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Brazing perovskite ceramics with silver/copper oxide braze alloys

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In this study the feasibility of eutectic braze alloys based on the silver/copper oxide (Ag/CuO) system were investigated for use in joining lead magnesium niobate (PMN) ceramics. PMN was successfully brazed in air at 1050 and 1100°C using Ag/CuO alloys. The brazed samples had an average four-point-bend fracture strength of approximately 40 percent of the average monolithic PMN strength (with an actual value of 19 ± 11 MPa). The fracture strength was relatively constant for all brazing conditions tested. No significant reaction product layer was observed at the silver/PMN interface and the electrical properties of the PMN were changed only slightly by presence of the braze alloy interlayers. © *2002 Kluwer Academic Publishers*

1. Introduction

A number of acoustic sensor and capacitor dielectric applications exist that would benefit from the development of metallic brazing alloys for electroding and bonding of lead magnesium niobate (PMN) ceramics. The chemical formula of PMN, which has the perovskite structure, is Pb $(Mg_{0.33}Nb_{0.67})$ O_3. Currently, limited information on the joining of PMN, or any other perovskite ceramic, is available in the published literature, and PMN stacks are soldered to copper alloy plates using conventional solder techniques. The current joining techniques requires relatively thick PMN and metal electrode plates while very thin plates are desired for optimum sensor performance.

In many electronic applications, a metal electrode is bonded to a ceramic substrate or ceramic multilayers are sandwiched between metal electrode layers. For electrode applications, a high electrical conductivity metal is desired. In order to accommodate the thermal stresses developed due to coefficient of thermal expansion (CTE) mismatch, a ductile material is also desired. Most candidate metals (e.g. silver, copper, gold, nickel and aluminum) do not wet and show poor adhesion to most oxide ceramics. One method of improving the strength of the metal/ceramic interface is the introduction of oxygen into the liquid metal either as a binary solution addition or as a low melting temperature oxide addition. The majority of the previous studies have evaluated metal systems in contact with their own oxides where the oxygen activity in the liquid is controlled by the oxygen partial pressure of the system. Studies have shown that copper/copper oxide (Cu/Cu_2O) braze alloys can be used to bond a number of oxide ceramic materials [1–6]. In addition to the need for careful atmosphere control, another shortcoming of this system is the potential for formation of thick interlayers via an oxide dissolution reaction. The reaction product creates additional interfaces with the potential for CTE mismatch and interfacial cracking. In theory, it should be possible to use similar eutectic systems, such as silver/copper oxide (Ag/CuO), to bond complex oxides, including perovskites. Silver/copper oxide braze alloys have been used to braze alumina [7]. The Ag/CuO alloys provide numerous advantages over the Cu/Cu_2O alloys, such as the ability to braze in air and higher electrical and thermal conductivity. The copper oxide is necessary to allow the silver to wet the Al_2O_3 [8, 9], and should also improve wetting of other oxide ceramics, such as PMN. The silver/copper oxide alloys could be used to bond PMN to other electroactive materials, to substrates and supports, and also could be used to form electrodes which are strongly bonded to the PMN. The current study demonstrates the feasibility of the Ag/CuO alloys for joining PMN. A continuous PMN silver interface was developed without the formation of an interfacial reaction product and without significantly altering the electrical properties of the PMN stacks.

2. Experimental procedure

The silver/copper oxide braze alloys studied in this experiment were produced by screen printing copper oxide paste, produced with copper oxide (CuO) powder (−200 mesh, 99.9% purity) and a Heraeus Inc. (Cermalloy Division) screen-printing vehicle (composed of ethyl cellulose and turpineol) onto 99.9% purity silver foils of various thickness. Copper oxide paste was printed onto one side of the silver foils using

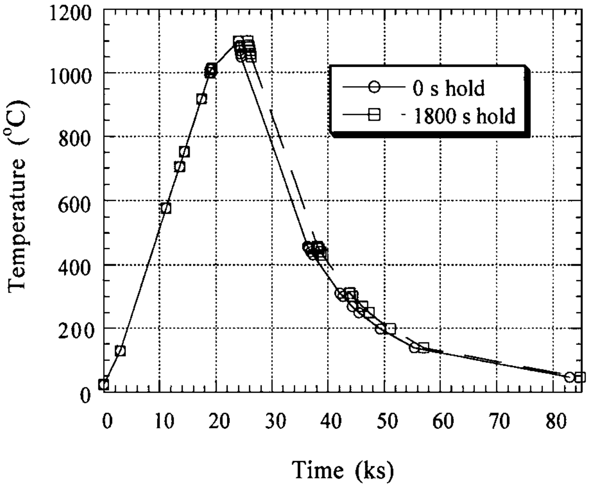

Figure 1 The furnace temperature profile for brazing hold times of 0 and 1800 s at 1100°C.

a Sel-Rex TF screen printer and was then dried at 100°C for approximately 3600 s.

PMN bars of the B300100 series were obtained from Lockheed-Martin Corporation. The PMN was produced with small amounts of lead titanate (PT) and barium titanate (BT) added to achieve the desired properties, such as dielectric constant, dissipation factor and mechanical response. The composition of the bars used in this study was 87.3 mole percent PMN–9.7 mole percent PT–3.0 mole percent BT. The joining surfaces were polished to a 600-grit finish to obtain a smooth, consistent surface for bonding.

The brazing procedure consisted of layering two silver foils between two PMN bars with the copper oxide layers adjacent to the PMN bars. The procedure is described in greater detail elsewhere [7]. PMN braze joints were produced with a full 2 × 3 × 3 test matrix with variable temperature (1050, 1100°C), isothermal hold times (0, 600, 1800 s) and initial silver interlayer thickness (0.15, 0.25, 0.38 mm).

A copper oxide layer thickness averaging 0.02 mm was prepared for all samples by screen-printing. The copper oxide thickness value of 0.02 mm was estimated based on the average measured thickness of the dry CuO layers and accounting for binder burnout during the brazing heat cycle. The overall braze alloy composition for each initial silver thickness was calculated assuming a uniform silver thickness and a uniform copper oxide thickness of 0.02 mm. The 0.15-mm-thick silver layer contained 88 weight percent silver and 12 weight percent CuO, the 0.25-mm-thick silver layer contained 92 weight percent silver and 8 weight percent CuO, and the 0.38-mm-thick silver layer contained 95 weight percent silver and 5 weight percent CuO. The furnace profile is shown in Fig. 1 for the 0 s and 1800 s hold times at 1100°C. The furnace profile was similar for the 1050°C brazing cycles. Each brazing cycle consisted of heating to 1000°C at 0.056°C/s (200°C/hr), heating to the maximum temperature at 0.017°C/s (60°C/hr), holding at the maximum temperature for the desired amount of time and then cooling to room temperature. The cooling cycle could not be controlled on the furnace that was used for brazing. The furnace turned off after the hold and cooled slowly to room temperature.

The brazed samples were cut into bend test bars with cross sectional dimensions of 4 ± 1 mm by 6 ± 1 mm. The test bars were approximately 38 mm in length. A total of 46 brazed test bars were obtained from the brazed samples. A number of the brazed bars were broken during the preparation of the test bars. Six monolithic test bars were also cut to the same dimensions from as-received PMN. The test bars were polished to obtain a rectangular cross section. The test bars were then broken in a standard 4-point bending test, with a crosshead speed of 0.008 mm/s (0.5 mm/min), and the fracture strength was determined using the standard four-point bending equation and the dimensions of each test bar:

$$\sigma_{\max} = \frac{3P}{2bw^2}(S_2 - S_1)$$

where $\sigma_{\max}$ is the fracture strength in Pa, P is the applied load in N, b is the dimension of the bar perpendicular to the loading direction (width) in m, w is the dimension of the bar parallel to the loading direction (thickness) in m, and S_1 and S_2 are the inner span (0.015 m) and the outer span (0.035 m), respectively, of the four-point-bend fixture [10].

The braze layer thickness of each test bar was measured prior to four-point-bend testing, using the eyepiece graticule on an optical microscope, on the side selected to be the tensile surface. The braze thickness varied between 0.04 mm and 0.28 mm, with an average thickness of 0.14 ± 0.06 mm. The braze layer thickness was correlated to the fracture strength for each test bar in order to determine the fracture strength as a function of the braze layer thickness.

The microstructures of the brazed joints and the fracture surfaces were examined with an optical microscope and a scanning electron microscope (SEM). Phase analysis of the brazed joints and fracture surfaces was also performed using energy dispersive spectroscopy (EDS) in order to determine the distribution of phases in the braze alloy and search for possible interface reaction products.

The electrical properties of brazed joints and monolithic samples were measured as a function of temperature. The test samples were cut and polished to a thickness of 2.0 ± 0.5 mm. The braze samples were cut with the braze layer centered in the sample. Monolithic samples were cut from as-received PMN that had not been subjected to the brazing heat treatment.

The samples were polished to the desired thickness and then electroded with silver electrode paste. The electrode paste was dried at 100°C for approximately 3600 s. The capacitance and dielectric loss were measured from 120°C to −10°C at a cooling rate of 0.03°C/s. Excel spreadsheets were used to calculate the dielectric constant (K) values from the capacitance (C) values and dimensions according to the formula:

$$K = \frac{Cd}{\varepsilon_0 A}$$

where C is capacitance, d is the thickness, ε_0 is the permittivity of free space and A is the electroded area of the PMN dielectric material [11].

3. Results and discussion

The fracture strengths of the brazed test bars varied from approximately 4 to 50 MPa with an average of 19 ± 11 MPa. The fracture strength of each test bar as a function of silver thickness is plotted in Fig. 2. The fracture strengths of the monolithic test bars varied from 38 to 54 MPa with an average strength of 46 ± 6 MPa. The most likely explanation for the lack of high strength joints is the large coefficient of thermal expansion (CTE) mismatch between PMN and silver. Approximately 20 percent of the test bars (8 out of 46) fractured in the bulk PMN, at a distance of 0.5 mm or greater from the braze layer. The majority of these test bars had the highest fracture strengths. The test bars which fractured in the PMN were not affected by thermal stresses in the braze joint region, since thermal stresses occur due to a mismatch in the thermal expansion coefficients of silver and PMN. The thermal stresses can create microcracks, which may act as fracture initiation sites. The joints that failed in the PMN fractured at flaws present in the bulk PMN, which may have formed during cutting or polishing of the test bars. The high fracture strengths of these test bars indicate that the thermal stresses at the braze joints were relatively low for these test bars and the braze joint had a very high strength. These test bars were produced at a variety of different combinations of silver thickness, temperature and hold time, but the majority (6 of 8) were brazed at 1050°C.

The fracture strengths of the brazed test bars were grouped according to the silver layer thickness of each test bar. The thickness range of the braze joints was divided into thickness intervals which were 0.05 mm wide and started at a thickness of 0.03 mm. The average strength for each thickness interval is shown in Fig. 3, which shows that the silver thickness did not have a significant effect on the strength of the PMN test bars. The fracture strength did vary slightly, but stayed within one standard deviation of the mean for each thickness interval. The larger standard deviations for the larger silver thickness intervals are due to a smaller number of test bars in those intervals.

The parameters of temperature and hold time did not have a significant effect on the fracture strength. The strength is plotted as a function of isothermal hold time and temperature in Fig. 4. The variation of the fracture strength with both parameters is well within the experimental error. No optimum brazing conditions could be determined from this study. The fracture strengths were relatively constant over the entire range of silver thickness, temperature and hold time.

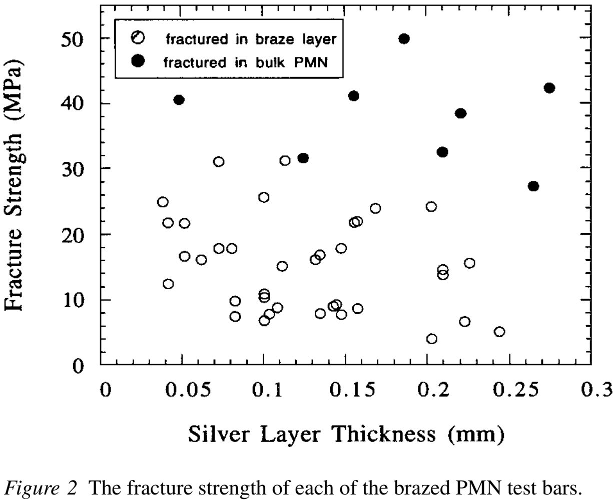

Figure 2 The fracture strength of each of the brazed PMN test bars.

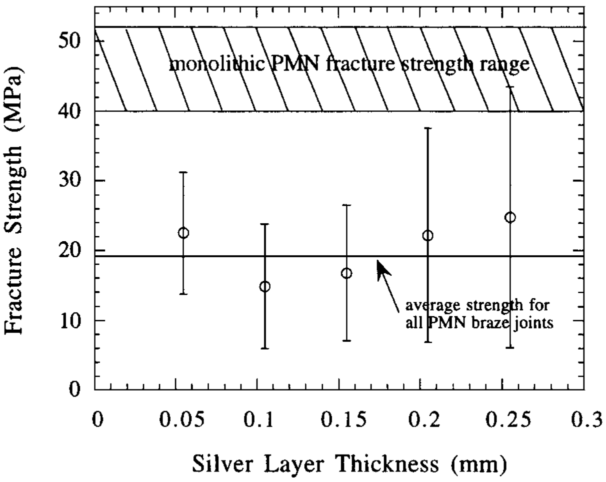

Figure 3 The average fracture strength for each silver thickness interval. The error bars represent ± one standard deviation of the mean.

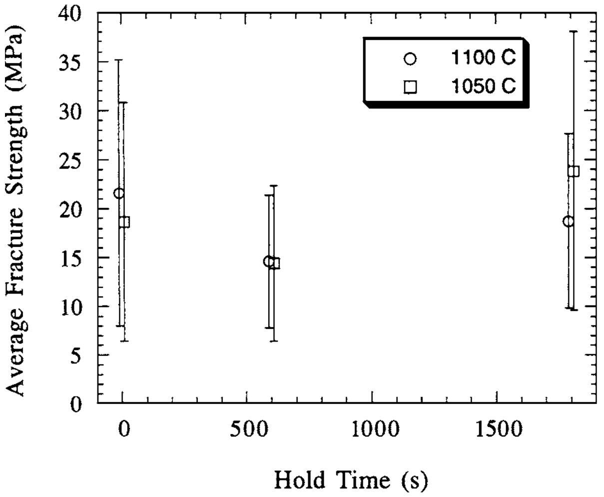

Figure 4 Average fracture strength as a function of hold time for PMN test bars brazed at 1050 and 1100°C. The error bars represent ± one standard deviation of the mean.

A typical PMN braze joint is shown in Fig. 5. No continuous copper oxide layer was observed in any of the joints. The copper oxide formed small second phase regions within the silver layer. A small number of these second phase regions were present at the surface of the PMN. The copper oxide did not react with the PMN to form a chemical bond or diffuse into the PMN. A continuous, crack-free interface was formed between the silver and the PMN due to the intimate contact between the molten silver and the surface of the PMN without the formation of a significant reaction product layer. The molten silver also flowed into pores in the surface of the PMN during brazing. The mechanical interlocking due to pore filling may have increased the joint strength above the strength obtained from the intimate contact between the PMN and the silver at the interface. Two types of fracture were observed in the brazed test bars. The first type was fracture

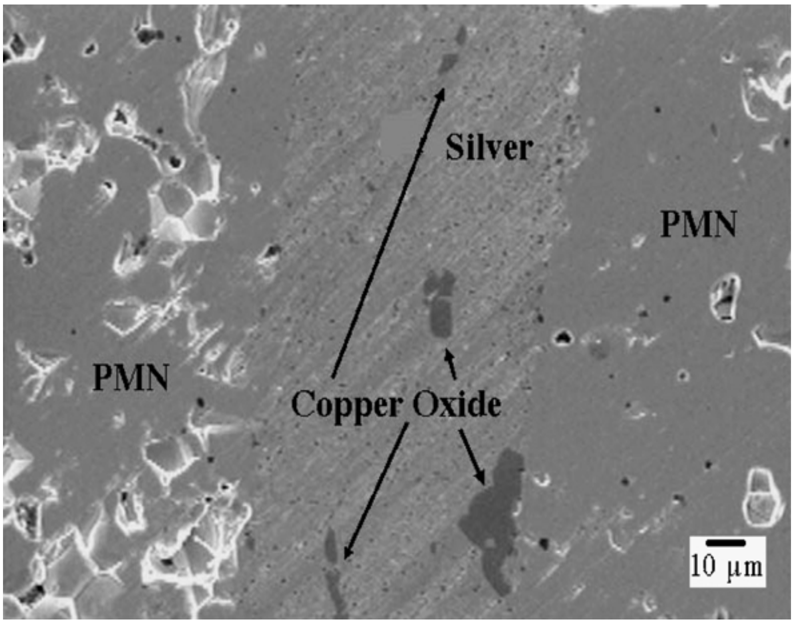

Figure 5 A typical silver/copper oxide braze between two PMN bars. The joint has been polished to a 1 μm surface finish.

in the PMN away from the braze layer. The majority of the test bars (38 out of 46), approximately 80 percent, failed at or directly adjacent to the braze/PMN interface. Many fractures occurred in the braze layer, or directly adjacent to the braze layer. The majority of the fractures appear to have initiated at the braze interface and continued at least partially through the PMN adjacent to the braze layer.

The electrical measurements show a small change in the dielectric constant between each set of samples. These changes indicate that the brazing had only a minor effect on the PMN microstructure and support the SEM observations that an insulating reaction product layer did not form at the PMN/braze alloy interface. Diffusion of silver, lead loss, oxygen loss or the formation of a second phase in the PMN are all possible explanations for the observed changes in the electrical properties of the PMN.

An increase in the maximum dielectric constant ($K_{\max}$), of approximately 1500 at 1 kHz, between the as-received and the monolithic samples was observed. The as-received samples were cut from PMN that was not subjected to a brazing heating cycle. The monolithic PMN samples were cut from PMN that had been subjected to the same brazing heating cycle as the brazed samples. The $K_{\max}$ decreased, by approximately 1100 at 1 kHz, between the monolithic and the braze samples. The temperature at which $K_{\max}$ occurs (T_c) also changed for each set of samples. The T_c increased by approximately 4°C at 1 kHz between the as-received and the monolithic samples. The T_c decreased by about 3°C at 1 kHz between the monolithic and the braze samples. The change in T_c was significant for these samples. These changes follow the general trends of previous studies concerning the effects of silver on PMN [12, 13]. The values of $K_{\max}$ and T_c are also frequency dependent. The values at 1 kHz are shown for a number of samples in Table I. Curves of the dielectric constant as a function of temperature are shown in Fig. 6. The dielectric loss was measured to be less than 0.12 for all the samples that were tested.

TABLE I The calculated $K_{\max}$ and T_c values for a number of PMN samples

Brazing conditions			Electrical properties	
Temperature (°C)	Hold time (s)	Ag thickness, (mm)	$K_{\max}$	T_c (°C)
As-received	–	Monolithic	9100	11.7
As-received	–	Monolithic	8000	10.0
1050	1800	Monolithic	10600	15.8
1050	1800	0.15	8900	15.2
1100	600	Monolithic	10900	16.1
1100	600	0.25	9900	14.9
1050	0	Monolithic	9600	17.3
1050	0	0.15	8900	11.4
1100	1800	Monolithic	4200	13.8
1100	1800	0.25	11900	9.1

The samples from the test bar brazed at 1100°C for 1800 s with a silver thickness of 0.25 mm exhibited results that did not follow the general trends observed for the other samples. Small amounts silver or copper oxide may have diffused into the PMN and had an effect on the electrical properties. No silver or copper oxide were detected in the PMN within the detection limits of the EDS scans, which was approximately 0.5 weight percent. The brazing conditions of this sample had the highest temperature and longest hold time. The silver did not affect the joints as much at the lower temperature or at shorter hold times. The observed results may also be caused by lead loss or by oxygen loss due to a change in the oxidation state of lead. The density of the samples decreased, by roughly 7 percent, after brazing from 8.0 to 7.5 g/cm^3. The formation of a second phase in the PMN at 1100°C and 1800 s hold time could also cause the observed results.

Additional research is needed to explain the bonding and the effects of the braze alloy on the electrical

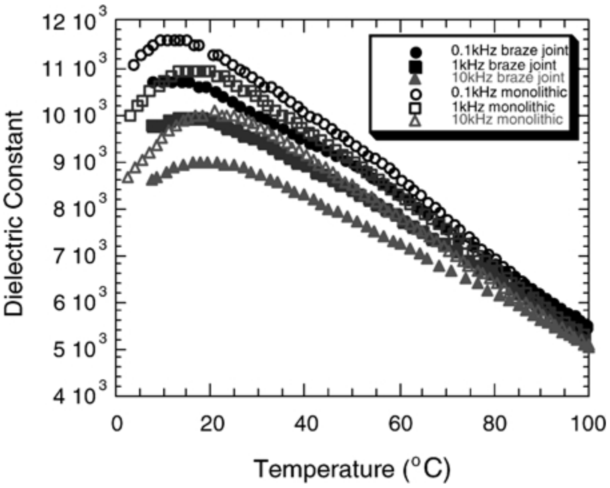

Figure 6 Dielectric constant as a function of temperature for monolithic and brazed samples produced at 1100°C with a 600 s hold.

properties. A study of the wetting behavior of PMN by silver and silver/copper oxide alloys should be performed. Future experiments with the brazing of PMN should also study the diffusion of silver into the PMN and the control of lead loss during brazing. Studies should also be performed to determine the magnitude of the residual stress caused by CTE mismatch.

4. Conclusions

Silver/copper oxide braze alloys were used to bond PMN with moderate joint strengths (19 ± 11 MPa, or approximately 40 percent of the fracture strength of monolithic PMN). The thickness of the silver layer, in the studied range of 0.04 to 0.28 mm, has only a small effect on the strength of the joints. A continuous copper oxide layer was not found at the PMN interface. The dielectric constant decreased slightly between the monolithic and brazed samples and the temperature at which the maximum dielectric constant occurred also decreased slightly. These small changes in the electrical properties should not pose any significant obstacle to the use of these braze alloys in commercial applications of PMN and other similar perovskite ceramics.

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