in Table 1, and lattice parameters are listed in Table 2. The lattice parameter for Ag_2O given in Table 2 is taken from [62Pal]; similar data were reported by [22Nig], [44Fai], and

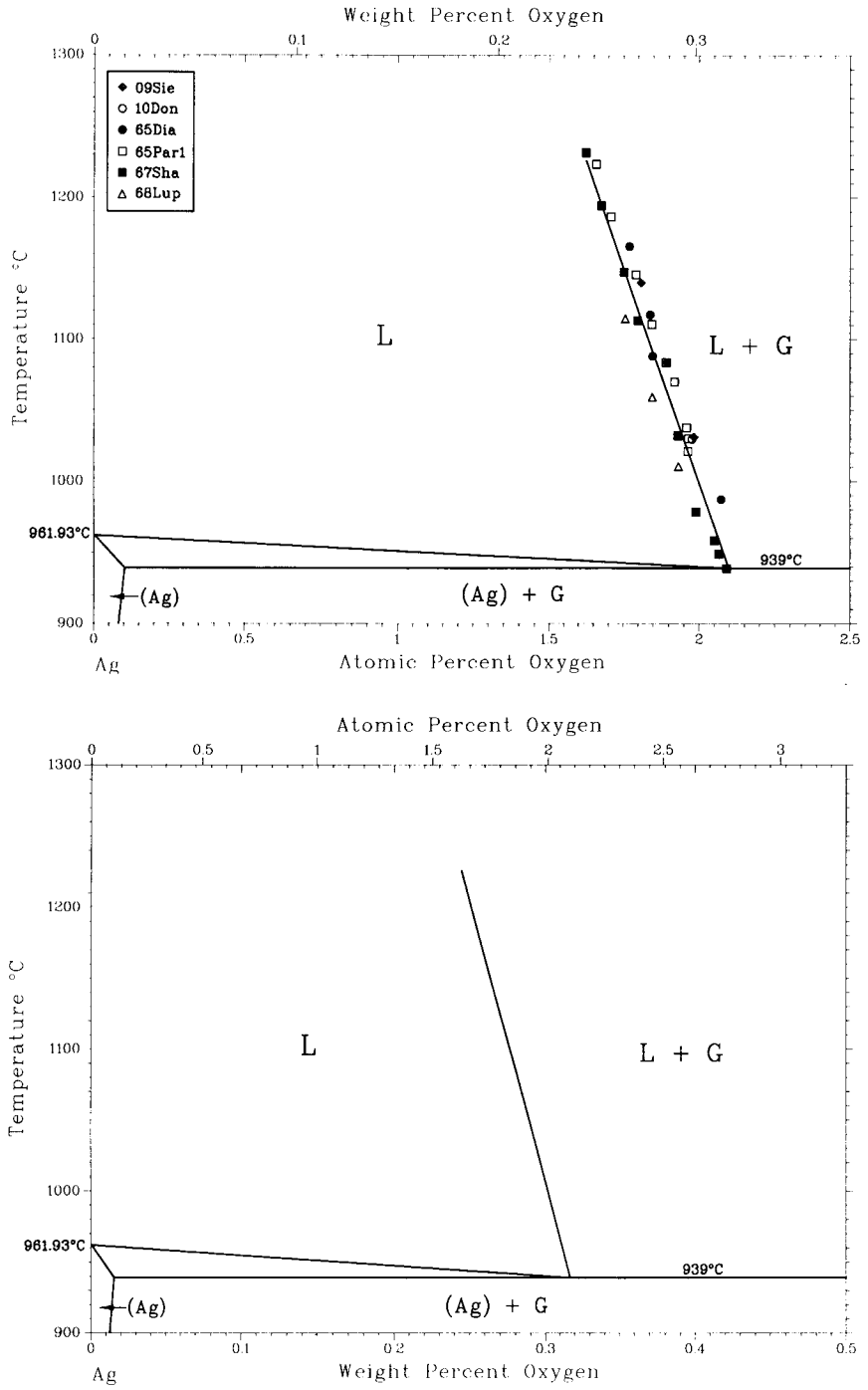

Fig. 1 Assessed Ag-O phase diagram (partial) at 1 atm (1.013 bar).

[62Swa]. A hexagonal, CdI_2-type, high-pressure modification of Ag_2O was reported by [64Kab]. The lattice parameters for this modification are a = 0.3072 and c = 0.4941 nm, respectively. The transformation was reported to occur at 1100 and 1300 °C at pressures of 250 and 125 kbar, respectively.

Crystal structures and lattice parameters of higher silver oxides have not been established conclusively. Proposed structures for these compounds are given in Table 3. Most of the studies indicated a monoclinic structure for AgO, but a tetragonal structure also has been proposed. X-ray and neutron diffraction studies [86Yvo] indicated a tetragonal structure and lattice parameters similar to those found by [63Mck], [70Kaz], and [74Ere] from high-intensity diffraction lines. The remaining lines were indexed on a bct cell with a and c lattice parameters of 0.6933 and 0.9122 nm, respectively [86Yvo]. Limited structural information available on other oxides is provided in Table 3.

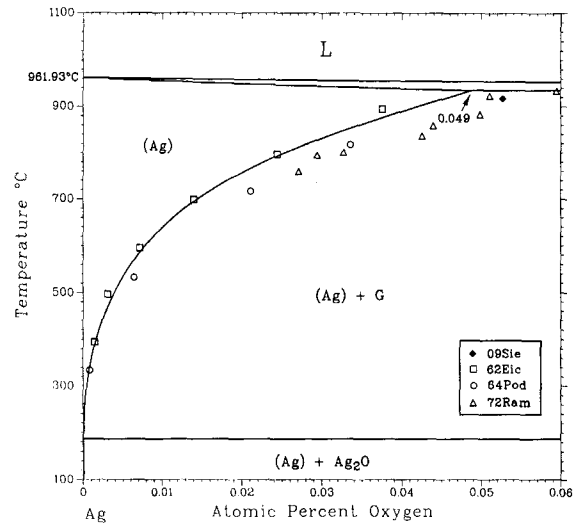

Fig. 2 Solubility of oxygen in solid (Ag).

Thermodynamics

The thermodynamic equilibrium between Ag, Ag_2O, and O_2 is well established. Using the data of [22Key], [32Ben], and [66Ott], the equilibrium O_2 partial pressure as a function of temperature can be expressed by:

$$2\,Ag(s) + 1/2\,O_2(g) \leftrightarrow Ag_2O(s)$$

$$\log_{10}P_{O_2}(atm) = 6.48773 - 2996.83/T$$

This yields a dissociation temperature of 189 °C for Ag_2O at 101.3 kPa O_2 pressure.

Several investigators have examined the thermodynamic behavior of dilute solutions of O in liquid Ag. These include Henrian activity coefficients derived from solubility data [66Bes, 68Bak, 68Lup] and activities of O obtained from electrochemical measurements [65Dia, 81Ots]. There is reasonable agreement among these data. The most recent electrochemical data [81Ots] that yield:

$$1/2\,O_2\,(g, 1\ atm) \leftrightarrow \underline{O}\ (1\ atom\ percent)$$

$$\Delta G^0 = -16\,140 + 6.52\,T \quad J/mol$$

were used in this assessment, where $\underline{O}$ represents O at infinite dilution in Ag. A small composition and temperature dependency to the excess Gibbs energy of liquid Ag-O solution was added to fit the scatter of the L/L + g phase boundary data shown in Fig. 1.

$$G^{ex} = (2300 - 1.2\,T)\,X_{Ag}X_O \quad J/mol$$

Table 3 Crystal Structure Data for Higher Oxides of Ag

Phase	Proposed structure	Lattice parameters, nm a	b	c	Comment	Reference
AgO	Monoclinic	0.579	0.350	0.551	β = 107°27′	[54Mcm]
		0.5852	0.3475	0.5495	β = 107°30′	[58Sca]
		0.5842	0.3480	0.5487	β = 107°27′	[58Gra]
		0.585	0.348	0.550	β = 107°30′	[60Mcm]
		0.5852	0.3478	0.5495	β = 107°30′	[61Sca]
	Tetragonal	0.4816	...	0.4548	...	[63Mck]
		0.483	...	0.4578	...	[70Kaz]
		0.6833	...	0.9122	...	[86Yvo]
	Cubic	0.4816	...	...	...	[59Ste1]
Ag_4O_3	Cubic	0.455	...	...	...	[60Vla]
Ag_3O_4	Monoclinic	0.3582	0.9212	0.5687	β = 106.18°	[86Sta]
Ag_2O_3	fcc	0.990	...	...	...	[35Bra]
	Cubic	0.493	...	...	...	[59Ste2]
	Orthorhombic	1.2874	1.0478	0.3660	...	[85Sta]

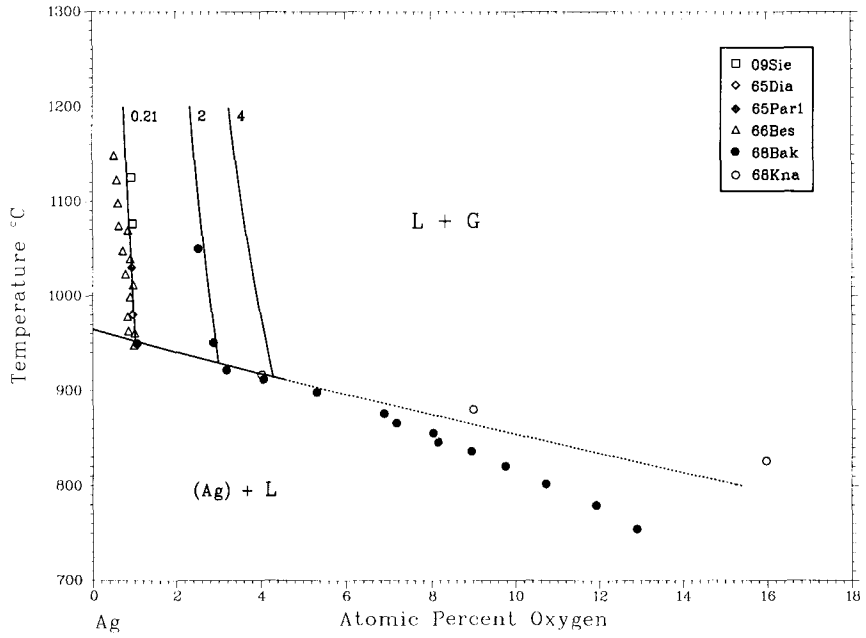

Fig. 3 Effect of pressure on oxygen solubility and the (Ag) liquidus temperature. Horizontal invariant lines (*e.g.*, 952 °C for 0.21 atm) have been omitted for clarity.

Table 4 Ag-O Thermodynamic Data

Standard Gibbs energies with respect to liquid Ag, J/mol

G^0(Ag,L) = 0

G^0(Ag,fcc) = $-266\,500/T - 1218.86 - 90.7247\,T - 0.247 \times 10^{-2}\,T^2 + 13.74\,T \ln T$

G^0(Ag,g) = $281\,525 - 214.495\,T + 12.686\,T \ln T$

Gibbs energy of formation data (from solid Ag and O_2 gas), J/mol of formula unit

$\Delta_f G^0(Ag_2O) = -24\,916 + 53.94\,T$

$\Delta_f G^0(Ag_2O_2) = -24\,686 + 175.73\,T$

This yields the following equation for the solubility of O, X_O, in liquid Ag:

$$8.314\,T(\ln X_O - \ln P_{O_2}^{1/2}) = 16\,140 - 44.807\,T - (2300 - 1.2T)(1 - X_O)^2$$

where $P_{O_2} \leq 5$ atm.

The small solubility of O in solid (Ag) was expressed by

$$-RT \ln (X_O/P_{O_2}^{1/2}) = 49\,000 + 23T$$

where P_{O_2} is the partial pressure in atm and X_O is the atomic fraction of dissolved O in the solid Ag-rich phase.

Other thermodynamic data used in connection with the phase diagram calculations for this system are listed in Table 4. Data on the properties of pure Ag are taken from [87Kar]. The standard Gibbs energy of formation for Ag_2O_2 was taken from [63Wic].

The thermodynamic treatment described in this section was adjusted to generate the Ag-O system at standard atmospheric pressure. An attempt was made to calculate this system at higher pressures. Unfortunately, at about five times higher than atmospheric pressure, deviations between the calculated diagram and the experimental data [68Bak] occurred; the liquidus temperatures appear to be too low above ~0.05 atomic fraction O. Liquidus temperature O reported by [68Kna] for O concentration >0.05 atomic fraction are higher than those calculated (Fig. 3). In view of this gross discrepancy between [68Kna] and [68Bak], the present evaluation is considered reliable for O partial pressure not exceeding 5 atm.

Cited References

09Sie: A. Sieverts and J. Hagenacker, "The Solubility of Hydrogen and Oxygen in Solid and Molten Silver," *Z. Phys. Chem.*, *68*, 115-128 (1909) in German. (Equi Diagram; Experimental)

10Don: F.G. Donnon and T.W.A. Shaw, "The Solubility of Oxygen in Molten Silver," *J. Soc. Chem. Ind.*, *29*, 987-989 (1910). (Equi Diagram; Experimental)

22Key: F.G. Keyes and H. Hara, "The Pressure of Oxygen in Equilibrium with Silver Oxide," *J. Am. Chem. Soc., 54,* 479-485 (1922). (Thermo; Experimental)

22Nig: P. Niggli, "The Crystal Structure of Several Oxides," *Z. Krist., 57,* 253-299 (1922). (Crys Structure; Experimental)

26Ste: E.W.R. Steacie and F.M.G. Johnson, "The Solubility and Rate of Solution of Oxygen in Silver," *Proc. R. Soc. (London) A, 112,* 542-558 (1926). (Equi Diagram; Experimental)

32All: N.P. Allen, "The Effect of Pressure on the Liberation of Gases from Metals (with Special Reference to Silver and Oxygen)," *J. Inst. Met., 49,* 317-340 (1932). (Equi Diagram; Experimental)

32Ben: A.F. Benton and L.C. Drake, "The Dissociation Pressure of Silver Oxide Below 200°," *J. Am. Chem. Soc., 56,* 2186-2194 (1932). (Thermo; Experimental)

35Bra: H. Braekken, "Crystal Structure of Silver Peroxide, Ag_2O_3," *Kgl. Norsk. Videnskab. Selskavs. Forh., 7,* 143-146 (1935). (Crys Structure; Experimental)

44Fai: R. Faivre, "Solid Solutions Formed During Dissociation of Ag_2O," *Ann. Chim. (Paris), 19,* 59-101 (1944) in French. (Crys Structure; Experimental)

54Mcm: J.A. McMillan, "The Crystalline Structure of AgO," *Acta Crystallogr., 7,* 640 (1954). (Crys Structure; Experimental)

58Gra: W.S. Graff and H.H. Stadelmaier, "Higher Oxides of Silver," *J. Electrochem. Soc., 105,* 446-449 (1958). (Equi Diagram, Crys Structure; Experimental)

58Sca: V. Scatturin, P. Bellon, and R. Zannetti, "Crystal Structure of Silver(II)-Oxide," *Collect. Czech. Chem. Commun., 24,* 1416-1419 (1958) in German. (Crys Structure; Experimental)

59Ste1: B. Stehlik, P. Weidenthaler, and J. Vlach, "Crystal Structure of Silver(II)-Oxide," *Collect. Czech. Chem. Commun., 24,* 1416-1419 (1959) in German. (Crys Structure; Experimental)

59Ste2: B. Stehlik, P. Weidenthaler, and J. Vlach, "Crystal Structure of Silver(III)-Oxide," *Collect. Czech. Chem. Commun., 24,* 1581-1588 (1959) in German. (Crys Structure; Experimental)

60Mcm: J.A. McMillan, "Magnetic Properties and Crystalline Structure of AgO," *J. Inorg. Nucl. Chem., 13,* 28-31 (1960). (Crys Structure; Experimental)

60Vla: J. Vlach and B. Stehlik, "X-Ray Studies of the Transformations of Silver Oxides," *Collect. Czech. Chem. Commun., 25,* 676-681 (1960) in German. (Crys Structure; Experimental)

61Sca: V. Scatturin, P.L. Bellon, and A.J. Salkind, "The Structure of Silver Oxide Determined by Means of Neutron Diffraction," *J. Electrochem. Soc., 108,* 819-822 (1961). (Crys Structure; Experimental)

***62Eic:** W. Eichenauer and G. Muller, "Diffusion and Solubility of Oxygen in Silver," *Z. Metallkd., 53,* 321-324 and 700 (correction) (1962) in German. (Equi Diagram; Experimental)

62Pal: T. Palagyi and I. Naray-Szabo, "On the Oxides of Silver," *Acta Chim. Hung., 30,* 1-9 (1962) in German. (Crys Structure; Experimental)

62Swa: H.E. Swanson, "Standard X-Ray Diffraction Powder Patterns," Natl. Bur. Stand. Monograph 25, Section 1, 45 (1962). (Crys Structure; Compilation)

63Mck: A.S. McKie and D. Clark, Proc. 3rd Int. Symp. Batteries, D.H. Collins, Ed., Pergamon Press, New York, 285-295 (1963). (Crys Structure; Experimental)

63Miz: E.A. Mizikar, R.E. Grace, and N.A. Parlee, "Diffusion of Oxygen in Liquid Silver," *Trans. ASM, 56,* 101-106 (1963). (Equi Diagram; Experimental)

63Wic: C.E. Wicks and F.E. Block, "Thermodynamic Properties of 65 Elements—Their Oxides, Halides, Carbides and Nitrides," Bur. Mines Bull. 605 (1963). (Thermo; Compilation)

64Kab: S.S. Kabalkina, S.V. Popova, N.R. Serebryanaya, and L.F. Vereshchagin, "New Ag_2O Modification with Layer Structure," *Sov. Phys. Dokl., 8,* 972-974 (1964). (Crys Structure; Experimental)

64Pod: H.H. Podgurski and F.N. Davis, "The Solubility of Oxygen in Silver and the Thermodynamics of the Internal Oxidation of a Silver-Copper Alloy," *Trans. Metall. Soc. AIME, 230,* 731-735 (1964). (Equi Diagram; Experimental)

64Ver: J.E. Verfurth and R.A. Rapp, "The Solubility and Diffusivity of Oxygen in Silver and Copper from Internal-Oxidation Measurements," *Trans. Metall. Soc. AIME, 230,* 1310-1313 (1964). (Equi Diagram; Experimental)

65Dia: C. Diaz, C.R. Masson, and F.D. Richardson, "Electrochemical Determination of Oxygen in Liquid Silver," *Trans. Inst. Min. Metall. C, 75,* 183-185 (1965). (Equi Diagram, Thermo; Experimental)

65Par1: N.A.D. Parlee and E.M. Sacris, "The Solubility of Oxygen in Liquid Silver," *Trans. Metall. Soc. AIME, 233,* 1918-1919 (1965). (Equi Diagram; Experimental)

65Par2: N.A.D. Parlee and H. Seibel, "Effect of Cell Geometry and Oxygen Pressure on the Diffusion of Oxygen in Liquid Silver," *Trans. Metall. Soc. AIME, 233,* 1923-1924 (1965). (Equi Diagram; Experimental)

66Bes: J. Besson, C. Deportes, R. Schmitt, and G. D'Anger, "Study of the Kinetics of Absorption of Oxygen by Liquid Silver in Air," *Bull. Soc. Chim. Fr.,* 3394-3398 (1966) in French. (Equi Diagram, Thermo; Experimental)

66Ott: E.M. Otto, "Equilibrium Pressure of Oxygen over Ag_2O-Ag at Various Temperatures," J. Electrochem. Soc., *113,* 643-645 (1966). (Thermo; Experimental)

67Cha: J.C. Chaston, "Oxygen in Silver," *Silver—Economics, Metallurgy and Use,* A. Butts and C.D. Coxe, Ed., Van Nostrand, New York (1967). (Equi Diagram; Compilation; #)

67Sha: I.D. Shah and N.A.D. Parlee, "The Diffusivity of Oxygen in Liquid Silver," *Trans. Metall. Soc. AIME, 239,* 763-764 (1967). (Equi Diagram; Experimental)

68Bak: E.H. Baker and M.I. Talukdar, "Silver-Oxygen System in the Pressure Range 0.25-750 atm and Some Measurements on Silver-Nitrogen and Gold-Oxygen Equilibria," *Trans. Inst. Min. Metall. C, 79,* 128-133 (1968). (Equi Diagram, Thermo; Experimental)

68Kna: O. Knacke and M. Meixner, "Bubble Formation in Solidifying Silver," *Z. Metallkd., 59,* 114-117 (1968) in German. (Equi Diagram, Thermo; Experimental)

68Lup: C.H.P. Lupis and J.F. Elliott, "Oxygen-Alloying Element Interaction in Liquid Silver," *Trans. Metall. Soc. AIME, 242,* 929-935 (1968). (Equi Diagram, Thermo; Experimental)

70Bou: R. Boulet, H. Pham, and M. Rolin, "Thermogravimetric Study of Oxygen Solubility in Molten Silver," *Bull. Soc. Chim. Fr.,* (4), 1306-1310 (1970) in French. (Equi Diagram; Experimental)

70Kaz: H.Z. Kazakevich, V.A. Kirkinskii, and I.E. Yablokova, "Behavior of Silver in Alkali During Anodic Polarization by Asymmetric Current," *Sov. Electrochem., 6,* 355-359 (1970). (Crys Structure; Experimental)

72Ram: T.A. Ramanarayanan and R.A. Rapp, "The Diffusivity and Solubility of Oxygen in Liquid Tin and Solid Silver and the Diffusivity of Oxygen in Solid Nickel," *Metall. Trans., 3,* 3239-3246 (1972). (Equi Diagram; Experimental)

74Ere: G.P. Ereiskaya, T.A. Losovskaya, V.I. Goncharov, N.P. Gaivoronskaya, and F.I. Kukoz, "Structure of Products of the Anodic Disintegration of Silver in a Potassium Hydroxide Solu-

tion by Large Currents," *Sov. Electrochem.*, *40*, 1236 (1974). (Crys Structure; Experimental)

81Ots: S. Otsuka and Z. Kozuka, "Activities of Oxygen in Liquid Copper and Silver from Electrochemical Measurements," *Metall. Trans. B*, *12*, 501-507 (1981). (Thermo; Experimental)

85Sta: B. Standke and M. Jansen, "Ag_2O_3, A Novel Binary Silver Oxide," *Angew. Chem. Int. Ed. Engl.*, *24*, 118-119 (1985). (Crys Structure; Experimental)

86Mog: F.K. Moghadam and D.A. Stephenson, "Oxygen Diffusivity and Solubility Studies in Ag and Pt Using AC Impedance Spectroscopy," *J. Electrochem. Soc.*, *133*, 1329-1332 (1986). (Equi Diagram; Experimental)

86Sta: B. Strandke and M. Jansen, "Ag_3O_4, The First Silver(II,III) Oxide," *Angew. Chem. Int. Ed. Engl.*, *25*, 77-78 (1986). (Crys Structure; Experimental)

86Yvo: K. Yvon, A. Bezinge, P. Tissot, and P. Fischer, "Structure and Magnetic Properties of Tetragonal Silver (I,III) Oxide, AgO," *J. Solid State Chem.*, *65*, 225-230 (1986). (Crys Structure; Experimental)

87Kar: I. Karakaya and W.T. Thompson, "The Ag-Pb (Silver-Lead) System," *Bull. Alloy Phase Diagrams*, *8*(4), 326-334 (1987). (Thermo; Compilation)

*Indicates key paper.

#Indicates presence of a phase diagram.

Ag-O evaluation contributed by **I. Karakaya,** Department of Metallurgical Engineering, Middle East Technical University, Ankara, Turkey, 06351, and **W.T. Thompson,** Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario, K7K 5L0. This work was supported by a grant from ASM International. Literature searched through 1988. Dr. Thompson is the Alloy Phase Diagram Program Co-Category Editor for binary silver alloys.