JPEDAV (2006) 27:92-101
DOI: 10.1361/105497106X92862
1547-7037/$19.00 ©ASM International

Effect of Pd Additions on the Invariant Reactions in the Ag-CuO$_x$ System

Jens T. Darsell and K. Scott Weil

(Submitted December 13, 2004; in revised form November 11, 2005)

Palladium was added as a ternary component to a series of copper oxide-silver alloys in an effort to increase the use temperature of these materials for potential ceramic brazing applications. Phase equilibria at low palladium and copper oxide concentrations in the Pd-CuO$_x$-Ag system were determined experimentally using differential scanning calorimetry, microstructural analysis, and x-ray diffraction. Small additions of palladium were generally found to increase the temperature of the eutectic reaction present in the pseudobinary system but have little effect on a higher temperature monotectic reaction. However once enough palladium was added (~5 mol%) to increase the new eutectic temperature to that of the original pseudobinary monotectic reaction, the pseudoternary monotectic temperature correspondingly began to move upward as well. The addition of palladium also forced the eutectic point to slightly lower silver concentrations, again causing a convergence with the former monotectic line.

Keywords eutectic composition, eutectic temperature, palladium-silver-copper oxide pseudoternary system

1. Introduction

Over the past couple of years, several groups have independently developed a new method of ceramic-ceramic and ceramic-metal brazing [2000Sch, 2002Ers, 2003Har]. Referred to as air brazing, the technique can be used to form a predominantly metallic joint directly in air without the need of an inert cover gas or the use of surface reactive fluxes. The resulting bond is hermetic, offers excellent room temperature strength, and is inherently resistant to oxidation at high temperatures [2005Kim, 2005Wei]. The key to developing a successful filler metal composition for air brazing is to identify a metal oxide wetting agent that is mutually soluble in a molten noble metal solvent. One particular oxide-metal combination that appears readily suited for this purpose is CuO$_x$-Ag, a system originally of interest in the development of silver clad cuprate-based superconductors. Results from equilibrium phase studies performed by Suzuki et al. [1995Suz] indicate that there are two invariant points in the pseudobinary CuO$_x$-Ag phase diagram around which new braze compositions could be developed: a monotectic reaction at 969 ± 1 °C, where CuO and a Ag-rich liquid L$_1$ coexist with a second CuO$_x$-rich liquid phase L$_2$ at a composition of $x_{Ag}/(x_{Ag} + x_{Cu}) = 0.36 \pm 0.03$ Ag and a eutectic reaction at 942 ± 1 °C, where CuO and Ag coexist with L$_1$ at a composition of $x_{Ag}/(x_{Ag} + x_{Cu}) = 0.99 \pm 0.005$.

In a series of sessile drop experiments conducted under inert atmosphere, Meier et al. demonstrated that the addition of copper oxide to molten silver greatly reduces the contact angle formed between this liquid and a solid alumina substrate [1995Mei]. The improvement in wetting was speculated to result from an increase in the oxygen activity of the melt and the formation of an interfacial compound, $CuAlO_2$. Schüler et al. [2000Sch] were the first to recognize that the CuO$_x$-Ag system could be exploited to bond ceramics directly in air and demonstrated this by joining blocks of alumina with a 1 mol% CuO-Ag braze composition. More recently, our group has been investigating the use of CuO$_x$-Ag based air brazes as a means of hermetically sealing solid-state electrochemical devices such as solid oxide fuel cells and gas concentrators [2005Wei].

Because the high-temperature application of the CuO$_x$-Ag brazes is ultimately limited by the eutectic transformation present in this system, the authors sought to extend the use temperature by adding a higher melting point noble metal element; in this case palladium. It was previously observed that the addition of palladium to the Cu-O-Ag system increases both the liquidus and solidus temperatures [2004Dar and 2004Har] but have not attempted a more detail study of this phenomenon until now. In the study described below, the authors examine the effect of small compositional deviations (i.e., minor palladium additions) on the formation of equilibrium solid and liquid phases in the pseudobinary CuO$_x$-Ag system.

2. Experimental

The alloy compositions investigated in this study were prepared by ball-milling the appropriate ratios of constituent metal powders, silver (99.9%, 0.75 μm average particle size, Alpha Aesar Company, Ward Hill, MA), copper (99%, 1.25 μm average particle size, Alpha Aesar Company), and palladium (99.9+%, submicron average particles size,

---

This paper was presented at the International Symposium on User Aspects of Phase Diagrams, Materials Solutions Conference and Exposition, Columbia, Ohio, 18-20 October, 2004.

Jens T. Darsell, Washington State University, PO Box 642920, Pullman, WA 99164-2920; and **K. Scott Weil,** Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352. Contact e-mail: Scott.Weil.pnl.gov.

Aldrich Chemical Company, Milwaukee, WI), in high purity ethanol (99.95%, Aldrich Chemical Company; using an approximate 1:10 volumetric ratio of powder to solvent) for 2 h. As will be described, the copper was allowed to oxidize in situ as part of the specimen preparation. The samples used in the differential scanning calorimetry (DSC) experiments measured 2 mm in diameter and were fabricated by cold pressing 5-10 mg of a given powder mixture in a small pellet die. Samples used in a subsequent series of isothermal soak and quench experiments were also prepared by uniaxial cold pressing, in this case, as 4 mm diameter pellets that each weighed approximately 200 mg.

The subdense pellets were homogenized with respect to composition by annealing in reducing gas (Ar/4mol% H_2) at 700 °C for 12 h x-ray diffraction (XRD; Philips, XRG3100, Mahwah, NJ) and microstructural analysis, via scanning electron microscopy (SEM; Jeol, JSM-5900 LV, Tokyo, Japan) and energy dispersive x-ray spectrometry (EDS; EDAX Inc., Mahwah, NJ), conducted on randomly selected specimens after this initial heat treatment step confirmed that the materials were single phase face-centered cubic (fcc) Ag-Cu-Pd alloys. The resulting compacts, which still contained substantial interconnect porosity (>30 vol%), were subsequently oxidized in situ during the air heating processes used in the respective DSC and quenching experiments. A comparison was made between samples that were preoxidized by heating in air at 900 °C for 4 h and those that were allowed to oxidize in situ during testing. DSC measurements indicated no difference in the recorded thermograms, and microstructural analysis showed no substantial difference in composition or phase formation. Other alternative sample preparation routes, yielded identical results but tended to lead to more coarse, less homogeneous microstructures within the specimens; these included the formation of homogeneously melted alloy buttons subsequently oxidized in an air treatment step or the ball-milling of silver and palladium powders with CuO, in place of copper, prior to forming the pellet specimens. Thus, the initial fabrication procedure was adopted for use in preparing all of the specimens used in this study.

Thermal analysis was conducted from room temperature to 1030 °C using a combined DSC/thermogravimetric analysis system (DSC/TGA; Netzsch, STA 449C Jupiter, Burlington, MA) equipped with a high-temperature furnace and a Type-S sample carrier. The alumina crucibles used in these experiments were 99.8% alumina with less than 0.1% Na_2O, 0.07% SiO_2, 0.05% CaO, and 0.04% Fe_2O_3. Prior to use, the crucibles were preheated to 1550 °C in static air to ensure thermal stability and to burn off any extraneous organic contamination. The DSC experiments were generally performed at a heating rate of 10 °C/min in dry flowing air (10 ml/min). Preliminary experiments conducted at slower heating rates, 5 and 2 °C/min, showed little difference in onset temperature for specific phase changes, but the peaks in these traces tended to be much smaller and more difficult to identify relative to background noise using the corresponding dE/dT curves. However, for several of the compositions, conducting the thermal measurements at the faster rate led to a suspicious amount of broadening in a given endotherm. Often when rerun at 2 °C/min, the single peak would reproducibly resolve into several distinct endotherms, which were ultimately the ones used in our analysis. A minimum of three heating and cooling curves were recorded for each sample to ensure good reproducibility. A number of the samples were found to undercool and thus only the heating curves were used to derive our data. The Pt/Pt-10%Rh thermocouples in the DSC instrument were calibrated using indium, tin, CsCl, and gold standards. Verification of our experimental procedure was conducted using a series of homogenized Pd-Ag alloy pellets fabricated by the powder-based technique described above. Measurements of the solidus and liquidus temperatures as a function of alloy composition from 0-50 mol% Pd in Ag differed by less than 1% with the previously calculated phase boundaries [1988Kar] for this binary system.

A series of quenching experiments were conducted to investigate the equilibrium phases originally present at temperatures above the liquidus as a function of composition and isothermal temperature. The 4 mm diameter samples used in this study were homogenized under reducing conditions in the same manner as the DSC samples, then placed on an alumina plate and heated in static air at 3 °C/min to the temperature of interest, where they were isothermally held for 15 min before quenching in a room temperature water bath. Subsequently, the samples were sectioned and mounted for SEM, EDS, and XRD analyses. Commercial Ag, Cu, NiO, and Pd standards were used in the EDS measurements.

3. Results and Discussion

Prior to discussion the experimental details and results found in this study, phase equilibria in the relevant consitutent binary and ternary systems are reviewed below. Because the experiments undertaken in the present work were conducted in ambient air ($p = 0.21$ atm), the primary focus is discussing the equilibrium phases formed under this condition. Information pertaining to invariant transformations in these systems in ambient air is summarized in Table 1.

3.1 Binary Cu-O, Pd-O, Ag-O, and Ag-Pd Systems

In the Cu-O system, two compound oxides exist, Cu_2O (κ; Cu:O = 67:33) and CuO (τ; Cu:O = 50:50) [1989Cha]. Cu_4O_3 (π; Cu:O = 57:43) has also been shown to exist [1978Oke], although the region of stability of this compound cannot be defined because its thermodynamic properties are not known [1989Cha]. In air at ambient temperature and pressure ($T \sim 25$ °C and $p \sim 0.21$ atm), the equilibrium phase is CuO, which decomposes to Cu_2O when heated to 1027 °C [1994Hal]. Upon further heating in air, Cu_2O melts to form a liquid and excess oxygen at 1124 °C [1994Hal]. Under a controlled partial pressure of oxygen less than ambient, copper displays a eutectic reaction with Cu_2O at 1067 °C and a monotectic reaction at 1223 °C, which lead to a liquid miscibility gap at higher temperatures [1994Hal].

Pd and PdO are the only solid phases that exist in the Pd-O system. Under ambient conditions, PdO is the thermodynamically stable phase, although in practice metallic

Table 1 Phase equilibria in the consitutent binary and ternary systems for Pd-Cu-O-Ag at PO_2 = 0.21 bar

System	Reaction	Temperature, °C	Compositions	Reference
Ag-O	$Ag_2O \rightarrow 2Ag + 0.5O_2$	147	…	… 1997Ass
	$Ag + O_2 \rightarrow L$	951	liquid $x_o = 0.00981$	1997Ass
Cu-O	$2CuO \rightarrow Cu_2O + 0.5O_2$	1027	…	1994Hal
	$Cu_2O \rightarrow L + O_2$	1124	$x_o = 0.377$	1994Hal
Pd-O	$PdO \rightarrow Pd + 0.5O_2$	798	…	1999Lyu, 2002Zha
	$Pd + O_2 \rightarrow L$	1550	N/A	1988Kar
Ag-Cu-O	$CuO + Ag \rightarrow L_1$	942	CuO:pure CuO Ag:$X_{Ag}/(X_{Cu} + X_{Ag}) = 1.00$ L_1:$X_{Ag}/(X_{Cu} + X_{Ag}) = 0.99 \pm 0.005$	1995Suz, 1998Nis
	$CuO + L_1 \rightarrow L_2$	969	CuO:pure CuO L_1:$X_{Ag}/(X_{Cu} + X_{Ag}) = 0.98 \pm 0.005$ L_2:$X_{Ag}/(X_{Cu} + X_{Ag}) = 0.36 \pm 0.03$	1995Suz, 1998Nis
	$CuO + L_2 \rightarrow Cu_2O$	1029	CuO:pure CuO Cu_2O:$X_{Ag}/(X_{Cu} + X_{Ag}) = 0.03\text{-}0.14$ L_2:$X_{Ag}/(X_{Cu} + X_{Ag}) = 0.10 \pm 0.03$	1995Suz, 1998Nis

Table 2 Results of the DSC experiments on the Pd-CuO_x-Ag system

		Onset temperature, °C			
$\frac{x_{Pd}}{x_{Pd}+x_{Ag}+x_{Cu}}$	$\frac{x_{Ag}}{x_{Ag}+x_{Cu}}$	Endothermic peak 1	Endothermic peak 2	Endothermic peak 3	Endothermic peak 4
0	1.000	950	…	…	…
0	0.990	942	949	…	…
0	0.986	941	…	…	…
0	0.980	942	966	…	…
0	0.960	943	966	…	…
0	0.900	943	967	…	…
0.010	1.000	959	968	…	…
0.010	0.995	946	953	964	…
0.010	0.990	947	949	960	…
0.010	0.986	946	950	957	…
0.010	0.980	948	951	…	…
0.010	0.960	947	952	968	970
0.010	0.920	948	952	967	973
0.020	1.000	967	979	…	…
0.020	0.995	950	957	972	…
0.020	0.990	951	969	…	…
0.020	0.986	952	959	967	…
0.020	0.980	952	959	…	…
0.020	0.960	951	957	969	971
0.020	0.920	952	959	967	974
0.050	1.000	982	1006	…	…
0.050	0.995	967	1002	…	…
0.050	0.990	965	1001	…	…
0.050	0.986	967	976	998	…
0.050	0.980	969	980	982	…
0.050	0.960	969	974	982	985
0.050	0.920	970	975	983	987

Pd is generally observed due to kinetic limitations in forming the oxide. When heated in air, pure PdO decomposes to form metallic Pd at 798 °C [1999Lyu, 2002Zha]. With further heating, palladium melts at 1550 °C [1988Kar]. Earlier work by Raub and Plate [1957Rau] and Krier and Jaffee [1963Kri] demonstrated a direct temperature dependence of oxygen solubility in solid palladium, but due to data scatter possibly caused by chemisorption, quantitative values for this and for the solubility of oxygen in liquid palladium are not well established.

Like palladium, metallic Ag is metastable in air at room temperature. The equilibrium phase is Ag_2O (Ag:O = 67: 33), which decomposes in air at 147 °C to form metallic Ag and oxygen gas [1997Ass]. The high solubility of oxygen in both solid and molten silver has been well studied [1909Sie, 1962Eic, 1992Kar, 1997Ass]. An invariant reaction between silver and oxygen occurs at 939 °C, forming a liquid containing 2.1 at.% oxygen in silver [1992Kar]. Under inert gas, metallic silver melts at 961 °C and in air at 951 °C [1932All]. Other silver oxide compounds such as AgO and Ag_3O_4 exist under higher partial pressures of oxygen and low temperatures [1958Gra, 1990Fis].

The equilibrium phases present in the binary Ag-Pd system are a liquid, fcc solid solution (α), and vapor [1906Rue]. The system shows complete miscibility at all compositions, although it deviates in a negative manner from the ideal solution model. A phase diagram for the binary Ag-Pd system was calculated by Karakaya and Thompson [1988Kar] and found to match the liquidus and solidus values previously determined experimentally by Ruer [1906Rue]. Evidence of two possible intermetallic phases in this system appears to be inconclusive [1988Kar].

3.2 Ternary Cu-O-Ag, Cu-O-Pd, and Ag-O-Pd Systems

A ternary Cu-O-Ag isothermal section [1230 °C] was originally constructed by Chang and Hsieh [1989Cha] based on the prior work of Leroux and Fröhlich [1931Ler] and Kohlmeyer and Sprenger [1948Koh]. Subsequent thermal analysis performed independently by Shao et al. [1993Sha] and Suzuki et al. [1995Suz, 1998Nis] demonstrated that the pseudobinary CuO_x-Ag system contains both a eutectic and a monotectic reaction joined by a liquid phase miscibility gap. The two data sets differ slightly, although the more recent investigations consider the effects of low subambient oxygen pressure on the various invariant equilibria in the system and are more thorough with respect to the copper oxide-rich end of the phase diagram. For these reasons, the authors refer to the data reported in the latter study [1998Nis]. The reported eutectic reaction occurs at 942 ± 1 °C, where CuO and Ag coexist with the Ag-rich liquid phase L_1 at a concentration of $x_{Ag}/(x_{Cu} + x_{Ag}) = 0.99 \pm 0.005$, and the monotectic reaction occurs at 969 ± 1 °C, where CuO_x and L_1 coexist with a second CuO_x-rich liquid phase L_2 at a composition of $x_{Ag}/(x_{Cu} + x_{Ag}) = 0.36 \pm 0.03$. At the monotectic temperature, the miscibility gap extends from the monotectic point to a concentration of $x_{Ag}/(x_{Cu} + x_{Ag}) = 0.98 \pm 0.005$. Below the monotectic temperature, the copper oxide was found to exist as CuO, whereas above this temperature both CuO and Cu_2O formed. Neither in this work nor in later theoretical studies of the Cu-O-Ag system [1998Ass, 2003Hal] were intermediate compounds found nor subsequently considered to form between CuO_x and Ag.

Two isothermal sections of the Cu-O-Pd system at 900 and 1000 °C were reported by Schmahl and Minzl [1965Sch]. At $p \sim 0.2$ atm, both sections indicate that at Pd-rich compositions [$x_{Pd}/(x_{Cu} + x_{Pd}) > 0.96$ at 900 °C and > 0.86 at 1000 °C], the equilibrium phase is a fcc-structured metallic alloy, whereas at Cu-rich compositions [$x_{Pd}/(x_{Cu} + x_{Pd}) < 0.51$ at 900 °C and < 0.24 at 1000 °C], a substituted copper-palladium oxide with the PdO crystal structure is the only phase present. In between, a two phase oxide-metal region exists. No ternary compounds were found in this system [1965Sch, 1989Cha].

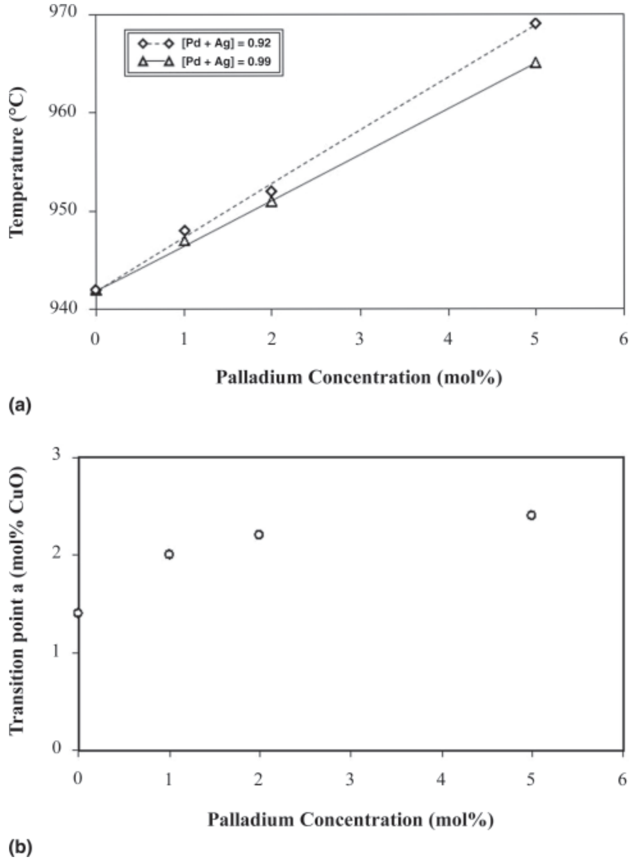

Fig. 1 (a) Liquidus temperature as a function of palladium concentration for several Pd-CuO_x-Ag compositions of constant noble metal content. (b) Plot of the α transition point as a function of palladium content for Pd-CuO_x-Ag, where α corresponds to the invariant eutectic composition for the binary system, i.e., $L_1 \rightarrow \alpha + CuO$, and to the $L_1 \rightarrow L_1 + \alpha + CuO$ transition for the ternary system. The compositions reported for palladium concentrations of 2% and 5% are extrapolated values.

Prior work on Ag-O-Pd has demonstrated that the addition of silver to palladium lowers the temperature at which the resulting alloy begins to oxidize upon cooling [1963Hof, 1985Col, 1986Mah]. Pepin determined that in high Pd-content alloys, PdO forms readily in air, and at higher temperatures, reduces to metallic form over a narrow temperature range [1988Pep]. With higher concentrations of silver in the initial alloy, less PdO forms and its reduction to metallic Pd takes place over a larger temperature range, with the onset occurring at lower temperatures. Wang and Huebner found that this phenomenon is directly related to the nonlinear change in the thermodynamic activity of palladium in Ag-Pd solid solutions as a function of silver concentration [1991Wan].

3.3 Thermal Analysis

Reported in Table 2 are the results of the DSC studies conducted on the 27 sample compositions. Listed for each

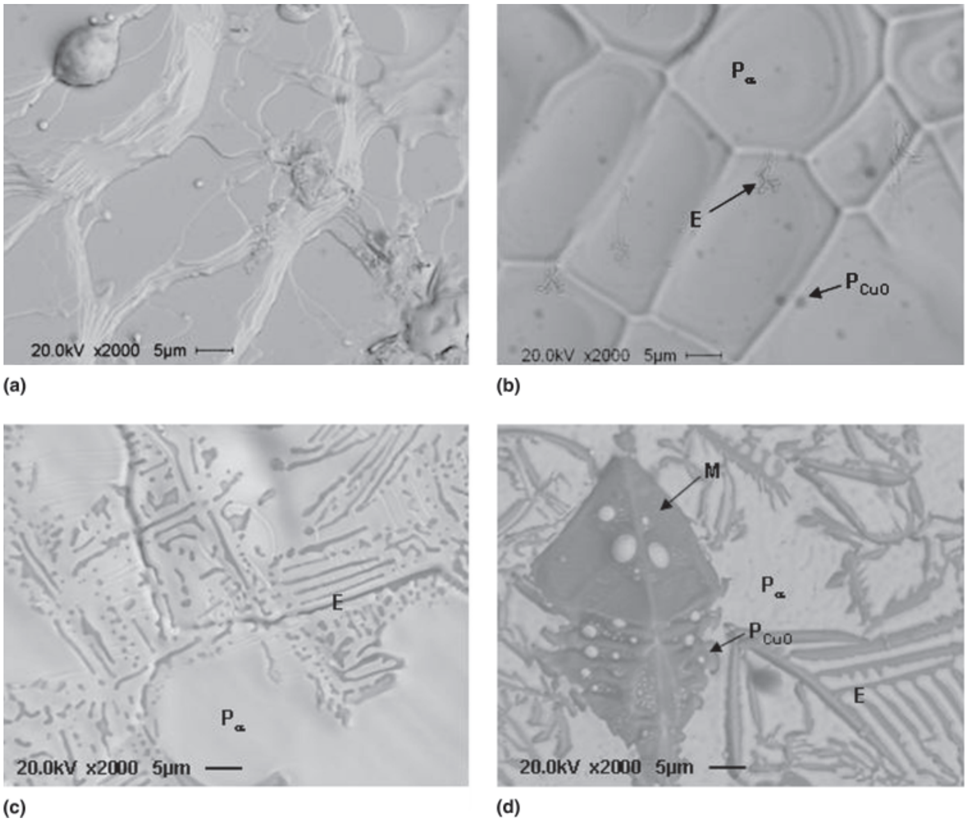

Fig. 2 SEM micrographs of specimens containing $x_{Pd}/(x_{Cu} + x_{Ag} + x_{Pd}) = 0.01$ that were heated to 980 °C, held for 15 min, and quenched to room temperature. These samples contain the following noble metal concentrations, $(x_{Ag})/(x_{Ag} + x_{Cu})$: (a) 1.000, (b) 0.995, (c) 0.986, and (d) 0.96. E = eutectic-type α + CuO, M = monotectic-type CuO_x, P_{CuO} = primary CuO_x, and P_α = primary α.

are the corresponding temperatures at which a given endotherm could be repeatably identified. In the case of the pseudobinary CuO_x-Ag compositions, i.e., no palladium added, the results correlate quite well with the previously discussed studies of this system. The data obtained in the present investigation indicates that the pseudobinary eutectic temperature is 942 ± 2 °C and the monotectic is 967 ± 2 °C, which match those reported by Nishura et al. [1998Nis] within experimental error. A single sharp endotherm is observed at the eutectic temperature for $x_{Ag}/(x_{Cu} + x_{Ag}) = 0.986$, suggesting that this is the invariant composition at which solid CuO and silver form a single silver-rich liquid, L_1. This finding yields a better match with the results of Shao et al. [1993Sha] than of Nishura et al. [1998Nis], who reported this invariant at a silver concentration of 0.99 ± 0.005.

Within each series of palladium-alloyed compositions, i.e., 1%Pd, 2%Pd, and 5%Pd, the emergence of two three-phase fields is apparent as endotherms corresponding to the original Ag-CuO eutectic and monotectic reactions split. Figure 1(a) shows the effect of increasing palladium content on the original monotectic temperature, which forms a liquidus boundary in the ternary system, for several silver concentrations, i.e., $(x_{Ag})/(x_{Ag} + x_{Cu})$. The liquidus boundary, either $CuO + \alpha \rightarrow CuO + L_1$ or $CuO + \alpha \rightarrow CuO + \alpha + L_1$, respectively, for the binary and ternary systems, shifts to steadily higher temperatures as palladium is added. Similarly the addition of palladium modifies the original eutectic composition as well, causing it to drift to higher CuO_x content with increasing amounts of palladium. This transition point, which corresponds the $CuO + \alpha \rightarrow L_1$ and $CuO + \alpha + L_1 \rightarrow + L_1$ transitions respectively for the binary and ternary systems, is identified as *a* and is plotted as a function of palladium concentration in Fig. 1(b). Trends in the non-invariant endotherms in Table 2 can also be recognized for any given series of compositions. For example, those associated with the liquidus boundary on the silver-rich side of the original eutectic composition (*E*), or *a* for the ternary compositions, occur at increasingly higher temperatures as the palladium content increases.

3.4 Quenching Studies

Phase equilibria at high temperature were evaluated by microstructural and crystallographic observation of quenched specimens, examples of which are shown in Fig. 2 and 3. The backscattered SEM micrographs in Fig. 2(a)-(d) are for a series of samples containing $x_{Pd}/(x_{Cu} + x_{Ag} + x_{Pd}) = 0.01$ that were heated to 980 °C (which according to the data in Table 2 is above both the original pseudobinary eutectic and monotectic temperatures), held for 15 min, and quenched to room temperature. In the specimen that contained no copper oxide, shown in Fig. 2(a), EDS and XRD analyses confirm that only single phase α (Ag-Pd alloy, fcc)

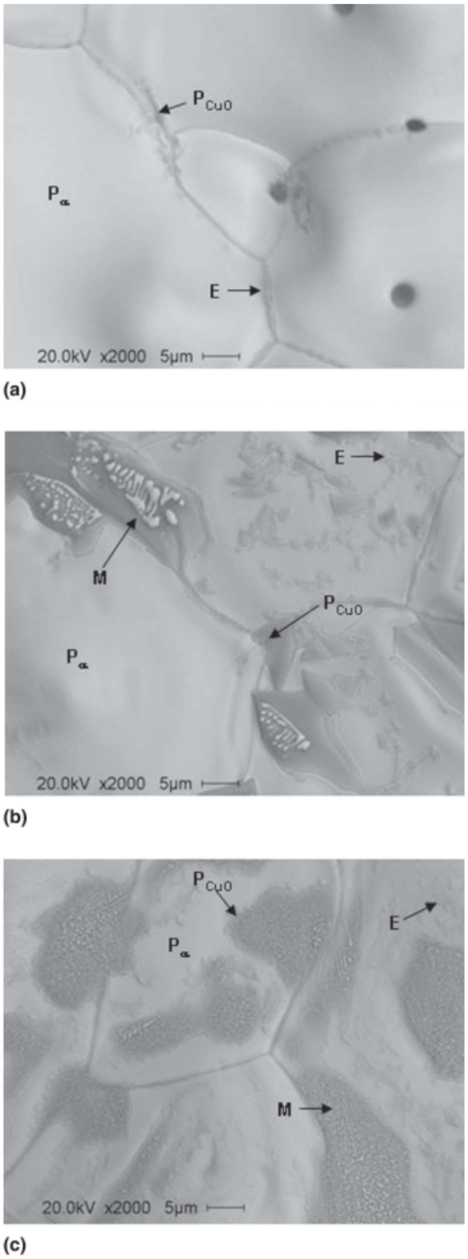

Fig. 3 SEM micrographs of specimens containing $x_{Pd}/(x_{Cu} + x_{Ag} + x_{Pd}) = 0.05$ that were heated to 1010 ℃, held for 15 min, and quenched to room temperature. These samples contain the following silver concentration, $x_{Ag}/(x_{Cu} + x_{Ag} + x_{Pd})$: (a) 0.995, (b) 0.986, and (c) 0.96. E = eutectic-type α + CuO, M = monotectic-type CuO_x, P_{CuO} = primary CuO_x, and P_α = primary α.

forms. Within experimental error, the measured lattice parameter for this cubic structured alloy matches that previously reported by Karayaka and Thompson [1988Kar].

Shown, respectively, in Fig. 2(b)-(d) are microstructures for compositions containing noble metal concentrations $[(x_{Ag})/(x_{Ag} + x_{Cu})]$ of 0.995, 0.986, and 0.96, which display hypereutectic, eutectic, and hypoeutectic features, respectively. In Fig. 2(b) for example, equiaxed primary copper oxide particles are observed within a proeutectic α matrix. Fine-scale eutectic material (α + CuO_x) is also found widely dispersed throughout the matrix. EDS analysis indicates that the copper-to-oxygen ratio of the copper oxide phase corresponds to stoichiometric CuO. Although not enough CuO is present to verify by XRD, the α alloy again exhibits a lattice parameter that corresponds to Ag-1Pd [1988Kar].

The specimen in Fig. 2(c) displays a predominantly lamellar eutectic-type microstructure, although regions of primary α and primary CuO_x (not shown) were observed. The composition in Fig. 2(d) displays a coarser microstructure with features that suggest a hypereutectic alloy. Large crystallites of CuO_x can be observed, which form due to the monotectic reaction, $L_2 \rightarrow L_1 + CuO_x$. Note that some Ag-rich L_1 liquid remains trapped in the immiscible L_2 liquid as this transformation takes place, resulting in a dispersion of a particles within the CuO_x. Upon further cooling, primary α forms, along with additional copper oxide. The remaining L_1 liquid eventually transforms to the fine-scale eutectic α and CuO_x material indicated in the figure. The observation of both primary α and CuO_x in Fig. 2(b)-(d) is evidence that a ternary α + CuO_x + L_1 region is present in the corresponding pseudoternary CuO_x-Ag-Pd phase diagram.

EDS analysis of the large monotectic copper oxide crystallites in Fig. 2(d) indicate a copper-to-oxygen ratio of 2:1, which corresponds to stoichiometric Cu_2O. Corresponding thermogravimetric analysis (TGA) data for these compositions indicate a slight but reproducible weight loss that could be attributed to the reduction of a fraction of the CuO to Cu_2O as the samples were heated at 980 ℃. As discussed previously, pure Cu_2O is not stable below 1027 ℃. However, Nishiura et al. identified Cu_2O in binary samples quenched from temperatures just above the monotectic reaction (969 ℃), the stabilization of which they suggested was due to a measurable uptake of silver within the lattice of the reduced oxide [1998Nis]. Attempts to verify this in the authors' samples by XRD proved inconclusive.

A second set of micrographs is shown in Fig. 3(a)-(c) for a series of specimens containing $x_{Pd}/(x_{Cu} + x_{Ag} + x_{Pd}) = 0.05$. These compositions were heated to 1010 ℃ and held for fifteen minutes prior to quenching in water. The specimen in Fig. 3(a), with a noble metal concentration of $(x_{Pd} + x_{Ag})/(x_{Cu} + x_{Ag}) = 0.995$, displays a microstructure dominated by primary α-phase, with a small amount of primary CuO_x and an apparent eutectic material observed within the boundaries between α grains. Primary α and CuO_x are also observed in Fig. 3(b), along with a mixture of α and CuO_x (labeled M) and regions of fine-scale α + CuO_x (labeled E). Although finer in scale, the microstructure is comparable to that observed in Fig. 2(c) and presumably forms in the same fashion; i.e., as will be discussed in the section, starting sequentially with the precipitation of CuO_x within the diphasic $L_1 + L_2$ liquid, followed by cooling through a binary $CuO_x + L_1$ phase field and the ternary α + CuO_x + L_1 field, and final conversion of the L_1 liquid to lamellar α + CuO_x. Similarly, the as-quenched microstructure in Fig. 3(c) for a silver concentration of 0.96 displays evidence of two immiscible liquids, one CuO_x-rich and the other Ag-rich, that when cooled underwent the same sequence of phase transformations. In addition, primary α is observed in regions

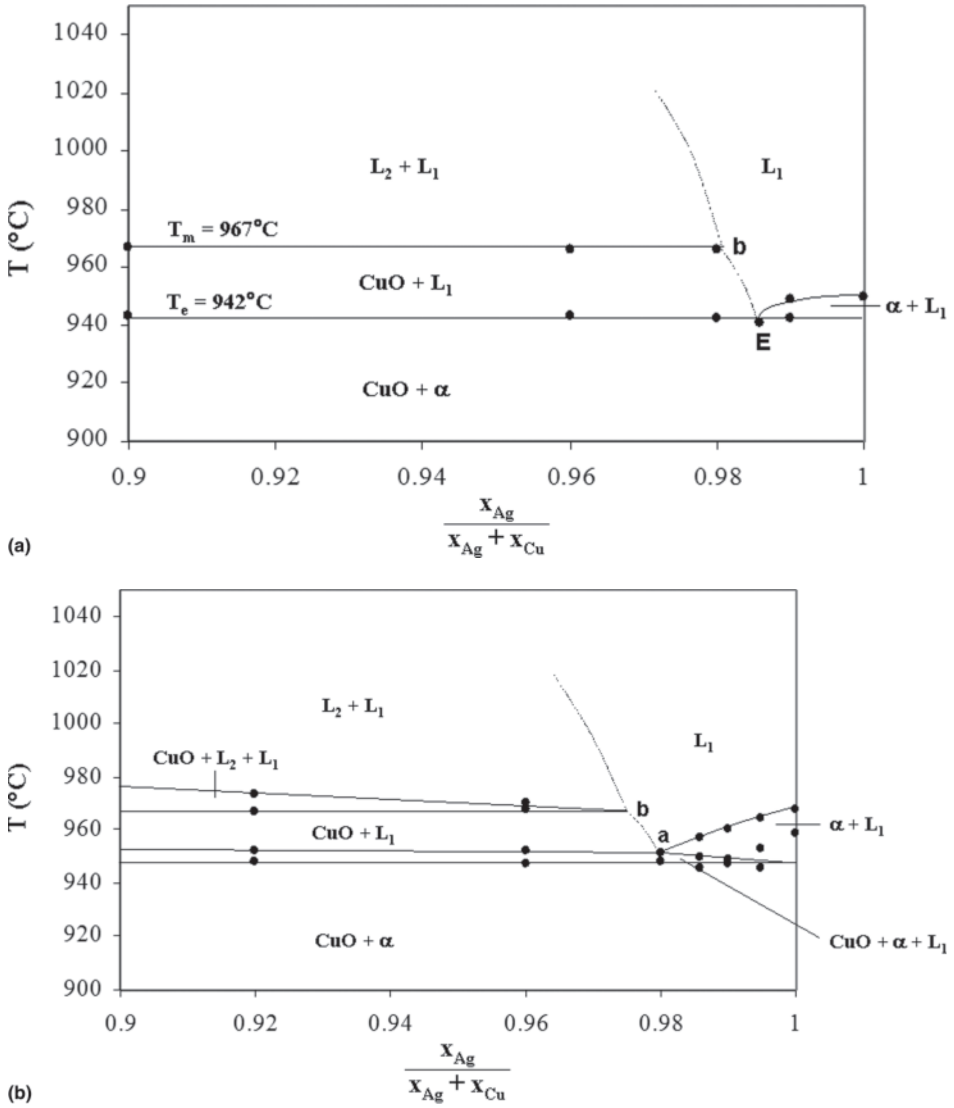

Fig. 4 Isopleths at palladium concentrations of (a) 0%, (b) 1%. The experimental data points are shown.

between the monotectic-type CuO_x and eutectic-type mixture, while proeutectic CuO_x is found as a thin rim of material around each crystallite. The copper-to-oxygen ratio of the monotectic-type copper oxide phases in all of the 5%Pd series specimens is 2:1, again corresponding to stoichiometric Cu_2O.

3.5 Invariant Reactions at Low Pd Content

Based on the data from the DSC and quenching experiments, a series of isopleths have been constructed in Fig. 4(a)-4(d) for $x_{Pd}/(x_{Cu} + x_{Ag} + x_{Pd}) = 0.00$, 0.01, 0.02, and 0.05. The pseudobinary diagram shown in Fig. 4(a) is quantitatively consistent with those previously reported [1993Sha, 1998Nis, and 1998Ass]. As palladium is added to the system to this system, the eutectic point separates from the original eutectic line forming a triangular ternary phase field, $\alpha + CuO_x + L_1$, in between. A corresponding ternary field, $CuO_x + L_1 + L_2$, also extends from the monotectic line. Similar phenomena have been observed in a number of ternary systems, a particularly germane example of which is found in the Au-Ag-Cu braze filler metal system [1963Har]. A general description of how these ternary fields develop and how the invariant temperatures are affected by the addition of a small amount of a third component to a binary system have been previously derived [1954Pri, 1983Lup]. In the present system, this type of analysis is applicable as long as the original pseudobinary can be approximated as a true binary system. It would be instructive to eventually conduct this analysis to determine its predictive capability for Pd-CuO_x-Ag and apply it to other pseudoternary systems such as Pt-CuO_x-Ag.

As noted previously in Fig. 2(a), our experimental results show that small additions of palladium raise the solidus temperature on average 5 °C/mol% Pd. The boundary corresponding to the $CuO_x + L_1 \rightarrow CuO_x + L_1 + L_2$ transfor-

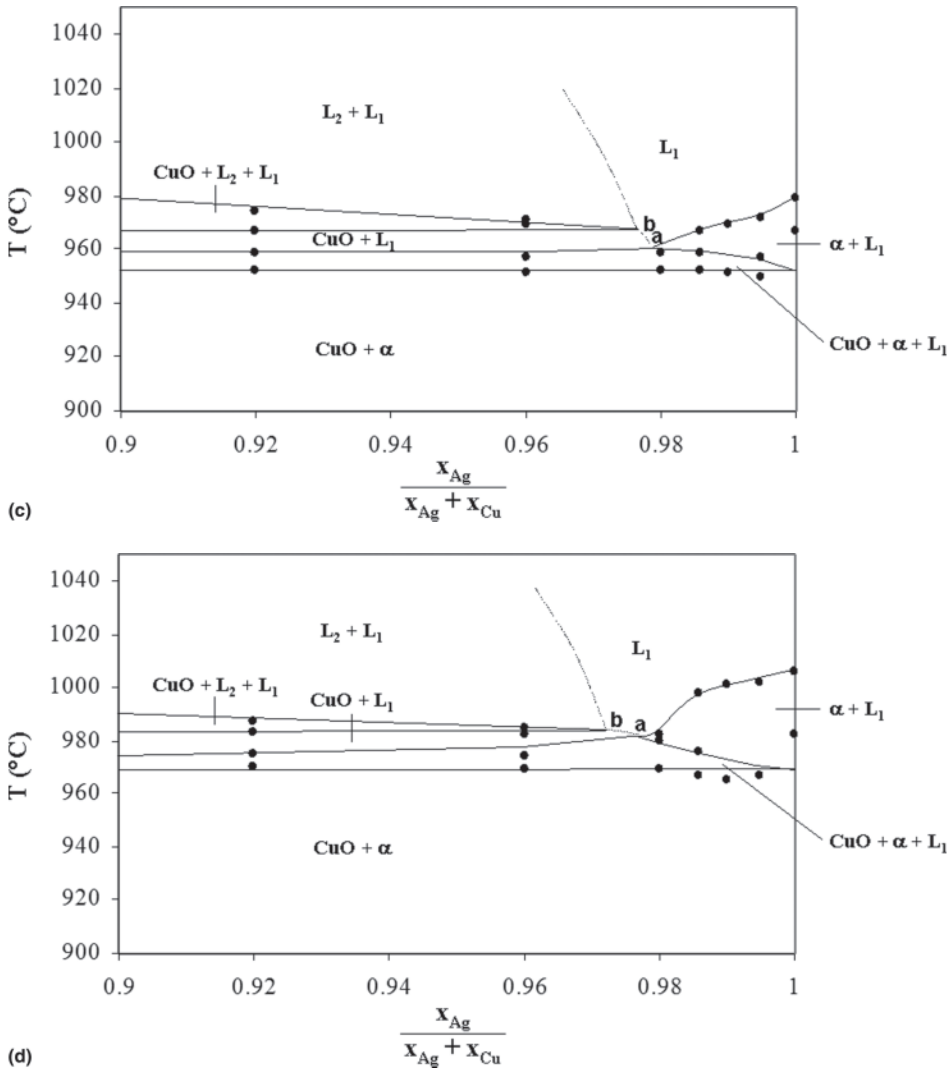

Fig. 4 cont. Isopleths at palladium concentrations of (c) 2%, and (d) 5%. The experimental data points are shown.

mation (derived from the original monotectic reaction in the pseudobinary Ag-CuO_x system) remains at ~970 °C until the solidus temperature eventually reaches this point, which causes a corresponding contraction in the $\alpha + CuO_x + L_1$ and $CuO_x + L_1$ phase fields. In addition, these phase fields narrow compositionally as the *a* transition point converges to the silver-rich end of the $CuO_x + L_1 + L_2 \rightarrow L_1 + L_2$ boundary line, point *b*. The convergence of the two three-phase fields indicates that with higher palladium content, a peritectic reaction will likely be observed, $\alpha + L_1 + L_2 \rightarrow CuO_x$. Although the exact nature for this phenomenon is not known, it is presumed to be related to palladium solubility in both CuO and silver, i.e., very little in the case of the former and complete solubility in the latter. Consequently, the initial addition of palladium primarily affects the thermodynamic equilibria of the silver-rich phases, α and L_1, and thereby modifies the original pseudobinary eutectic reaction. Because the original monotectic reaction is driven by the decomposition of the copper oxide-rich L_2 liquid, the effect of palladium at low concentrations is minimal.

4. Conclusions

The phase equilibria in the Pd-CuO_x-Ag pseudoternary system at low palladium and copper oxide concentrations have been investigated by DSC analysis and microstructural examination of quenched specimens. Based on the experimental results, a series of isopleths of constant Pd-concentration were constructed. These indicate that small additions of palladium (<5 mol%) increase the solidus temperature on average 5 °C/mol% palladium added but have little effect on the original monotectic reaction other than to cause an anticipated three-phase field ($CuO_x + L_1 + L_2$) to arise. However, once enough palladium was added (~5 mol%) to increase the pseudoternary solidus temperature to that of the lower boundary for this three-phase field (~970 °C), the lower boundary begins to increase in temperature as well. The addition of palladium also causes the original eutectic point *E* to move to lower silver concentrations, which also causes a convergence of the two new three-phase fields, $CuO_x + L_1 + L_2$ and $CuO_x + \alpha + L_1$. This suggests that with higher palladium concentrations, a peritectic reaction, $\alpha + L_1 + L_2 \rightarrow CuO_x$, may eventually be observed in the system.

Acknowledgments

This work was supported by the U.S. Department of Energy (US DOE), Office of Fossil Energy, Advanced Research and Technology Development Program. Thermal analysis equipment used was provided by Office of Basic Energy Sciences, Division of Materials and Engineering Physics. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the US DOE under Contract DE-AC06-76RLO 1830.

References

1906Rue: R. Ruer, On the Alloys of Palladium with Silver, *Z. Anorg. Allg. Chem.,* 1906, 51, p 315-319, in German

1909Sei: A. Sieverts and J. Haganacker, The Solubility of Hydrogen and Oxygen in Solid and Molten Silver, *Z. Phys. Chem.,* 1909, 68, p 115-128, in German

1931Ler: J.A.A Leroux, and K.W. Fröhlich, The Quasi-Binary Section Silver-Cuprous Oxide in the System Silver-Copper-Oxygen, *Z. Metallkde.,* 1931, 23, p 250-254, in German

1932All: N.P. Allen, The Effect of Pressure on the Liberation of Gases from Metals (with Special Reference to Silver and Oxygen), *J. Inst. Met.,* 1932, 49 (2), p 317-346

1948Koh: E.J. Kohlmeyer and K.V. Sprenger, The Oxidation of Liquid Silver-Copper Alloys, *Z. Anorg. Chem.,* 1948, 257, p 19914, in German

1954Pri: I. Prigogine and R. Defay, *Chemical Thermodynamics,* D.H. Everett, transl., Longmans Green Co., New York, 1954, p 250

1957Rau: E. Raub and W. Plate, The Solid State Reaction Between the Precious Metals or Their Alloys and Oxygen at High Temperature, *Z. Metallkde.,* 1957, 48, p 529-539, in German

1958Gra: W.S. Graff and H.H. Stadelmaier, Higher Oxides of Silver, *J. Electrochem. Soc.,* 1958, 105 (8), p 446-449

1962Eic: W. Eichenauer and G. Muller, Diffusion and Solubility of Oxygen in Silver, *Z. Metallkde.,* 1962, 53, p 321-324 and 700 (correction), in German

1963Har: W.B. Harding and H.B. Pressly, Soldering to Gold Plating, P*roc. 50th Ann. Conf. Amer. Electroplaters Soc.,* 1963, 90-106

1963Hof: L.C. Hoffman, Precision Glaze Resitors, *Am. Cer. Soc. Bull.,* 1963, 42 (9), p 490-493

1963Kri: C.A. Krier and R.I. Jaffe, Oxidation of the Platinum-Group Metals, *J. Less-Common Met.,* 1963, 5, p 411-431

1965Sch: N.G. Schmahl, and E. Minzl, Formation of (CuO, PdO) Mixed Crystals and Their Participation in the Equilibrium of the Cu-Pd-O System, *Z. Phys. Chem.,* 1965, 47, p 142-163, in German

1978Oke: M. O'Keeffe and J.O. Bovin, The Crystal Structure of Paramelaconite, Cu_4O_3. *Am. Mineral.,* 1978, 63, p 180-185

1983Lup: C.H.P. Lupis, *Chemical Thermodynamics of Materials,* Elsevier, New York, 1983, p 315-324

1985Col: S.S. Cole, Oxidation and Reduction of the Palladium in the Presence of Silver, *J. Am. Cer. Soc.,* 1985, 68 (4), p C-106-C-107

1986Mah: G.H. Maher, Method for Making Ag/Pd Electroding Powder, U.S. Patent 4,568,384, 1986

1988Kar: I. Karayaka and W.T. Thompson, The Ag-Pd (Silver-Palladium) System, *Bull. Alloy Phase Diagrams,* 1988, 9 (3), p 237-243

1988Pep: J.G. Pepin, Subsolidus Phase Relations in the System Pd-Ag-O and Application to Multilayer Ceramic Capacitor Electrodes, *Adv. Cer. Mats.,* 1988, 3 (5), p 517-519

1989Cha: Y.A. Chang and K.C. Hsieh, *Phase Diagrams of Ternary Copper-Oxygen-Metal System,* ASM International, Metals Park, OH, 1989

1990Fis: P. Fischer and M. Jansen, Cyclic Voltammetry and X-ray Powder Techniques Applied to Anodic Crystallization of Higher Silver Oxides, *Solid State Ionics,* 1990, 43, p 61-67

1991Wan: S.F. Wang and W. Hubner, Thermodynamic Modeling of Equilibrium Subsolidus Phase Relations in the Ag-Pd-O_2 System, *J. Am. Cer. Soc.,* 1991, 74 (6), p 1349-1353

1992Kar: I. Karayaka and W.T. Thompson, The Ag-O (Silver-Oxygen) System, *J. Phase Equilib.,* 1992, 13 (2), p 137-142

1993Sha: Z.B. Shao, K.R. Liu, and L.Q. Liu, Equilibrium Phase Diagrams in the Systems PbO-Ag and CuO-Ag, *J. Am. Ceram. Soc.,* 1993, 76 (10), p 2663-2664

1994Hal: B. Hallstedt, D. Risold, and L.J. Gauckler, Thermodynamic Assessment of the Copper-Oxygen System, *J. Phase Equilib.,* 1994, 15 (5), p 483-499

1995Mei: A.M. Meier, P.R. Chidambaram, and G.R. Edwards, A Comparison of the Wetability of Copper-Copper Oxide and Silver-Copper Oxide on Polycrystalline Alumina, *J. Mater. Sci.,* 1995, 30 (19), p 4781-4786

1995Suz: R.O. Suzuki, H. Nishiura, K. Ono, and L.J. Gauckler, Thermodynamics and Phase Diagram of the Ag-Cu-O System, *Advances in Superconductivity VII,* Proceedings of the 7th International Symposium on Superconductivity (Kita-kyushu, Japan November 8-11, 1994), K. Yamafuji and T. Morishita, ed., Springer-Verlag, Tokyo, Japan, 1995 p 373-376

1997Ass: J. Assal, B. Hallstedt, and L.J. Gauckler, Thermodynamic Assesment of the Silver-Oxygen System, *J. Am. Ceram. Soc.,* 1997, 80 (12), p 3054-3060.

1998Ass: J. Assal, B. Hallstedt, and L.J. Gauckler: Thermodynamic Assessment of the Ag-Cu-O System, *J. Phase Equilib.,* 1998, 19 (4), p 315-360

1998Nis: H. Nishiura, R.O. Suzuki, K. Ono, and L.J. Gauckler: Experimental Phase Diagram in the Ag-Cu_2O-Cuo System, *J. Am. Cerm. Soc.,* 1998, 81 (8), p 2181-2187

1999Lyu: M. Lyubovsky and L. Pfefferle, Complete Methane Oxidation over Pd Catalyst Supported on α-alumina. Influence of Temperature and Oxygen Pressure on the Catalyst Activity, *Catal. Today,* 1999, 47, p 29-44

2000Sch: C.C. Schüler, A. Stuck, N. Beck, H. Keser, and U. Täck, Direct Silver Bonding—An Alternative for Substrates in Power Semiconductor Packaging, *J. Mater. Sci: Mater. Electron.,* 2000, 11 (3), p 389-396

2002Ers: K.M. Erskine, A.M. Meier, and S.M. Pilgrim: Brazing Perovskite Ceramics with Silver/Copper Oxide Braze Alloys, *J. Mater. Sci.,* 2002, 37, p 1705-1709

2002Zha: H. Zhang, J. Gromek, G.W. Ferdando, S. Boorse, and H.L. Marcus: PdO/Pd System Equilibrium Phase Diagram Under a Gas Mixture of Oxygen and Nitrogen, *J. Phase Equilib.,* 2002, 23 (3), p 246-248

2003Hall: B. Hallstedt and L.J. Gauckler: Revision of the Thermodynamic Descriptions of the Cu-O, Ag-O, Ag-Cu-O, Bi-Sr-O, Bi-Ca-O, Bi-Cu-O, Sr-Cu-O, Ca-Cu-O and Sr-Ca-Cu-O Systems, *CALPHAD,* 2003, 27, p 177-191

2003Har: J.S. Hardy, J.Y. Kim, and K.S. Weil, Joining Mixed Conducting Oxides Using an Air-Fired Electrically Conductive Braze, *J. Electrochem. Soc.,* 2004, 151 (8), p J43-J49

2004Dar: J.T. Darsell, J.S. Hardy, J.Y. Kim, and K.S. Weil:

Microstructure, Melting and Wetting Properties of Pd-Ag-CuO Air Braze on Alumina, *Surfaces, Interfaces and Science of Ceramics Joining,* Ceramic Transaction Volume 158, K.S. Weil, I.E. Reimanis, and C.A. Lewinsohn, Ed., American Ceramic Society, Westerville, OH, 2004, p 173-182

2004Har: J.S. Hardy, J.Y. Kim, J.T. Darsell, and K. Scott Weil: Pd-Modified Reactive Air Braze for Increased Melting Temperature, *Surfaces, Interfaces and Science of Ceramics Joining,* Ceramic Transaction Volume 158, K.S. Weil, I.E. Reimanis, and C.A. Lewinsohn, Ed., American Ceramic Society, Westerville, OH, 2004, p 14-154

2005Kim: J.Y. Kim, J.S. Hardy, and K.S. Weil, Novel Metal-Ceramic Joining for Planar Solid Oxide Fuel Cells, *J. Electrochem. Soc.,* 2005, 152, p J52-J58

2005Wei: K.S. Weil, J.Y. Kim, and J.S. Hardy, Reactive Air Brazing: A New Method of Sealing Solid Oxide Fuel Cells and Other Solid State Electrochemical Devices, *Electrochem. and Sol. St. Lett.,* 2005, 8, p A133-A136