Liquid-phase oxidation joining of oxide ion conducting ceramics via Al/heat resistant alloy/Al multilayer interlayers

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A joining technique for oxide ion conducting ceramics, such as yttria-stabilized zirconia, was developed, utilizing oxidation of transiently formed aluminum melt. Two yttria-stabilized zirconia (YSZ) blocks were joined via Al/Ni alloy/Al interlayers at 1273 to 1473 K for 3.6 to 28.8 ks in a vacuum (< 0.2 Pa) with an applied load of 80 MPa. The average fracture strength increased with increasing the joining time and temperature. A strong four-point bend strength of 170 MPa was obtained for the specimen joined at 1473 K for 14.4 ks, which was fractured at YSZ block. Alumina interlayer, which is expected to act as a protective layer for further oxidation of Ni alloy, was formed between YSZ and Ni alloy in the specimen after joining.

Key-words : Joining, Oxidation, Aluminum, Yttria-stabilized zirconia, Ni alloy, Fracture strength

1. Introduction

Joining of oxide ion conducting ceramics is one of the most important techniques for electrochemical applications, such as solid oxide fuel cells (SOFCs), gas sensors, and oxide ion pumps. This study suggests a joining technique for oxide ion conducting ceramics, for example, stabilized zirconia, doped ceria, and doped hafnia, and so on. Many joining techniques have been developed for ceramics, but most of them were for the joining of non oxide-ion-conducting ceramics of silicon nitride and aluminum oxide. Some of the joining techniques for non oxide-ion-conducting ceramics were applied to join oxide ion conducting ceramics, but they could not obtain reliably strong joints for high temperature applications. For example, fully stabilized zirconia ceramics joined using Ni alloy and Ag–Cu–Ti solder as interlayers had a weak fracture strength of 30 MPa, and yttria-stabilized zirconia joined via Ni–NiO eutectic liquid had a joining strength of only 51 MPa by a shear test.

Joining techniques of heat resistant alloys to oxide ion conducting ceramics have also been studied, and strong joints were obtained by diffusion bonding of stainless steel to zirconia (720 MPa by four-point bend test) and diffusion bonding of Ni alloy to zirconia (620 MPa by four-point bend test). However, high temperature annealing resulted in the degradation of the strength to 0 MPa for stainless steel/zirconia and 66 MPa for Ni alloy/zirconia, which was caused by void formation at the joined interface.

Figures 1(a) and (b) compare the expected oxygen chemical potentials across the joined interface between alloy and alumina (a) and between alloy and yttria-stabilized zirconia (YSZ) (b). For the joined interface between alloy and alumina (Fig. 1(a)), the chemical potential of oxygen at alloy/alumina interface is low because of low oxide ion conductivity of alumina. Therefore, the alloy is stable even at higher temperatures, resulting in a relatively strong and durable joint. On the other hand, for the joined interface between alloy and YSZ (Fig. 1(b)), the chemical potential of oxygen at the interface is high and therefore several oxides form between alloy and zirconia. These oxides are brittle in some cases, and voids form in the oxide layer during oxidation of some heat resistant alloys. This is one of the reasons why joining between alloy and zirconia is difficult. In this case, oxide ion diffuses along the interface predominantly, not through YSZ, because of low electronic conduction in YSZ, which establishes electrical neutrality while oxide ions diffuse. In order to prevent

Fig. 1. Interface structure and expected chemical potential across interfaces between alloy and ceramics.
the brittle oxide formation and void formation by oxidation, a protective layer is necessary between alloy and YSZ as shown in Fig. 1(c), which is the proposed interface for a strong and durable joint between alloy and YSZ in this study. If the protective layer forms at the interface as shown in Fig. 1(c), the chemical potential of oxygen at the interface of alloy/protective layer decreases, and brittle oxide and void formation can be avoided.

In order to fabricate the interface as in Fig. 1(c), we modified the PTLP (partial transient liquid-phase) joining technique8)–10) to form a protective layer after joining. Figure 2 illustrates the joining mechanism proposed in this study. Before heat treatment, interlayers of Al/heat resistant alloy/Al interlayers were sandwiched by oxide ion conducting ceramics of YSZ blocks. The assembly was heated at a higher temperature than the eutectic point in alloy-Al system, and then the Al interlayers were melted and filled gaps along the YSZ/alloy interfaces and open pores in YSZ blocks. In the idea of conventional PTLP joining, the entire Al melt is dissolved in alloy and no remnant is formed between alloy and ceramics. In this study, some of Al melt is intentionally oxidized to form a protective alumina layer at the oxidation and homogenization step as shown in Fig. 2. Since alumina has high electric insulation, the alumina layer is expected to act as an alternative of the potentially brittle glass seal for planar SOFCs.20),21) The complex interface between YSZ and alumina after the oxidation and homogenization step (see Fig. 2) is expected to form a strong joint by the anchor effect.

Ni alloy (Inconel 600) was used as a heat resistant alloy, because it has excellent high temperature oxidation resistance up to 1450 K and Ni has a high solid solubility of Al from room temperature to higher temperatures as shown in Ni–Al phase diagram (Fig. 3).22) Remnant Al without oxidation could be soluble in the Ni alloy layer, and therefore the transiently formed Al melt and Ni–Al intermetallics are expected to disappear after heat treatment.

2. Experimental procedure

Yttria-stabilized zirconia (YSZ) powder (TZ–8Y, Tosoh Corp.), whose grain size was 50 μm, was sintered by hot pressing at 1773 K for 3.6 ks with an uniaxial applied load of 24 MPa in vacuum (< 0.2 Pa), and annealed at 1673 K for 7.2 ks in air. The sintered YSZ block (relative density: 97%) was cut into blocks of 10 × 10 × 17.5 mm³, and the joining surface (10 × 10 mm²) was polished flat with a diamond plate and polished with 9 μm, 3 μm, and 0.5 μm diamond pastes. Polished blocks were cleaned ultrasonically in acetone, ethanol, and distilled water. Aluminum foils (Nilaco Corp., thickness: 0.8 μm, purity: > 99%) were placed between polished surfaces of the YSZ block and Ni alloy plate (Inconel600, Nilaco Corp., thickness: 50 μm, composition: Ni(+Co): > 72, Cr: 14.0–17.0, Fe: 6.00–10.00, C: < 0.15, Mn: < 1.00, S: < 0.015, Si: < 0.50, Cu: < 0.50 (mass%)). YSZ blocks were joined using Al/Ni alloy/Al interlayers at 1273, 1373, and 1473 K (see dashed lines in Fig. 3), for 3.6 to 28.8 ks in vacuum (< 0.2 Pa) with an applied load of 80 MPa. Joining at 1473 K for 28.8 ks wasn’t carried out, because the joining was completed for 14.4 ks. The joined YSZ block was cut into rectangular beams with the interlayer at the midpoint. A surface of beam was polished down to 0.5 μm diamond paste and beveled with 3 μm diamond paste. The beams were subjected to the four-point bend testing to initiate the failure from the polished surface. Phases on the fracture surfaces were identified by X-ray diffraction analysis, and cross sections were observed by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) with EDS. YSZ blocks joined at 1273 K for 0 ks were also prepared to observe layers between YSZ blocks right after melting of Al and clarify the reaction mechanism during joining at 1273 K.

3. Results and discussion

Figure 4 shows cross sectional SEM images joined at 1273 K and concentration profiles of each element by EDS line analysis on dashed lines. In the all specimens joined at 1273 K for 0 ks to 28.8 ks (Figs. 4(a)–(d)), dark layers were seen between Ni alloy and YSZ. In the dark layer, aluminum and oxygen were detected, indicating that the alumina layer was formed after joining. In the specimen joined at 1273 K for 3.6 ks (Fig. 4(b)), Ni–Al intermetallic layer, in which Ni and Al were detected by EDS line analysis, were observed at the left side of the dark alumina layer. At the left side of the Ni–Al intermetallic layer, chromium-rich phase was observed. The Ni–Al intermetallic layers became

Fig. 2. Mechanism of liquid-phase oxidation joining.

Fig. 3. Phase diagram of Al–Ni system.22)
thinner with increasing the joining time, and the Ni–Al intermetallic layers and chromium-rich phase disappeared at 28.8 ks, with the alumina layer remaining (Fig. 4(d)). The alumina layer is expected to act as a protective layer for further oxidation and an insulating layer for electrochemical applications.

**Table 1.** Fracture Strength of Joined YSZ by Four-Point Bend Test

<table>
<thead>
<tr>
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<th>3.6 ks</th>
<th>14.4 ks</th>
<th>28.8 ks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273 K</td>
<td>&lt; 1 MPa</td>
<td>26 MPa</td>
<td>49 MPa</td>
</tr>
<tr>
<td>1373 K</td>
<td>16 MPa</td>
<td>38 MPa</td>
<td>133 MPa</td>
</tr>
<tr>
<td>1473 K</td>
<td>44 MPa</td>
<td>170 MPa</td>
<td>–</td>
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</tbody>
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Some of the beams with a relatively low fracture strength were fractured at the interface, and the intermediate alloy layers remained on one side of the fractured beams. X-ray diffraction analysis was carried out for the fracture surface with alloy layers (alloy side) and without alloy layers (YSZ side). Table 2 lists phases identified by X-ray diffraction analysis for the Ni alloy side of fracture surfaces after the four-point bend test. Phases identified on the fracture surface of the specimen joined at 1273 K for 0 ks were also shown. This specimen was easily fractured after joining, and therefore was not subjected to the four-point bend testing. In the alloy side of specimen joined at 1273 K for 0 ks, Ni₃Al, Ni₅Al₃, Al₂O₃ were identified in addition to Ni. The Ni₃Al phase disappeared at 1273 K for 3.6 ks, the Ni₅Al₃ and NiAl disappeared at 1273 K for 28.8 ks, and only the polycrystalline Al₂O₃ phase remained on the fracture surface of the Ni alloy layer. These are in good agreement with the phase diagram of the Ni–Al system. (Fig. 3) On the other hand, in the X-ray diffraction pattern from the YSZ side of fracture surface, only peaks for ZrO₂ were identified. Iron-rich compounds such as Fe₂O₃ and Fe₃O₄ could not be identified by XRD analysis. Iron might exist as a solid solution in the Ni–Al intermetallic layer.

**Figure 5.** Cross sectional TEM image of the specimens joined at 1273 K for 3.6 ks.

**Table 2.** Identified Phases on Alloy Side of Fracture Surfaces by X-ray Diffraction Analysis

<table>
<thead>
<tr>
<th></th>
<th>0 ks</th>
<th>3.6 ks</th>
<th>14.4 ks</th>
<th>28.8 ks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273 K</td>
<td>Ni, Ni₃Al, NiAl, Ni₅Al₃, Al₂O₃</td>
<td>Ni, Ni₃Al, NiAl, Ni₅Al₃, Al₂O₃</td>
<td>Ni, Ni₃Al, NiAl, Ni₅Al₃, Al₂O₃</td>
<td>Ni, Al₂O₃</td>
</tr>
<tr>
<td>1373 K</td>
<td>Ni, Ni₃Al, NiAl</td>
<td>Ni, Ni₃Al, NiAl</td>
<td>(Fractured at YSZ)</td>
<td></td>
</tr>
<tr>
<td>1473 K</td>
<td>Ni</td>
<td>(Fractured at YSZ)</td>
<td></td>
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Fig. 4. Cross sectional SEM image and concentration profiles of elements by EDS analysis of the specimens joined at 1273 K for 0 ks (a), 3.6 ks (b), 14.4 ks (c) and 28.8 ks (d).
Al 
formation of crystalline Al₂O₃ layers. From EDS analysis of the 
an increased joining time and joining temperature. The strong 
layer was expected to act as a protective layer for further oxida-
tion of Ni alloy and inhibit degradation of the joined interface at 
higher temperatures. The four-point bend strength increased with 
an increased joining time and joining temperature. The strong 
fastening. The four-point bend strength of 170 MPa were obtained for 
specimens joined at 1473 K for 14.4 ks. The disappearance of Ni–Al 
intermetallic layers led to a stronger four-point bend strength. 

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Fig. 6. Reaction mechanism between Ni alloy and YSZ during liquid-
phase oxidation joining of YSZ via Al/Ni alloy/Al interlayers at 1273 K 
from 0 ks to 28.8 ks.