Interfaces and Wetting Properties between PLZT Ceramics and Electrode Metals

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The wetting of (Pb, La) (Zr, Ti)O₃ ceramics with various electrode metals were studied by measuring the contact angle in a vacuum atmosphere. Two kinds of PLZT were used: \( x=0.07, \ y=0.35 \) and \( x=0.12, \ y=0.60 \) in \( (Pb_{1-x}, La_x)(Zr_{1-y}, Ti_y)O_3 \). The metals studied were Ag, Al, In, Sn, Bi and Cu. The metals forming thermodynamically unstable oxides showed low contact angles: 98° with Ag and less than 90° with Cu. The contact angles were dependent on the composition of PLZT. The other metals indicated the obtuse contact angles as large as 140° since the metals forming the stable oxides can not move by being protected with the oxide. The wettability of a metal on the oxide ceramics can be predicted by the redox reactions of metal and a certain element in the ceramics. In and Sn were bonded with the PLZT but not with BaTiO₃.

Key-words : PLZT ceramics, Wetting, Contact angle, Oxidation potential, Electrode metal, Interface, Adherence

1. Introduction

The interfacial issues between an electrode metal and ceramics are important to achieve ohmic contact for an electronic packaging including inner electrodes for a multi-layer ceramics in a basic study and applications as well. The interfacial issues can be treated from the viewpoint of bondability of ceramics and metal with its mechanical strength. There are a lot of studies for bondability relating to the structural ceramics including the development of materials for joining between them.¹,²

The selection of proper metal for joining has been mainly based on the experiences at the industries. Wetting of ceramics is one of characteristics for their bondabilities. In application to the electronic ceramics, a metal with glass frit is usually used for the bonding of ceramics with an electrode metal since a metal does not wet ceramics generally. Basic studies of BaTiO₃³ and Pb(Zr, Ti)O₃ ceramics⁴ (hereafter PZT) with electrode metals including glass frit have been studied by Sugihara and Okazaki.

For the purpose of characterizing wetting, a reactivity parameter \( P \) is introduced by the relationship between the difference of oxidation potentials of a metal and a selected element in a ceramic, and ionic radius of the metal. The values of \( P \) were found to have the relation with a contact angle.⁴ There has not been a wetting study of (Pb, La) (Zr, Ti)O₃ (hereafter, PLZT) with an electrode metal. This paper describes the wetting study of PLZT with the electrode metals such as Ag, Al, In, Sn and Cu in a vacuum and the qualitative evaluation of adherence properties in each case. Furthermore, the cross-sectional interfaces will be evaluated and the reactivity parameter \( P \) will be discussed on the PLZT wetting as compared with PZT.

2. Experiments

The substrates of wetting experiments were \( (Pb_{1-x}, La_x)(Zr_{1-y}, Ti_y)O_3 \) with different compositions such as \( x=0.07, y=0.35 \), and \( x=0.12, y=0.60 \). These PLZT wafers were fabricated by Hayashi Chemical Co. Ltd. They were cut in a size of 14×14 mm and thickness of 0.5 mm. The surface roughness of each specimen is 0.6 \( \mu m \) approximately.

The electrode metals were Ag, Al, In, Sn, Bi and Cu. The purity of every metal was higher than 99.9% and the weight was 60-100 mg in a lump. The purity of every metal was higher than 99.9% and the weight was 60-100 mg in a lump.

The experiments were carried out using a high temperature surface tension measuring equipment as shown in Fig. 1. The atmosphere was a vacuum (4-5×10⁻³ Pa), and the temperatures were general-
ly raised up to higher than the melting point of each metal. On heating, the photographs were taken with a telescope to measure the contact angle. After wetting experiments, the system was mounted into resin to cut with a diamond cutter, then followed by the analysis of the cross sectional interface with a SEM and an EPMA.

3. Results and discussion

3.1 Wetting properties

Figures 2(a) and (b) show the wetting properties at various temperatures with the contact angle for every system of PLZT (7/65/35) and PLZT (12/40/60). The contact angle of Cu was 68° on PLZT (12/40/60) and 73° on PLZT (7/65/35). Since the contact angle can be measured by photographs with an error of 2°-3° in a good producibility, the difference in the contact angles of the system Cu/PLZT is considered to be significant. But it could not be explained why the asymmetrical angle at left/right on the photograph was caused in the system of Cu/PLZT (12/40/60). Ti is an active element and changes the valence from +3 to +4 and vis-a-vis in oxide depending on the ambient conditions so that it has been used as bonding media between ceramics/ceramics or ceramics/metal. However, there were not big differences in the contact angle from that of the other metal such as Al, In and Sn, being independent upon the amount of Ti. Although Al on PLZT (7/65/35) did not show any round shape at 700°C, the shape became round to be a contact angle of 120° with increasing temperature up to 980°C, and the contact angle became smaller with increasing temperatures in the system of Al/PLZT (12/40/60) as well. The fact can be explained by the phenomenon that the oxide films on Al were partially eliminated. These phenomena will be elucidated by the larger amount of Ti in PLZT (12/40/60) rather than an amount of La.

Generally, Sn and Al have the Gibbs free energy for the oxide formation as large as 105 and 220 kcal/g·mol, respectively, compared with the value smaller than 50 kcal/g·mol in Cu and Ag, which indicates that Al and Sn can be easily oxidized to form more stable oxides than Ag and Cu. Furthermore, Fig. 3 shows the changes of the contact angle of Ag with the composition of PLZT in a vacuum. PLZT (12/40/60) was rather wetted with Ag, indicating the least contact angle of 98° among those of the other composition of PLZT. It may be due to the largest amount of Ti in the composition as well as the Cu/PLZT system.

Figure 4 indicated the cross sectional interface be-

Fig. 2. Contact angles of various metals on PLZT in vacuum. (a) PLZT (7/65/35), (b) PLZT (12/40/60).

Fig. 4. EPMA analysis at the interfaces of Cu/PLZT.

Fig. 3. Contact angles of Ag on PLZT with different compositions in vacuum. (a) PLZT (7/65/35), (b) PLZT (9.5/65/35), (c) PLZT (12/40/60).
between PLZT and Cu, measured on Cu, Zr, Ti and La with EPMA. Neither Zr nor Ti migrated toward the interface whereas La seemed to be gathered at the position closer to the interface than Zr and Ti, although the EPMA results have not quantitatively been elucidated yet. The observation reveals that Cu did not react with any element in the ceramics at the interface and did not migrate into PLZT as shown in a SEM photograph (Fig. 5).

Wettability of PLZT (7/65/35 and 12/40/60) with the metals are summarized in the periodic table as shown in Table 1. The small contact angle with Bi will be explained from the fact that Bi has the lowest oxidation potential among other metals examined in this study on the group of VA, WA and VA in the periodic table and also Bi with the chemically-active characteristic, which can change the valence readily, can be easily oxidized by oxygen from PLZT, where Ti (+4) will be reduced to Ti (+3).

The tendency in the periodic table from the view point of the contact angle must be relating to the wettability of those metals on the oxide ceramics. The contact angle will be described by the reactivity parameter P which associates with the difference of oxidation potential between metal and a certain element in the ceramics, and an ionic radius of metal. P is defined as follows,

\[ P = \frac{(E_{Ti} - E_m)}{R_m} \]  

where \( E_{Ti} \) and \( E_m \) indicate the oxidation potential of Ti and a metal, respectively, and \( R_m \) means the ionic radius of a metal. \( E_{Ti} \) in Eq. (1) is selected as the oxidation potential energy in the PLZT since Ti is the element with the smallest ionization energy in the constituents of the ceramics. In the system of Cu/PLZT, for instance, the oxidation potentials are \(-0.337\) V (defined at Cu (solid) \(2e^- = Cu^{2+}\)) and \(+1.63\) V with Ti\(^{2+}\), respectively. PLZT will be rather reduced to provide oxygen to Cu. And the ionic radius of Cu\(^{2+}\) is 0.057 nm, then \( P \) is calculated to be 34.5 by the Eq. (1).

The metals except for Ag and Cu can easily form the oxides by oxygen from the ceramics in a vacuum, and their oxides are more stable than the oxides of Ag and Cu, comparatively. The group of stable oxides of metals will not wet the ceramics to show the obtuse contact angle regardless of the compositions of PLZT. The migrations of Zr and Ti in the ceramics into a melted metal will be hindered by the stable oxide formation on the surface of the metal. The contact angles were plotted against a reactivity parameter \( P \) for each metal in the system of metal/PLZT as illustrated in Fig. 6. These results were essentially similar to those in the system of metal/PZT, showing the parabolic curve of contact angles with the reactivity.

### 3.2 Adherence of metal with ceramics

![Fig. 5. SEM photograph of the interfaces of Cu/PLZT scanned by Cu.](image)

![Table 1. Contact angles of metal/PLZT in the periodic table (angle/degree).](table)

<table>
<thead>
<tr>
<th>Metal</th>
<th>PZT</th>
<th>PLZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Sn</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Bi</td>
<td>O</td>
<td>X</td>
</tr>
<tr>
<td>Ag</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Al</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

![Fig. 6. Dependence of contact angle on reactivity parameter, \((E_{Ti} - E_m)/R_m\) where \( E_{Ti} \) and \( E_m \) indicate the oxidation potentials, and \( R_m \) means an ionic radius of a metal.](image)

![Table 2. Adherence of metal on oxide ceramics of BaTiO\(_3\), PZT and PLZT (O: adhered, X: not adhered, --: none available).](table)
Table 2 shows the qualitative evaluation of adherence for every metal with PLZT (7/65/35) and (12/40/60) as compared with BaTiO3 and PZT. Sn and In bonded with PLZT although they did not wet the ceramics to show the obtuse contact angles. The definition of a bonding here means that a metal after wetting experiments does not come off when the system is vertically cut with a diamond wheel rotating at the speed of 150 rpm. It is also interesting that Sn was not bonded with BaTiO3 and PZT ceramics. This is the case that a bonding happens even though a metal does not wet the oxide ceramics. The strength of bonding, however, will be weak in this case because the work of adherence (W) becomes smaller when the contact angle is obtuse as described in the following Young’s equation,

$$W = \gamma (1 + \cos \theta)$$  \hspace{1cm} (2)

where $\gamma$ is a surface energy of a metal and $\theta$ is a contact angle. Therefore, it is sure that the wetting is necessary for strong bonding of a metal with ceramics.

As described in Section 3.1, the metals studied here did not wet the PLZT except for Cu. However, the adhesion was observed although the mechanism was not elucidated in this study. The analysis by a SEM and an EPMA of the interfaces between the ceramics and the metals reveals neither the mutual diffusion nor inter layer formation through reactions. In the bonding of Ag with Si single crystal, the formation of epitaxial interface was revealed by TEM analysis. Ag reacted with Si in eutectic, and wetted Si to show a contact angle of 42° at 950°C. The examination at an atomic level is necessary to discuss the mechanism of adhesion of a metal with ceramics although it is difficult to clear up unless there are distinguishing mutual diffusions, reaction layers and epitaxial lattice structures.

4. Conclusion

1. Wettability of metal on PLZT is essentially the same as wetting on PZT although there are slight differences of contact angle between PLZT and PZT substrates.

2. Wettability of a metal on an oxide can be predicted by the reactivity parameter defined by preferable reactions of a melted metal with a particular element in a substrate ceramics.

3. Ti may lead to the improvement for wetting of Ag and Cu on PLZT.

4. Sn and In adhered to PLZT as well as Ag and Cu although Sn was not bonded with the other ceramics such as BaTiO3 and PZT that Ag and Cu did. The bonding mechanism should be studied and classified on every electrode metal in order to predict their bonding strength.

References