J Mater Sci (2007) 42:705–713
DOI 10.1007/s10853-006-1381-0

# Development of silver–metal oxide reactive air braze alloys for electroding PZT ceramics

**E. J. Pavlina · A. M. Meier · P. Monteleone ·
J. D. Weigner**

Received: 4 August 2004 / Accepted: 30 January 2006 / Published online: 31 December 2006

**Abstract** Existing multi-layer devices using lead-based piezoelectric ceramics utilize an internal electrode that does not bond the ceramic layers. Improvements in device performance and processing could be gained if the electrode also acted as a bond between the ceramic layers. In the current work, the feasibility of brazing lead zirconate titanate (PZT) in ambient conditions utilizing silver-based alloys containing low melting temperature metal oxides was investigated. Wettability, joint fracture strength, and microstructural analyses were conducted for various PZT/silver–metal oxide systems. The metal oxide additions included copper (II) oxide, vanadium pentoxide, lead (II) oxide, and eutectic lead oxide-titanium (IV) oxide. The silver–copper oxide (Ag–CuO) system demonstrated the most potential; exhibiting an apparent contact angle of approximately 64° and an average braze joint fracture strength that was approximately 62% of the monolithic PZT strength. In addition, no significant reaction product formation was observed at the silver/PZT interface. However, a preliminary investigation of multi-layer devices electroded with Ag–CuO alloys indicated a decrease in the resistivity of the brazed PZT by several orders of magnitude.

## Introduction

Piezoelectric ceramics such as lead zirconate titanate (PZT) are used in sensor and actuator applications where a multi-layer configuration is typically utilized to realize a lower drive voltage and a higher capacitance [1]. These devices employ an internal co-fired silver electrode that does not provide any structural integrity through bonding of the ceramic layers. Instead an external compressive load is used to mechanically join the layers. An internal electrode that also provides a structural bond between the PZT layers would result in higher device sensitivity, improved reliability, and a simplified handling procedure.

In order to bond the ceramic layers, the electrode braze alloy must adequately wet the ceramic substrate. Wetting behavior is often described by an equilibrium contact angle less than 90° as given by the Young equation [2]. Most pure ductile metals, including silver, do not wet most ceramics [3]. In order to promote wetting of the liquid metal, several alloying additions can be combined with the braze filler. In reactive brazing, small amounts of a reactive metal such as titanium, zirconium, or hafnium are alloyed with the filler [4]. The reactive elements promote spreading due to a reduction of the substrate resulting in reaction product formation at the liquid/substrate interface.

E. J. Pavlina (✉)
Department of Metallurgical and Materials Engineering,
Colorado School of Mines, 1500 Illinois Street, Golden, CO
80401, USA
e-mail: epavlina@mines.edu

A. M. Meier · P. Monteleone
School of Engineering at Alfred University, 2 Pine Street,
Alfred, NY 14802, USA

J. D. Weigner
Lockheed-Martin Corporation, Electronics Park EP5-H20,
Liverpool, NY 13088, USA

Reactive brazing typically requires either high vacuum or an inert atmosphere to inhibit oxidation of the reactive element. A second method of joining oxide ceramics is eutectic brazing [5]. In this process a liquid solution of copper and oxygen, or a eutectic composition of copper and cuprous oxide is formed at the metal/ceramic interface allowing for an intimate bond to develop. The process is carried out in a controlled oxygen-containing atmosphere. An alternative to reactive brazing and eutectic brazing is referred to as reactive air brazing (RAB) which is conducted in ambient conditions without the need for careful atmosphere control. In this method, a noble metal, typically silver (Ag), is alloyed with a low melting temperature metal oxide ($Me_xO_y$) in order to promote wetting on oxide ceramics. The compositions of interest are regions where either two immiscible liquids or a low melting temperature eutectic liquid are present at the brazing temperature. The oxide-rich phase is surface active, lowering the liquid-vapor and solid-vapor interfacial energies, thereby lowering the contact angle described by the Young equation [6]. Interfacial reaction product formation is typically limited and is not required for wetting in this technique.

RAB has been studied for several oxide ceramics using silver alloys containing 1–10 wt.% copper (II) oxide (CuO) or vanadium pentoxide ($V_2O_5$) [7–26]. Low oxide additions, 1–2 wt.%, were sufficient to promote wetting of the liquid metals on the ceramic substrates. Weil et al. [14] demonstrated that small additions of titanium (IV) oxide ($TiO_2$) to Ag–CuO alloys effectively decreased the contact angle on lanthanum strontium cobalt ferrite by approximately one-half for constant CuO concentrations. Furthermore, joint strengths 30–65% of the monolithic ceramic strength were achieved after brazing between 1,000 and 1,100 °C under ambient conditions. Minimal non-continuous interfacial reaction products were observed at the ceramic/braze interface for some systems [9–11, 23]. No significant effects from brazing were observed on the electrical properties of PMN [12]. The use of Ag–CuO braze alloys has been demonstrated in solid oxide fuel cell applications as viable interconnects between the oxide ceramic and the electrode [14].

The goal of the current study is to develop a technique for the reactive air brazing of metal electrodes that can be used for multi-layer PZT devices. Certain performance requirements must be achieved for the application: (1) the electrode braze alloy needs to be electrically conductive across the interface, (2) the electrode/PZT interface must be continuous and absent of voids or cracks so that high joint strengths can be achieved, and (3) the interactions with the braze alloy and the brazing thermal cycle must not adversely affect the piezoelectric properties of the PZT. In this study, the effects of braze time, temperature, and braze alloy composition on the wetting behavior and mechanical strength of the substrate/braze alloy interface are presented for a number of PZT/Ag–$Me_xO_y$ systems. Where possible, correlations between the braze microstructure and resulting properties are made. The braze alloy oxide additions investigated were CuO, $V_2O_5$, lead (II) oxide (PbO), and eutectic PbO–$TiO_2$.

## Experimental procedure

The wetting behavior, braze joint strength, and microstructural evolution of silver alloys containing metal oxides on PZT substrates was investigated. The PZT substrate composition was $(Pb_{0.94}, Sr_{0.04})(Ti_{0.53}, Zr_{0.47})O_3$ (Lockheed-Martin) which is known as PZT-4 or a Navy Type 1 PZT ceramic (referred to as PZT hereafter). The metal oxide additions included CuO powder (99.9%, Alfa Aesar), $V_2O_5$ powder (99.8%, –10 mesh, Alfa Aesar), PbO powder (99.9%, Aldrich) and a PbO–$TiO_2$ powder eutectic composition, made by mixing PbO powder with $TiO_2$ powder (>99.8%, Fisher Scientific), which were then alloyed with silver foil (99.9%, Lucas-Milhaupt) in concentrations between 1 and 10 wt.%. The PbO–$TiO_2$ eutectic contains 14 mol% $TiO_2$ [27]. A more detailed procedure is available elsewhere [22, 25].

Wettability tests were conducted to determine the apparent contact angle of the liquid braze alloy on the PZT substrate. Silver foil was fashioned into a boat and up to 10 wt.% oxide powder was added. The boat was then placed onto a PZT substrate and heated at a rate of 0.067 °C/s up to 1,000 °C and then held for 1,800 s under ambient conditions. In the case of Ag–CuO compositions, temperatures of 1,050 and 1,100 °C were utilized based upon previous work with Ag–CuO alloys [9, 10]. Following a furnace cool to room temperature the apparent contact angle of the resulting sessile drop was measured using a procedure outlined by Meier et al. [6]. A spherical cap geometry and constant drop volume were assumed for the calculation. Based on this geometry, the apparent contact angle can be determined [6, 9–13, 22, 23, 25, 26]. Fisher [28] showed that methods of this type are as accurate as direct contact angle measurement for wetting contact angles. Also, he stated that noncircularity of the drop was found to have little effect on the scatter of calculated contact angles.

The mechanical strength of brazed joints was determined using a standard four-point flexure test configuration. Mechanical test specimens were prepared by placing a 0.254 mm silver interlayer with oxide addition between 1 and 20 wt.% between the narrow faces of two 34 mm × 31 mm × 5 mm PZT substrates. The brazing cycle was conducted under ambient conditions with a heating rate of 0.067 °C/s up to 1,000, 1,050, or 1,100 °C and then isothermally held for 300, 1,800, or 3,600 s followed by a furnace cool to room temperature. Attempts were made to then section the brazed substrates into 5 mm × 5 mm × 62 mm bars, with the braze oriented transversely in the center of the length. Following sectioning, the bars were polished with a 125-µm diamond pad. Only the Ag–CuO braze alloys did not fail during the sample preparation steps with Ag–$V_2O_5$ alloys failing during the polishing step. Braze samples prepared using all other braze alloy compositions did not survive sectioning and a larger cross-sectional area had to be utilized. The fracture strength of the braze joint was determined for a four-point flexure setup with an outer span of 35 mm and inner span of 15 mm. Although the testing fixture does not comply with ASTM C 1161-94 [29], which specifies a 2:1 span ratio, results are valid when strengths are compared within this study. A crosshead speed of 0.0083 mm/s was used.

Selected samples from the brazed joints and sessile drop tests were cross-sectioned, mounted in epoxy, and polished to a 1-µm finish using diamond paste. A thin coating of a gold–palladium alloy was sputtered onto the polished surface in order to minimize charging when viewed under the electron microscope. Microstructure and elemental analysis was conducted using a scanning electron microscope (SEM) equipped with a heavy element energy dispersive spectroscopy (EDS) detector.

Six-layer multi-layer devices were fabricated using the processing conditions and brazing procedure outlined for the mechanical test specimens. The PZT layer thickness in the device was 2 mm, with a cross-sectional area of approximately 10 mm × 10 mm. Only Ag–CuO alloys were chosen for initial device construction due to these alloys exhibiting the highest fracture strength when compared with the other systems evaluated. The CuO concentration in the alloys used for this study ranged from 1 to 7 wt.%. The initial braze interlayer thickness was 0.127 mm. Brazing was conducted at 1,050 and 1,100 °C for 300 and 3,600 s. Following the brazing cycle, wire leads were attached to the braze interlayers in a parallel connection. Dipole polarization of the devices was conducted at 90 °C in a heated oil bath using an electric field of 3 kV/mm. During the polarization process, a high leakage current developed causing the process to be aborted. The resistivity of the brazed PZT layers was determined by applying a DC voltage of 1 V across each layer and measuring the resulting current. The resistivity, $\rho$, of the layer was calculated using [30]:

$$\rho = \left(\frac{VA}{Id}\right) \tag{1}$$

where $V$ is the applied voltage, $A$ is the cross-sectional area, $I$ is the measured current, and $d$ is the PZT layer thickness. Complete coverage of the PZT layer by the braze alloy was assumed in the calculation.

## Results

### Wettability

The apparent contact angle of Ag–$Me_xO_y$ alloys on polycrystalline PZT is presented in Fig. 1. Again it is noted that contact angles below 90° indicate wetting behavior. Pure silver on PZT exhibited a contact angle near 90°. The addition of CuO to the silver in concentrations between 1 and 10 wt.% decreases the apparent contact angle to approximately 64° after an isothermal hold at 1,050 °C. When isothermally held at 1,100 °C, the apparent contact angle increased with increasing oxide concentration from a minimum for the alloy containing 1 wt.% CuO. The observed rise in apparent contact angle is a real phenomenon since the ratio of drop height to drop spreading radius increased

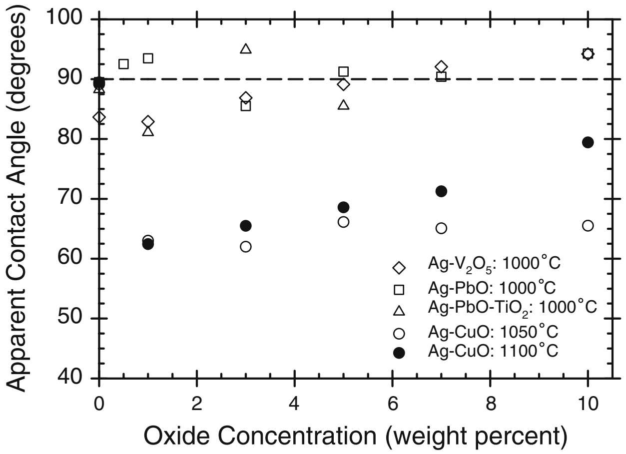

**Fig. 1** Apparent contact angle of Ag–$Me_xO_y$ alloys on polycrystalline PZT. Sessile drops were isothermally held for 1,800 s at 1,000 °C except were noted. The PbO–$TiO_2$ is a eutectic composition (14 mol% $TiO_2$)

with increasing CuO additions, increasing from 0.61 for 62° to 0.83 for 79°. Wetting behavior for liquid Ag–$V_2O_5$ alloys on PZT was observed with a $V_2O_5$ addition of 1 wt.%. With increasing $V_2O_5$ concentration the contact angle increased above 90°. The ratio of drop height to drop spreading radius increased with increasing $V_2O_5$ additions indicating that the observed rise in apparent contact angle is also a real phenomenon. The ratio increased from a minimum of 0.88 for 83° to 1.08 for 94°. Borderline wetting/non-wetting behavior was observed for Ag–PbO alloys with an apparent contact angle near 90° with the experimental error (±3°). The addition of $TiO_2$ to the silver in the form of the eutectic PbO–$TiO_2$ composition did not significantly affect the apparent contact angle over the composition range analyzed.

## Fracture strength of brazed joints

The fracture strength of PZT brazed with Ag–$Me_xO_y$ alloys is shown in Fig. 2. Fracture initiated at the braze interface for all conditions. The as-received monolithic fracture strength of PZT is 102 ± 17 MPa when tested in a three-point flexure test configuration [Unpublished data, Lockheed-Martin Corporation, Liverpool, NY]. The highest joint fracture strengths were observed for the Ag–CuO alloys. An overall average joint fracture strength of 64 MPa (~62% of monolithic strength) was observed for PZT brazed with the Ag–CuO alloys for all samples and test conditions. A general decrease in strength was observed with increasing CuO additions, from an average of 71 MPa to 41 MPa for CuO concentrations of 1 and 10 wt.%, respectively.

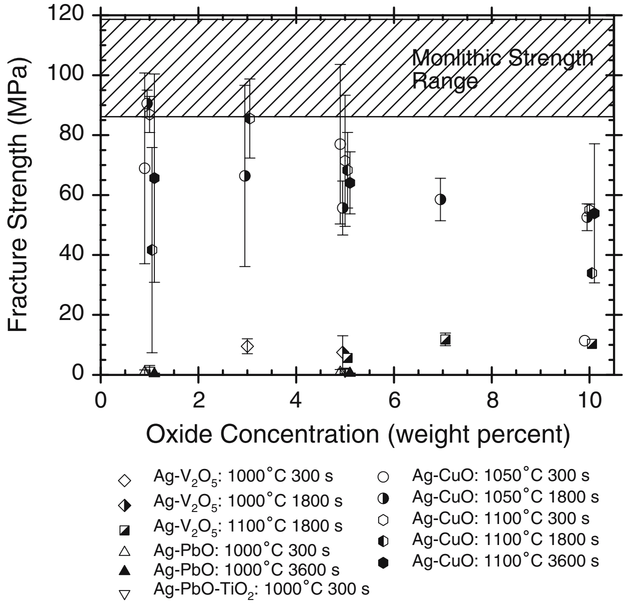

**Fig. 2** Joint fracture strength of PZT/Ag–$Me_xO_y$ brazed joints tested in a four-point flexure configuration. The monolithic values were obtained using a three-point flexure configuration [24]

Significantly lower joint fracture strengths were observed for the other alloy systems. In the case of Ag–$V_2O_5$ alloys, an average fracture strength of 9.2 MPa (~9% of monolithic strength) was observed for all test conditions. The lowest fracture strength was observed for the PZT/Ag–PbO system, exhibiting an average strength of 0.68 MPa (~0.7% of monolithic strength). The average strength of Ag–PbO–TiO alloys was 1.36 MPa (~1.3% of monolithic strength). The overall average strength was calculated only using the results for the small number of samples that could be sectioned for testing. The standard deviation for these tests was 3.4 MPa for PZT brazed with Ag–$V_2O_5$ alloys and approximately 1.0 MPa for PZT brazed with Ag–PbO and Ag–PbO–$TiO_2$ alloys. Within the test reproducibility, the resulting fracture strengths were independent of the processing conditions.

## Microstructural characterization

Typical microstructures of PZT/Ag–CuO joints brazed at 1,100 °C for 3,600 s are shown in Fig. 3. A zirconium-rich phase is observed at the PZT/braze interface for CuO concentrations of 1 and 10 wt.%. Increasing amounts of this phase are present with increasing CuO additions, temperatures, and isothermal hold times (Fig. 3b). Within detection limits of the SEM/EDS system, no dissolved copper is observed in the silver interlayer, which corresponds with the CuO–Ag phase diagram [31]. Instead, the copper exists in discrete regions within the silver in the form of copper oxide. With increasing amounts of CuO, silver infiltration into pre-existing pores in the PZT occurred. Minimal porosity is present in the silver interlayer and at the interface for all conditions.

Typical microstructures of PZT/Ag–$V_2O_5$ joints brazed at 1,050 °C for 3,600 s are shown in Fig. 4. The silver layer is discontinuous. A zirconium-rich phase is present along the length of the silver layer. A lead/vanadium-rich phase is also observed at high $V_2O_5$ concentrations (Fig. 4b). This phase is found as a distinct phase as well as within the zirconium-rich regions. Qualitative elemental analysis indicates a zirconium depletion of the PZT matrix near the interface. Large pores are also present at the interface.

In the Ag–PbO system, analysis of sessile drop cross-sections and brazed-joint cross-sections indicated differing reaction and wetting behavior (Fig. 5). In the case of sessile drop cross-sections, no interfacial

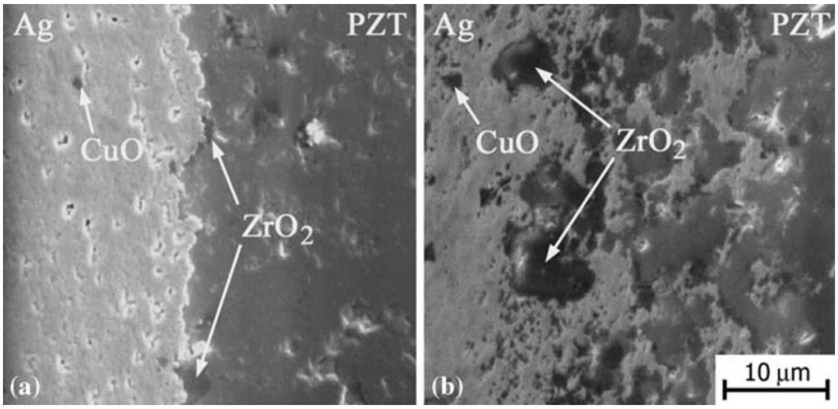

**Fig. 3** Cross-section of interface of PZT joint brazed with silver alloys containing (**a**) 1 wt.% CuO and (**b**) 10 wt.% CuO at 1,100 °C for 3,600 s

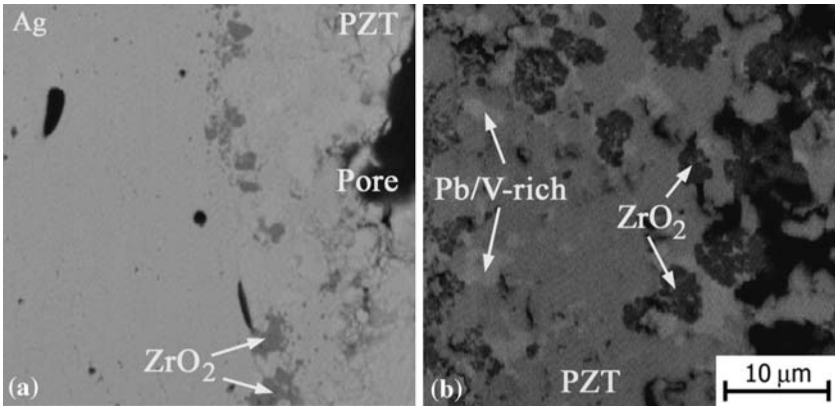

**Fig. 4** Cross-section of interface of PZT joint brazed with silver alloys containing (**a**) 1 wt.% $V_2O_5$ and (**b**) 10 wt.% $V_2O_5$ at 1,050 °C for 3,600 s

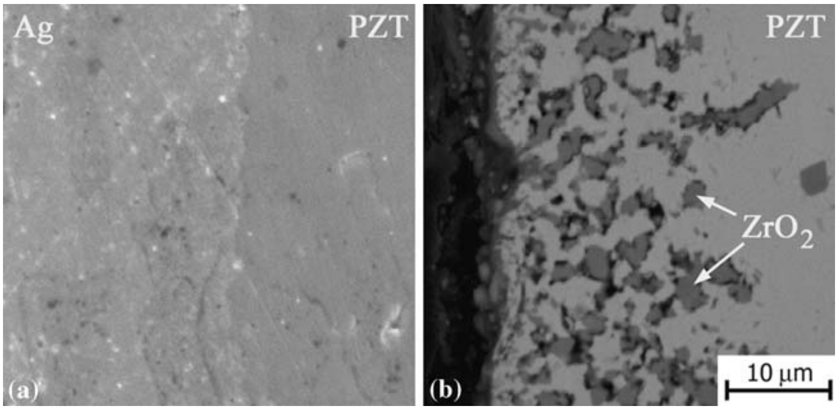

**Fig. 5** Cross-section of PZT/Ag–PbO interface of (**a**) sessile drop of Ag-1 wt.% PbO alloy brazed at 1,000 °C for 1,800 s and (**b**) braze joint interface brazed with an Ag-1 wt.% PbO alloy at 1,000 °C for 3,600 s

reaction products or porosity are observed. However, zirconium-rich regions and porosity are found at the interface of brazed joints. In both configurations, no discrete regions of PbO or dissolved lead are present in the silver interlayer.

Typical microstructures of PZT/Ag–PbO–$TiO_2$ joints brazed at 1,000 °C for 300 s are shown in Fig. 6. No interfacial reaction products or major porosity are observed. Cracking within the silver interlayer and along the interface was observed in some samples (Fig. 6a). Again, no dissolved PbO or $TiO_2$ are found in the silver. Furthermore, no titanium-rich regions are present in the PZT near the interface.

## Electrical resistivity of PZT electroded with Ag–CuO alloys

The resistivity of unpolarized, unbrazed monolithic PZT at room temperature is $2.0 \times 10^{14}$ Ω cm. Devices utilizing an Ag-7 wt.% CuO electrode brazed at 1,050 °C for 300 s exhibited a decrease in resistivity

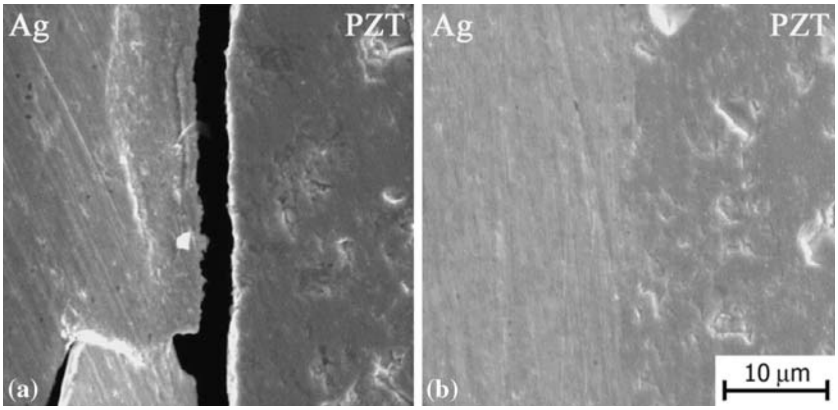

**Fig. 6** Cross-section of interface of PZT brazed with silver alloys containing (**a**) 1 wt.% eutectic PbO–TiO$_2$ and (**b**) 5 wt.% eutectic PbO–TiO$_2$ at 1,000 °C for 300 s

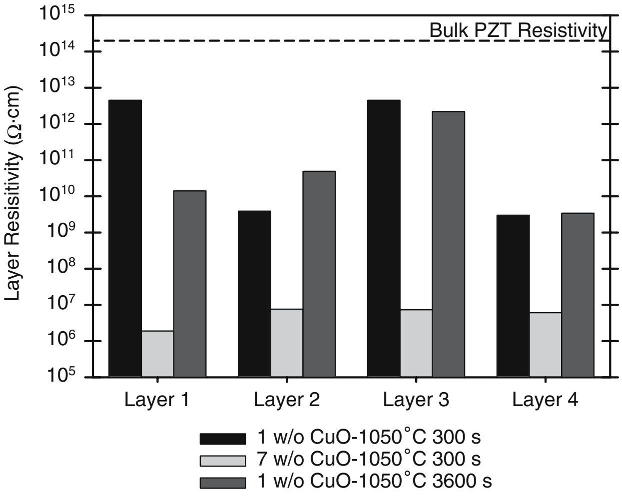

**Fig. 7** PZT layer resistivity of multi-layer stacks brazed with Ag–CuO electrodes

of 7 orders of magnitude to a minimum of $1.9 \times 10^6$ Ω cm (Fig. 7). Even after brazing devices at 1,050 °C for 300 s with an Ag-1 wt.% CuO alloy, the PZT layer resistivity decreased 2–5 orders of magnitude to a minimum of $5.3 \times 10^9$ Ω cm.

## Discussion

### Wettability of pure silver

The approximately wetting contact angle of pure silver on polycrystalline PZT ($\theta = 88° \pm 3°$) can be attributed to several different factors. Previous research has indicated a lowered contact angle for pure metals on titanium oxides due to an increase in metallic character resulting from the presence of titanium [32]. In a parallel study of liquid Ag–Me$_x$O$_y$ alloys on zirconia, which utilized the same apparent contact measurement procedure as this study, a wetting contact angle was also obtained for pure silver on zirconia [23].

### The PZT/Ag–CuO system

In the PZT/Ag–CuO system the CuO is surface active, resulting in wetting of the PZT by the Ag–CuO alloys with only a 1 wt.% CuO concentration. The zirconium-rich phases present at the braze interface are most likely zirconia. Nagata et al. [33] observed interfacial zirconia formation of PLZT, (Pb$_{0.9}$, La$_{0.1}$)(Zr$_{0.65}$, Ti$_{0.35}$)O$_3$, electroded with silver, after thermal cycling to 9,00 °C. The silver and the PLZT react to form the interfacial zirconia, as follows: PLZT + Ag → (Pb,La)-TiO$_3$) + ZrO$_2$ + (PbO + Ag). A similar crystal structure and chemistry is shared between PZT and PLZT, with A-sites in the PZT containing 6 at.% strontium and A-sites in PLZT contain 10 at.% lanthanum.

The silver/copper-rich phases found in pre-existing pores within the PZT near the interface are located approximately 15 μm from the interface. The porosity of the PZT is not open indicating that direct infiltration of the pores is not occurring. Instead, lattice diffusion or grain boundary diffusion of silver and copper oxide between the pores are possible transport mechanisms. The latter is more probable due to faster grain boundary diffusion of silver in lead-based perovskite ceramics [34].

The relatively high average fracture strength (64 MPa or ~62% of the monolithic PZT fracture strength) of the PZT/Ag–CuO joints is attributed to different elements of the interface. The absence of large pores in the silver interlayer and along the interface minimizes the concentration of stress risers that can compromise joint integrity. Also, no continuous reaction product layer is present at the interface. When present, these reaction product layers tend to be brittle in nature and create stresses at the PZT/reaction product interface due to thermal expansion mismatch. As indicated by Fig. 3b, it is expected that a thick, continuous reaction product layer of $ZrO_2$ will develop after long brazing times, resulting in a degradation of the mechanical properties of the brazed joint. Along with the reduction in mechanical strength, electrical and thermal conduction across the interface will be decreased if the reaction product layer is an insulator.

The decrease in resistivity of the PZT following brazing may be caused by an increase in the ionic or electronic conductivity of the monolithic PZT. Ionic conductivity could increase through increasing the concentration of oxygen vacancies in the PZT lattice. Oxygen vacancies can be created from zirconium depletion of the PZT. For every vacancy on a zirconium site, two oxygen vacancies need to be created in order to retain charge neutrality. Limited substitution of silver on lead sites can occur, although the solubility of silver is small, about 1 at.% [35]. If substitution does occur, the formation of oxygen vacancies is again required to retain charge neutrality.

The electronic contribution to the conductivity of monolithic PZT is not significant. A continuous network of metal-rich grain boundaries can increase the relative contribution of electronic conduction to the total conductance. Any excess silver in the PZT matrix, beyond the solubility limit, will migrate to the grain boundaries [36].

Zuo et al. [37] performed work on the electrical properties of silver-doped PMN-PNN-PZT ceramics at elevated temperature. A change from nearly complete lattice conductivity to lattice and grain boundary mixed conductivity was observed, resulting in an overall increase in electrical conductivity. At temperatures of approximately 500 °C grain boundary conductivity occurs due to excess silver ions aggregated in the grain boundary glass phases.

Visual examination of the PZT/Ag–CuO interface reveals a discolored region approximately 1–2 mm on each side of the interface. Device layers were only 2 mm thick, therefore exhibiting the discolored region throughout the layer thickness. Typically, discoloration is indicative of diffusion or reaction, and formation of $ZrO_2$ at the interface was observed. The diffusion of silver may also have contributed to the discoloration, although the analytical techniques that were used did not indicate the presence of silver in the bulk PZT. Regardless of the mechanism for the reduced electrical resistivity of the PZT, the effect occurs at a depth of at least 1 mm in less than 300 s at 1,050 °C.

## The PZT/Ag–$V_2O_5$ system

Wetting behavior for liquid Ag–$V_2O_5$ alloys on PZT was observed with a 1-wt.% $V_2O_5$ addition. With increasing $V_2O_5$ concentration the contact angle increased above 90°. The increased contact angle is attributed to dissolution of the $V_2O_5$ into the PZT resulting in a Pb/V-rich phase that changes the composition of the liquid silver alloy towards pure silver and borderline wetting behavior.

The microstructural features of the PZT/Ag–$V_2O_5$ joints exhibit several features that could explain the lower joint fracture strengths relative to the PZT/Ag–CuO brazed joints. For the samples tested, an average fracture strength of 9.2 MPa or ~9% of the monolithic PZT fracture strength was observed. A large reaction zone along with the large pores and a discontinuous silver layer were observed. All of these features would degrade the integrity of the joint and could act as stress risers and crack initiation sites, decreasing the strength of the joint.

The Ag–$V_2O_5$ alloys are too aggressive to use as an electrode material. The absence of a continuous silver interlayer for connecting to the electrode layer combined with the poor joint strengths indicates that this system is not feasible. Also, the migration of zirconium from the PZT matrix should alter the electrical response of the PZT considerably.

## The PZT/Ag–PbO system

Based on the apparent contact angle of Ag–PbO alloys on PZT, the addition of PbO to silver did not promote wetting of the PZT substrate. Dissolution of the PbO into the PZT would result in a sessile drop composed primarily of silver, which would then exhibit the near-wetting behavior observed for pure silver on PZT. Also, since PbO is an unstable oxide known to volatilize below its melting temperature, the volatilization of the PbO in the braze alloy may occur very rapidly resulting in a sessile drop composed solely of silver [36]. Volatilization of the PbO would account for the borderline wetting apparent contact angles exhibited over the composition range studied.

The poor brazed joint strengths of the PZT/Ag–PbO joints can be attributed to the poor wetting behavior displayed by Ag–PbO alloys. Generally, poor wetting behavior is indicative of poor adhesion. In some specimens, a zirconium-rich phase was observed at the braze interface, similar to that observed in the PZT/Ag–CuO system. Porosity surrounding this phase can act as stress risers and crack initiation sites, decreasing the strength of the braze joint. However, it is not likely that the loss of mechanical strength is due to interfacial reaction product formation alone. The PZT/Ag–CuO system exhibited similar reaction products but still maintained joint strengths that averaged 62% of the monolithic PZT strength as compared to less than 2% of the monolithic PZT strength for in the PZT/Ag–PbO system. Instead the decreased fracture strengths in the PZT/Ag–PbO system are most likely due to poor silver adhesion and poor wettability of the braze alloy on the ceramic substrate.

### The PZT/Ag–PbO–$TiO_2$ system

The apparent contact angle of Ag–PbO alloys on PZT remained virtually unchanged with the addition of $TiO_2$. Similar to the Ag–PbO alloys, volatilization or dissolution of the PbO would lead to the borderline wetting behavior that was observed. Even though some solid $TiO_2$ would remain in the silver matrix it would not be present in high enough concentrations to affect the wetting behavior of the silver.

Braze joint strengths for the PZT/Ag–PbO–$TiO_2$ system were very poor, less than 1% of the monolithic PZT strength. No interfacial reaction products or porosity were observed indicating that the low strengths were the result of poor adhesion of the silver interlayer.

## Conclusions

Adequate wetting behavior and braze joint strengths were only achieved for silver alloys containing CuO in concentrations up to 10 wt.%. Apparent contact angles between 62° and 79° and braze joint strengths averaging 64 MPa (62% of the monolithic PZT fracture strength) were obtained. An initial evaluation of Ag–CuO alloys as viable electrode materials indicates a decrease in the electrical resistivity of the brazed PZT by many orders of magnitude, effectively negating the potential advantages of this process. Silver alloys containing $V_2O_5$, PbO, and eutectic PbO–$TiO_2$ additives are not suitable as electrode compositions due to borderline wetting behavior and most importantly, braze joint strengths that were less than 10% of the monolithic PZT fracture strength. Aggressive reaction of the Ag–$V_2O_5$ alloys with the PZT resulted in reaction product formation and a discontinuous silver layer.

**Acknowledgements** PZT substrates were provided by Lockheed-Martin Corporation. Technical assistance was provided by Dr. W. Schulze and Mr. C. Williams at the School of Engineering at Alfred University.

## References

1. Jaffe B, Cook WR, Jaffe H (1971) Piezoelectric ceramics. R.A.N. Publishers, Marietta, OH, p 271
2. Eustathopoulos N, Nicholas M, Drevet B (1999) Wettability at high temperatures. Pergamon, New York, p 7
3. Nogi K, Oishi K, Oginio K (1989) Mater Trans JIM 30:137
4. Loehman R, Tomsia A (1988) Ceram Bull 67:375
5. Burgess JF, Neugebauer CA, Flanagan G (1975) J Electrochem Soc 122:688
6. Meier AM, Chidambaram PR, Edwards GR (1995) J Mater Sci 30:4781
7. Schuler CChr, Stuck A, Beck N, Keser H, Tack U (2000) J Mater Sci 11:389
8. Schuler C (1998) US Patent 5,767,029, June 16, 1998
9. Erkine KM (1999) MS Thesis, Alfred University, Alfred, NY
10. Kenefick MJP Sr (2000) Thesis, Alfred University, Alfred, NY
11. Dickson KR (2001) MS Thesis, Alfred University, Alfred, NY
12. Erskine KM, Meier AM, Pilgrim SM (2002) J Mater Sci 37:1705
13. Dickson K, Meier A, Erskine K (2002) In: Drew RAL, Pugh MD, Brochu M (eds) Proceedings of the international symposium on metal/ceramic interactions, Montreal, August 2002. Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, p 13
14. Weil KS, Hardy JS (2003) In: Lewinsohn CA, Singh M, Loehman R (eds) Advances in joining of ceramics: proceedings of the joining of ceramics symposium: held at the 104th annual meeting of the American Ceramic Society, St. Louis, April 2002. American Ceramic Society, p 18
15. Weil KS, Hardy JS, Kim JY (2003) US Patent Application 20030132270, July 17, 2003
16. Kim JY, Weil KS (2003) In: Lewinsohn CA, Singh M, Loehman R (eds) Ceramic transactions: advances in joining of ceramicsm, vol 138. American Ceramic Society, Westerville, OH, p 119
17. Weil KS, Paxton DM (2002) Ceramic engineering and science proceedings. American Ceramic Society, Westerville, OH, USA, p 785
18. Weil KS, Coyle CA, Kim JY, Hardy JS (2003) In: Knauth P, Gasteiger HA (eds) Solid state ionics-2002: symposium, Boston, December 2002, vol 756. Materials Research Society, Warrendale, PA, p 551
19. Weil KS, Hardy JS, Kim JY (2003) In: Indacochea JE, DuPont JN, Lienert TJ, Tillmann W, Sobczak N, Gale WF, Singh M (eds) Joining of advanced and specialty materials V proceedings 2002, Columbus, OH, October 2002. ASM International, Materials Park, OH, p 47
20. Hardy JS, Kim JY, Weil KS (2005) J Electrochem Soc 152:J52
21. Weil KS, Kim JY, Hardy JS (2005) J Mater Sci 40:2341
22. Pavlina EJ Sr (2003) Thesis, Alfred University, Alfred, NY
23. Sinnamon KE Sr (2003) Thesis, Alfred University, Alfred, NY
24. Meier AM, Miller DR, Dickson KR, Perkins RS, Ramarge MM (2004) US Patent 6,757,963, July 6, 2004
25. Monteleone P Sr (2003) Thesis, Alfred University, Alfred, NY
26. Zink NM Sr (2004) Thesis, Alfred University, Alfred, NY
27. Jaffe B, Cook WR, Jaffe H (1971) Piezoelectric ceramics. R.A.N. Publishers, Marietta, OH, p 117
28. Fisher LR (1979) J Colloid Interface Sci 72:200
29. Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature, ASTM Standard C 1161-94 (1998) 1998 Annual Book of ASTM Standards. American Society for Testing and Materials, West Conshohocken, PA, p 221

30. VanVlack LH (1985) Elements of materials science and engineering, 5th edn. Addison-Wesley Publishing, Reading, MA, p 14
31. Shao AB, Liu KR, Liu LQ, Liu HK, Dou SX (1996) J Am Ceram Soc 76:2663
32. Eustathopoulos N, Chatain D, Coudurier L (1991) Mater Sci Eng A135:83
33. Nagata H, Haneda H, Sakaguchi I, Takenaka T, Tanaka J (1997) J Ceram Soc Jpn 105:805
34. Lewis DJ, Gupta D, Notis MR (2001) J Am Ceram Soc 84:1777
35. Hwang HJ, Yasouka M, Sando M, Toriyama M (1999) J Am Ceram Soc 82:2417
36. Zuo R, Li L, Hu X, Gui Z (2002) Mater Lett 54:185
37. Ryu J, Choi J, Kim H (2001) J Am Ceram Soc 84:902