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Wettability of electrode metals on barium titanate substrate

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The wettability and bonding strength between electrode metals and dielectrics are very important for internal electrodes, terminations, and soldering of multilayer ceramic passive components. In this work, the contact angles of electrode metals, including Pb, Sn, Au, Ag, Ag/Pd, and Cu on $BaTiO_3$ were measured. Results showed that the addition of Pd into Ag significantly reduced the contact angle of Ag on $BaTiO_3$ substrate. The wettability of noble metals (Ag and Au) is nearly independent of the partial pressure of oxygen, under the circumstances of the investigated oxygen partial pressure and within the accuracy of the contact angle measurement. However, molten Cu changes its contact angle drastically when using purified Ar (102°) instead of as-received Ar (89°), and in an air atmosphere (64°). The work of adhesion, according to Young-Dupré equation, was also calculated for these metals. Results were compared with those on ZrO_2, SiO_2 and Al_2O_3. © *2001 Kluwer Academic Publishers*

1. Introduction

The bonding strength of a metal-ceramic interface is very important for many electrical and mechanical structures. Examples include multilayer capacitors and transducers, metallized hybrid microcircuit substrates, solid fuel cells, metal-ceramic composites, and Si_3N_4 turbocharger rotors joined to metal shafts [1, 2]. Bonding between materials is related to the interfacial energies. Usually, when bonding occurs, the overall energy of a system is lowered as the ceramic and metal are brought together and an interface is formed [3]. The change in energy associated with the interface formation depends on the surface energies of the ceramic and the metal as well as the energy that causes the physical bonding. If a chemical reaction is involved, the system's energy will be lowered further, and a chemical bonding is achieved. Chemical reactions occurring at an interface usually enhance the wetting, and thus adhesion.

The physical interaction between a metal and a ceramic can be characterized by the work of adhesion, W_{ad}. When clean, defect-free surface is brought into contact, energy is released in accordance with the Dupré equation [4, 5]:

$$W_{ad} = \gamma_c + \gamma_m - \gamma_{mc} \tag{1}$$

where γ_c, γ_m, and γ_{mc} are the surface energies of ceramic, metal, and metal-ceramic interface. Direct measurement of W_{ad} is not possible. In practice, W_{ad} is deduced by the measurement of a contact angle, θ, which is established using the sessile drop method. This method is based on the formation of a droplet of liquid metal on a solid substrate in an inert atmosphere (Fig. 1). In this case the following equation holds [5, 6]:

$$\gamma_c = \gamma_{mc} + \gamma_m \cos\theta \tag{2}$$

Combining equations 1 and 2 produces the Young-Dupré equation:

$$W_{ad} = \gamma_m(1 + \cos\theta) \tag{3}$$

The interfacial energies for liquid metal-ceramic and solid metal-ceramic are related. In general, the surface energy of a metal increases as the metal solidifies by ≈13% [3, 7]. Therefore, the interfacial surface energy, as well as the W_{ad}, of solid metal-solid ceramic can be calculated using $d\gamma_c/dT$ and $d\gamma_m/dT$, and a 13% correction for metal solidification.

Wettability studies of metals on SiO_2, AlN, ZrO_2, SiC, Al_2O_3, and rare earth oxides have been reported [8–12]. However, very little information concerning the

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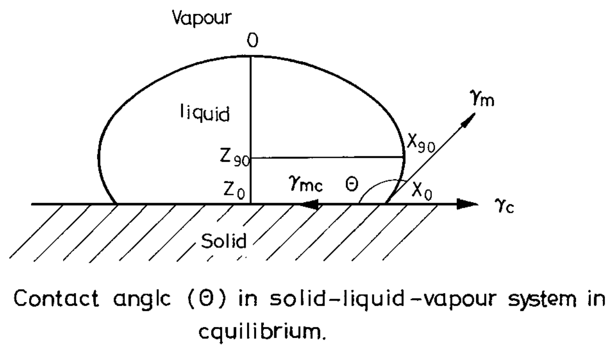


Figure 1 Configuration of a droplet of metal on a solid substrate.

wettability of metals on dielectrics is available in the literature [13]. The bonding strength between electrode metals and the dielectric is very important for internal electrodes, terminations, and soldering of MLC capacitors. If the electrode does not form a closed joint with the ceramic, it may contribute a parasitic capacitance to the capacitor. In addition, a low permittivity layer between the electrode and the ceramic significantly reduces the overall capacitance, especially when the dielectric layers become thinner.

In this work, the contact angle and W_{ad} of several electrode metals, including Pb, Sn, Au, Ag, Ag/Pd, and Cu, on $BaTiO_3$ were measured. Ni was not included in the experiment, even though it is a commonly used electrode. This is due to the instability of $BaTiO_3$ ceramic surfaces occurring at temperatures higher than the melting point of Ni (1453°C). After wetting experiments, the interfacial microstructure was also examined. The correlation of these results is evaluated especially with a view to their practical applications.

2. Design of the apparatus

Fig. 2 depicts the experimental arrangement. Samples were heated in a tube furnace utilizing $MoSi_2$ heating elements. The temperature was monitored with a Pt-Pt10%Rh thermocouple, which was calibrated against a standard thermocouple. The temperature of the substrate was controlled to ±2°C. The reaction tube was made of Al_2O_3. An optical-grade quartz window through which the sample could be observed and photographed was sealed to one end of the reaction tube.

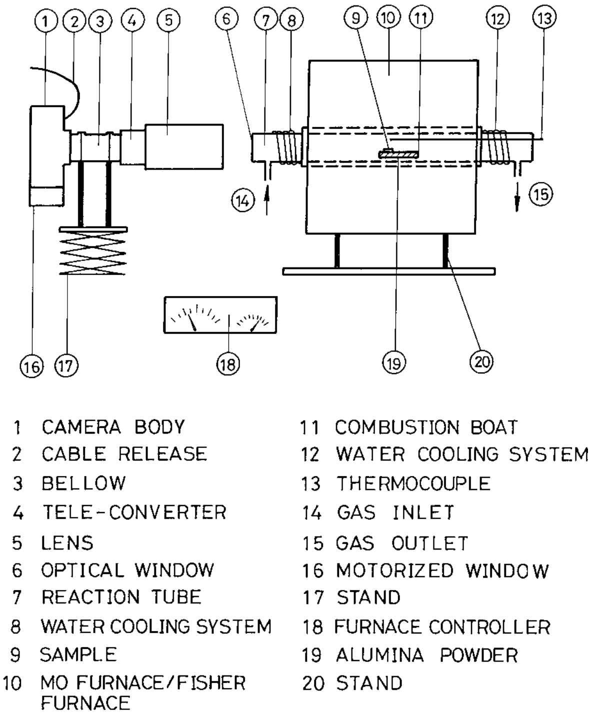


Figure 2 Arrangement for contact angle measurement.

An inert atmosphere was achieved by flowing argon gas over the sample. The Ar was scrubbed through a Drierite (granular $CaSO_4$) to remove H_2O, through an Ascarite to remove CO_2, through a Mg trap at 420°C to remove O_2, and through an active carbon to remove hydrocarbon materials.

3. Experimental procedure

High purity (TAM-HPB, 99.99%) and high density (>99% theoretical density) $BaTiO_3$ substrates were polished with sandpaper and diamond. The final polish was achieved with 0.05 μm diamond paste. After rinsing with deionized water, the substrates were cleaned in an acetone bath for 20 min using ultrasonic cleaner. Approximately 0.02 cm^3 of high purity metal (>99.99%) was then placed on a cleaned surface of polycrystalline $BaTiO_3$, which rested on a Pt sheet held in an Al_2O_3 boat. After careful placement of the Al_2O_3 boat in the furnace, the reaction tube was flushed with the inert gas for 3 h before heating.

Observation of the sample shape was possible by its emitted light at elevated temperatures. The shape of the liquid metal resting on the solid $BaTiO_3$ was photographed when the desired temperature was reached and held for 30 min. By assuring that the $BaTiO_3$ surface was horizontal, the system was not vibrating, and the atmosphere was consistently controlled, the contact angle could be repeatedly measured with an accuracy of about ±1°.

The solidified sessile drop samples were mounted in an epoxy, and then cut through the cross section using a diamond saw. These specimens were carefully polished and examined by SEM, microprobe, and EDAX.

4. Results and discussion

Since the wetting angle (θ) in all the systems examined was greater than 90°, the sessile drop had a spheroidal shape. Contact angles were calculated from the drop dimemsions using the tables of Bashforth and Adams [14]. The measured contact angles in the $BaTiO_3$-liquid metal systems, together with literature data on the surface energies of the liquid metals Au, Ag, Cu, Pb, and Sn in Ar atmosphere (Table I) were used for the calculation of W_{ad} (Equation 3) [9, 10]. Results are listed in Table II. Plots of θ and W_{ad} with respect to temperature are shown in Figs 3 and 4.

TABLE I Surface energies of electrode metals in their liquid state [9, 10]

Materials	Surface energy (mN/m)	
Ag	910–0.17 [T(°K)-1234]	$T \geq Tm = 1234$°K
Au	1105–0.28 [T(°K)-1336]	$T \geq Tm = 1336$°K
Cu	1320–0.28 [T(°K)-1356]	$T \geq Tm = 1356$°K
Sn	551–0.09 [T(°K)-505]	$T \geq Tm = 505$°K
Pb	468–0.13 [T(°K)-600]	$T \geq Tm = 600$°K

TABLE II Results of contact angle θ and calculated work of adhesion W_{ad} for various electrode metals on $BaTiO_3$ substrate

Metal	Temperature (°C)	γ (mN/m)	θ	W_{ad} (mJ/M^2)
Ag	1000	903	139	222
	1050	895	137	240
	1100	886	134	271
	1150	878	128	337
Au	1100	1095	124	483
	1150	1081	119	557
	1200	1067	116	599
Cu	1085	1319	103	1022
	1100	1315	102	1042
	1150	1301	93	1233
Pb	350	465	145	85
	550	439	140	103
	750	413	136	116
Sn	250	549	149	78
	450	531	143	107
	750	504	138	130
70 Ag/30Pd	1200	1087	92	1049

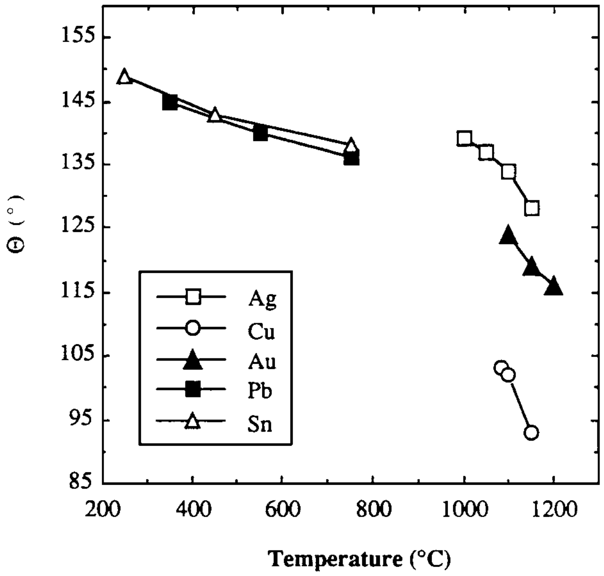


Figure 3 Contact angle θ on $BaTiO_3$ of various electrode metals versus temperature.

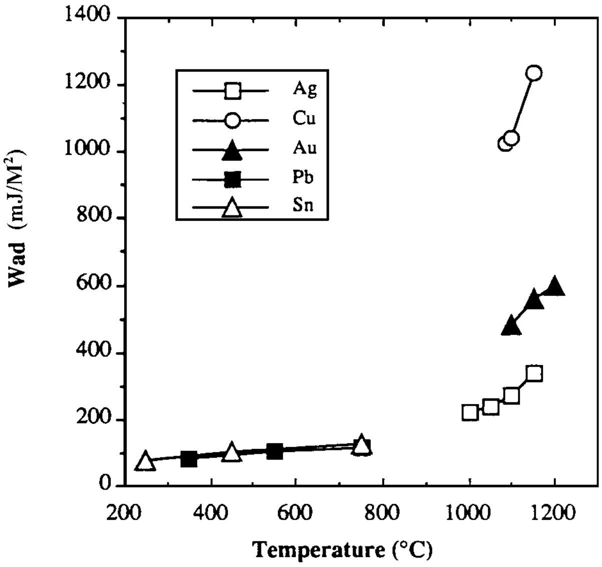
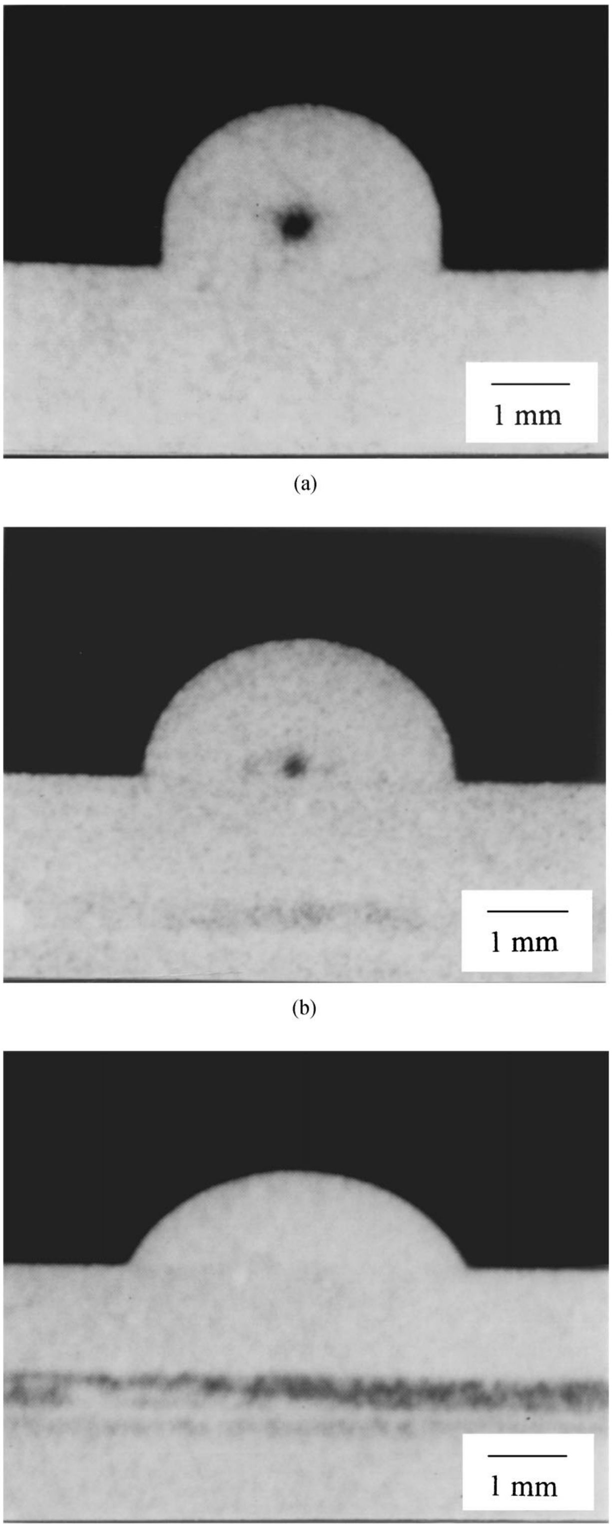


Figure 4 Work of adhesion θ on $BaTiO_3$ of various electrode metals versus temperature.

As indicated in Fig. 3, Ag, Au, Cu, Pb, and Sn do not wet the $BaTiO_3$ ceramic (i.e., $\gamma_{mc} > \gamma_c$). In addition, the contact angle decreases with increasing temperature. Pb and Sn have higher contact angles, but Cu has a lower contact angle. Fig. 4 indicates that metals with higher melting points and higher surface energies, such as Cu, have higher values of W_{ad}. According to Weyl's model [15], the larger size and higher polarizability of oxygen anions compared to the cations causes a reconstruction



(a)

(b)

(c)

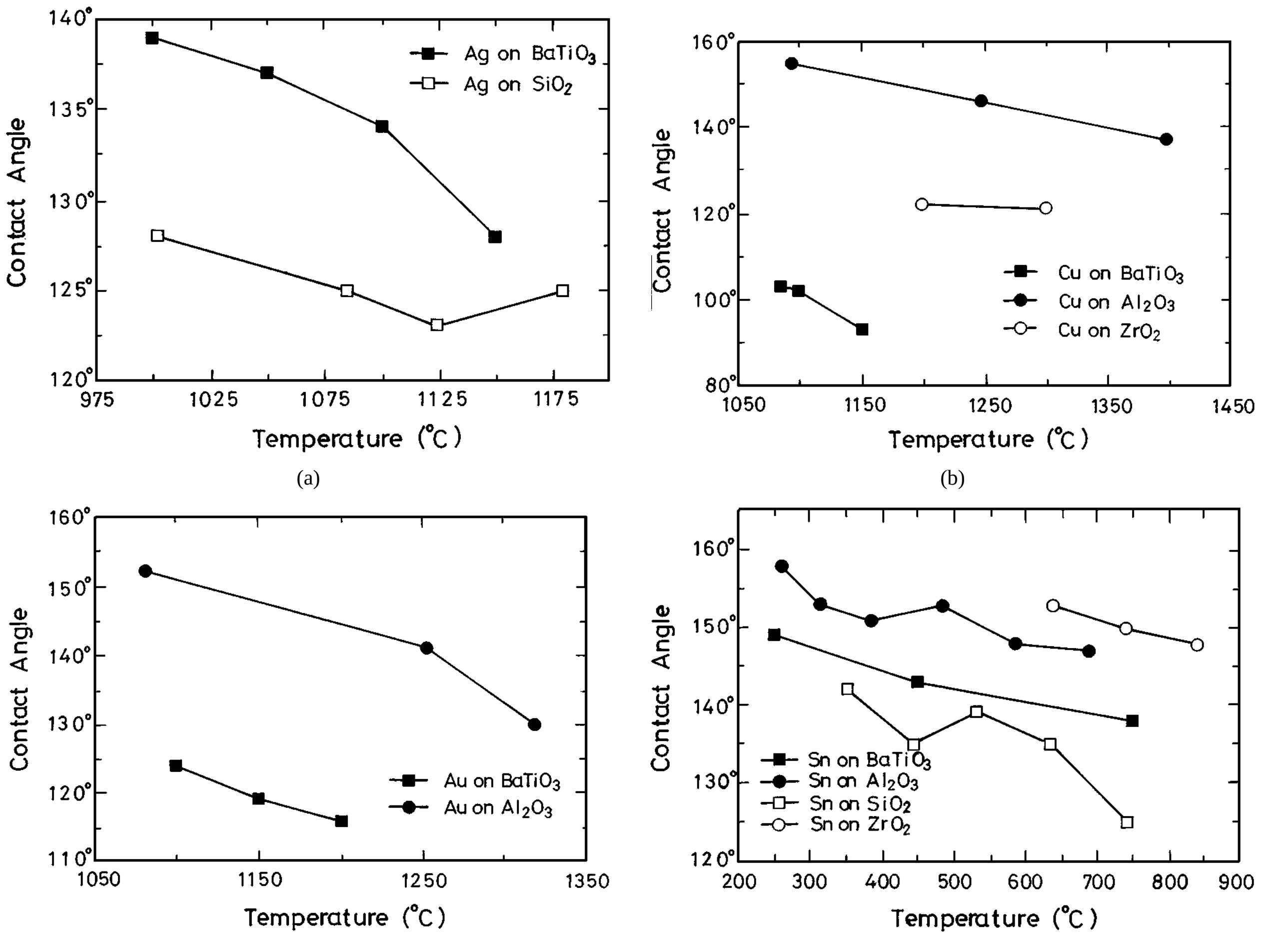
Figure 5 Photographs of the equilibrium droplet of molten Cu on $BaTiO_3$ substrate under (a) purified Ar and (b) as-received Ar, and (c) air atmospheres at 1100°C.

of the oxide surface with the displacement of the cations from the surface to the interior. A double layer is created in which the extreme outer layer contains only anions. It is generally agreed that the adhesion of metals to oxides is essentially governed by the interaction of the metal atoms with oxygen anions. Humenik and Kingery [16] suggested that the W_{ad} of liquid metals on oxide surfaces increase with an increasing affinity of the metal for oxygen (i.e., with increasing standard free energy of oxide formation).

Pb, Sn, and their alloys are used as internal electrodes in MLC capacitors using the injection technique, owing to their low cost [17]. However, results show that these metals have very high θs and low adhesion on $BaTiO_3$, as shown in Table II. Therefore, it is difficult to impregnate the Pb-Sn alloy into the thin interstices left by fugitive ink processes, resulting in electrode discontinuities. This, in turn, causes a wide variability in capacitance and poor reliability. Due to these considerations this method would not be acceptable for capacitors requiring small capacitance tolerance and high volumetric efficiency.

Pb, Sn, and Ag are also commonly used for end termination and solder materials. Because of the poor wetting and adhesion of these materials, glass frits are typically added to increase their wettability on the ceramic [18, 19]. However, the additions of glass frits generally compromise the conductivity of the metallic film, and can also lead to undesirable chemical reactions and interdiffusion between components. Results of this study show that with the addition of Pd to Ag, θ dramatically decreases and thus W_{ad} increases. This is probably due to the higher oxygen affinity of Pd compared with that of Ag. A number of investigators have shown that Ti additions to a metal in contact with an oxide result in a sharp decrease in θ. The Ti concentration at the liquid phase-ceramic interface was shown to be much higher than that within the liquid phase [11]. Another reason for the low θ may be related to the decrease in lattice parameter mismatch for the 70Ag/30Pd alloy. In Klomp's study [3], W_{ad} of the (111) plane of various metals on the (0001) plane of Al_2O_3 increased with decreasing lattice misfit. The original purpose of using Pd additions to Ag conductors was to reduce solder leaching and Ag migration under bias in humid environments for MLC applications. The results of the current study show that, in addition to these advantages, Ag/Pd shows a lower contact angle and higher adhesion to $BaTiO_3$ ceramic compared with pure Ag.

The θ of base metals on $BaTiO_3$ is very sensitive to pO_2 at high temperatures. Fig. 5 shows photographs of the equilibrium droplet of molten Cu on the $BaTiO_3$ substrate under purified and as-received Ar and air atmospheres at 1100°C. The molten Cu changes its θ drastically when using purified Ar (102°) instead of as received Ar (89°), and in an air atmosphere (64°). However, the study of the equilibrium droplet of molten Au on the $BaTiO_3$ substrate at 1100°C indicates that the θ of Au was not significantly changed under purified Ar (124°) and air (120°) atmospheres. The high sensitivity



(a) (b)

(c) (d)

Figure 6 Wettability of (a) Ag, (b) Cu, (c) Au, and (d) Sn on $BaTiO_3$ compared with those on ZrO_2, Al_2O_3, and SiO_2, from the literature [8, 10].

of the θ for base metals subjected to small amounts of oxygen is due to their high oxygen affinity. Under higher oxygen content, an eutectic melt of CuO and Cu_2O is formed at 1065°C [20, 21], acting as an intermediate layer responsible for bonding between Cu and $BaTiO_3$ and thus increasing its wettability on $BaTiO_3$.

Fig. 6 shows the wettability of Cu, Au, Ag, and Sn on $BaTiO_3$ compared with that on ZrO_2, Al_2O_3, and SiO_2, as cited in the literature [8, 10]. The θ is highest on ZrO_2, followed by Al_2O_3, $BaTiO_3$, and SiO_2, except for Cu. Naidich [22] concluded from his study that the θ of liquid metals is larger on the thermodynamically stable oxides compared to unstable oxides.

The θ and W_{ad} can be taken as indicators of the mechanical integrity of a sintered metal-ceramic interface only if a physical bonding is involved. However, when the nonwetting system has a chemical reaction or interdiffusion, the wettability and strength relation can be inaccurate. Macdonald and Eberhart [23] presented a model that correlates room-temperature strengths and the W_{ad}. Their results did not correlate with actual values because the interfacial microstructure and chemical reaction at the interface had a strong impact on the bonding, and they were not considered in this model. As a result, the interfacial microstructure is a very important factor to adhesion.

Interfacial microstructures were examined using SEM combined with EDS X-ray dot maps. In all cases except the Pb/$BaTiO_3$, SEM showed that the interface was sharp and clean without any apparent reaction. The X-ray mappings confirm that there was no interdiffusion of the metal elements into the ceramics within the detection limits of EDX ($\approx$0.1 wt%). SEM micrograph of the solidified Pb sessile drop on the $BaTiO_3$ ceramic cooled from 750°C showed that there is a Pb diffusion zone in the $BaTiO_3$ ceramic side. SEM observations also revealed that cracking occurs either along the interface or parallel to the interface inside the $BaTiO_3$ ceramic for the Ag/Pd metal system. This is probably due to the mismatch of thermal expansion during the cooling. In MLC capacitors, cracking is a major defect and it strongly affects reliability [24].

5. Summary and conclusions

The contact angle of the pure liquid metals Ag, Au, Cu, Pb, and 70Ag/30Pd on $BaTiO_3$ ceramic was measured over a wide range of temperatures. The corresponding work of adhesion was also calculated using Young-Dupré equation. These tested metals do not wet $BaTiO_3$ in a purified Ar atmosphere. Addition of Pd to Ag significantly reduced the contact angle. SEM and EDS X-ray maps showed that no chemical reaction or interdiffusion of Pd occurred at the interface. The wettability of base metals such as Cu on $BaTiO_3$ is sensitive to residual oxygen. However, the wettability of noble metals such as Au is nearly independent of pO_2 due to the difference in oxygen affinity of the metals, under the conditions of the investigated oxygen partial pressure and within the accuracy of the contact angle measurement.

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