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<td>Iwamoto, Nobuya; Makino, Yukio; Sera, Tokio</td>
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Osaka University
Joning of Zirconia Using Platinum Film and Characterization of Its Interface

Nobuya IWAMOTO*, Yukio MAKINO** and Tokio SERA#

Abstract

Strength of joint of zirconias using platinum film was investigated with shear strength testing method. Fracture shear strength over 100MPa was obtained from ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joint. The good strength of the joint is attributed to the formation of Pt-Zr-O compound in the interlayer, which was identified using XPS method. Partial charges of constituent ions show very large values but the detailed structure of the compound remains unclear.

KEY WORDS: (YTZ/Pt Joning) (XPS) (Fracture Shear Strength)

1. Introduction

Studies on stabilization of zirconia has been performed from the middle of this century$^1$ and it is believed that yttrium oxide is the most excellent stabilizer for transformation of zirconia. Recently, yttria partially-stabilized zirconia (YTZ) has been developed using various processes and it is successful to obtain highly strengthened YTZ.$^2$ However, practical applications of zirconias is not so wide on account of no good properties at high temperature. Further, zirconia-metal (especially-platinum) joints is not well investigated.$^3$ On the other hand, alumina-metal joint has well investigated and alumina-platinum joint has been fairly interested from the standpoint of sealing.$^4,5$ However, detailed mechanism of the joining and state of interlayer remain still unclear. Comparing with alumina-platinum joint, characterization of zirconia-platinum joint has less performed. In the present paper, zirconia/platinum/zirconia joint having good strength was tried to produce and fractured surfaces of the joint after fracture shear strength testing was investigated using x-ray photoelectron spectroscopy for the purpose of characterizing the state of interlayer of the joint.

2. Experiments

Two sorts of zirconias (Zr-11 (CaO-stabilized) and YTZ (3 mol%Y$_2$O$_3$), Nihon Kagaku Togyo Co.) and pure platinum films with 20µm and 50µm in thickness were used for ZrO$_2$/Pt/ZrO$_2$ joining. Rectangular zirconia disks with about 10 × 10 mm and 3 mm in thickness were used. Before joining, zirconias and platinum film were washed in trichloroethylene, acetone and 10% (vol.) HNO$_3$-ethanol solution in order using supersonic waves. After drying well, each zirconia disk and platinum film were pretreated in oxygen atmosphere at 1500°C for 2 hr. Zirconia/Pt/zirconia joints were produced in oxygen atmosphere at 1500°C for 4 hr as loading 1.5 kg in weight. Several joints were tried to produce in air.

Fracture shear strengths of these joints were measured with tensile strength testing machine using self-made attachment as shown in Fig. 1. Cross head speed was fixed at 1 mm/min for every test. In order to characterize interlayer of the joints, SEM observation, EDX and XPS analyses were performed. X-ray photoelectron spectra were measured using the fracture surfaces of the YTZ (50µm)/Pt/YTZ (50µm) joint (YTZ-V). XPS used was ESCA Lab-5, which was operated at 10kV × 20mA under 2 × 10$^{-9}$ Torr. Charging effect was corrected using C$_{1s}$ (284.6 eV) and Ag$_{3d(5/2)}$ (367.9 eV) peaks as standard peaks. SEM observation and EDX analysis of each zirconia/Pt/zirconia joint was performed before and after shear strength test.

3. Results

Typical value of fracture shear strengths obtained from several zirconia/Pt/zirconia joints are given Table 1. No high fracture shear strength was obtained from ZrO$_2$ (Zr-11)/Pt/ZrO$_2$ (Zr-11) joint. It was observed in these joints that fracture occurs sometimes not in Pt/zirconia interface but in bulk of zirconia. Fracture strength higher than 100 MPa was obtained from ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joints. In these joints using YTZ, it seems that fracture occurs in the platinum metal layer near interlayer region because grayish reacted region was observed.

† Received on Nov. 5, 1986
* Professor
** Instructor
# Collaborator (Seibu-Kogyo Gijutsu Center of Hiroshima Prefecture)

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at the overall surface of zirconia-side of fractured YTZ/Pt/YTZ joint.

Results of SEM observation and EDX analysis of ZrO$_2$ (ZR-11)/Pt/ZrO$_2$ (Zr-11) and ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joint after shear strength test are given in Figs. 2, 3 and 4.

It is found from Fig. 2 that stabilizer and impure element are enriched in the interface of ZrO$_2$ (ZR-11)/Pt/ZrO$_2$ (ZR-11) joint. In Fig. 3, it is observed that platinum film fractured after deforming practically. Figure 4 shows that zirconia surface reacted well with platinum film. Though both rough and smooth surfaces are observed in the picture, platinum was detected in both areas with EDX method.

O$_{1s}$, Pt$_{4f}$ and Zr$_{3d}$ photoelectron spectra obtained from the surface of zirconia-side of fractured ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joint after Ar$^+$ ion sputtering for 120 min are shown in Fig. 5. Table 2 gives the values of O$_{1s}$, Pt$_{4f}$ and Zr$_{3d}$ binding energies corresponding to each Ar$^+$ ion sputtering time. O$_{1s}$ binding energy changed drastically between 90 min and 120 min ion-sputtering and the difference is about 5 eV. On the other hand, Zr$_{3d}$ binding energy is weakly depend on Ar$^+$ ion sputtering time. After Ar$^+$ ion sputtering for 120 min, another broad Zr$_{3d}$ peak having no subpeak appears in lower energy position. Pt$_{4f}$ photoelectron spectra shows the complicated dependence on Ar$^+$ ion sputtering time as shown in Fig. 6. Three or four peaks are observed at every sputtering time except short sputtering time. Compared with standard values of ZrO$_2$, PtO$_2$ and α-Al$_2$O$_3$, the binding energies of Zr$_{3d}$, Pt$_{4f}$ and O$_{1s}$ were observed in about 2–5 eV higher energy positions as shown in Fig. 5.

4. Discussions

No good joint using ZR-11 zirconia was obtained in the present study on account of no good strength of the zirconia. Further, the enrichment of aluminum, silicon and calcium at the interface between zirconia and platinum metal seems to cause weak strength of the joint. High fracture shear strength of YTZ/Pt/YTZ joint can be at-

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**Table 1** Joining conditions and typical result of fracture shear strength.

<table>
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<tr>
<th>Specimen</th>
<th>Thickness of platinum film (μm)</th>
<th>Atmosphere</th>
<th>Pretreatment</th>
<th>Fracture shear strength (MPa)</th>
<th>Fracture position</th>
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</thead>
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<tr>
<td>ZB-I</td>
<td>1</td>
<td>air</td>
<td>(zirconia) was in acetone</td>
<td>5.9</td>
<td>zirconia &amp; interface</td>
</tr>
<tr>
<td>ZB-II</td>
<td>20</td>
<td>O$_2$</td>
<td>(zirconia) &amp; (Pt) was in trichloroethane (15 min), 1000°C (heating) in O$_2$</td>
<td>———</td>
<td>zirconia &amp; interface</td>
</tr>
<tr>
<td>YBS-I</td>
<td>20</td>
<td>O$_2$</td>
<td>same conditions as ZB-II</td>
<td>105.9</td>
<td>interface</td>
</tr>
<tr>
<td>YBS-II</td>
<td>20</td>
<td>O$_2$</td>
<td>same conditions as YBS-II</td>
<td>136.4</td>
<td>interface</td>
</tr>
<tr>
<td>YBS-III</td>
<td>20</td>
<td>O$_2$</td>
<td>same conditions as YBS-II</td>
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<td>interface</td>
</tr>
<tr>
<td>YBS-IV</td>
<td>50</td>
<td>O$_2$</td>
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<td>104.9</td>
<td>interface</td>
</tr>
<tr>
<td>YBS-V</td>
<td>50</td>
<td>O$_2$</td>
<td>same conditions as YBS-II</td>
<td>143.2</td>
<td>interface</td>
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88
Fig. 2  SEM image and EDX spectra obtained from the interface of $\text{ZrO}_2$ (ZR-11)/Pt/$\text{ZrO}_2$ (ZR-11) joint.

Fig. 3  SEM images of fracture surface of platinum metal side of $\text{ZrO}_2$ (YSZ)/Pt/$\text{ZrO}_2$ (YSZ) joint.
Fig. 4  SEM images and EDX spectra obtained from fracture surface of zirconia side of ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joint.

Table 2  Values of O$_{1s}$, Zr$_{3d}$($5/2$) and Pt$_{4f}$($7/2$) binding energies corresponding to each Ar$^+$ ion sputtering time.

<table>
<thead>
<tr>
<th>Sputtering Time</th>
<th>O$_{1s}$</th>
<th>Zr$_{3d}$($5/2$)</th>
<th>Pt$_{4f}$($7/2$)</th>
</tr>
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<tr>
<td>5 min</td>
<td>530.29 eV</td>
<td>189.49 eV</td>
<td>78.17 eV</td>
</tr>
<tr>
<td>30</td>
<td>539.90 eV</td>
<td>188.98 eV</td>
<td>3 peaks$^a$</td>
</tr>
<tr>
<td>60</td>
<td>529.97 eV</td>
<td>187.81 eV</td>
<td>3 peaks$^a$</td>
</tr>
<tr>
<td>90</td>
<td>528.92 eV</td>
<td>187.70 eV</td>
<td>3 peaks$^a$</td>
</tr>
<tr>
<td>120</td>
<td>535.72 eV</td>
<td>187.38 eV</td>
<td>77.99</td>
</tr>
<tr>
<td>150</td>
<td>535.03 eV</td>
<td>187.44 eV</td>
<td>76.16</td>
</tr>
<tr>
<td>200</td>
<td>535.18 eV</td>
<td>187.34 eV</td>
<td>70.82</td>
</tr>
</tbody>
</table>

$^a$ see fig. 6.

Fig. 5  X-ray photoelectron spectra of O$_{1s}$, Pt$_{4f}$ and Zr$_{3d}$ obtained from fracture surface of zirconia side of ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joint (after Ar$^+$ ion sputtering for 120 min.).

Contributed to the formation of some Pt-Zr-O compounds at the interface and to the original strength of YTZ. As indicated by many investigators, yttrium oxide is the excellent stabilizer for transformation of zirconia and thermal stability of Y$_2$O$_3$ in ZrO$_2$ is so higher than other stabilizer such as MgO and CaO. Therefore, it is expected that yttrium can diffuse homogeneously to platinum metal together with zirconium. The consideration can be supported by the fact that coexistence of yttrium and zirconium near fracture surface of zirconia-side of YTZ/Pt/ YTZ joint was detected by XPS. However, formation of Y$_2$O$_3$ or other compound containing yttrium remains unclear.

Fracture shear strength of YTZ/Pt/ YTZ joint seems to be determined by the strength of platinum metal because plastically-deformed platinum was observed in the SEM image of fracture surface. It is sometimes indicated that thermal stress affects fracture strength of ceramic-metal joint. Practically, thickness of insert metal is of important factor for compensating thermal stress. In the present study, dependence of fracture shear strength of the joint.
Joining of Zirconias Using Platinum

Fig. 6 Dependence of Pt$_{4f}$ photoelectron spectrum upon Ar$^+$ ion sputtering in the fracture surface of zirconia side of ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ).

upon thickness of platinum film was not investigated, so that higher fracture shear strength may be expected. Platinum metal with 1μm in thickness was used in several experiments but no good fracture shear strength was obtained in the present study.

XPS results support the formation of Pt-Zr-O compound containing yttrium. Taking into account the chemical shift of each spectrum, it is suggested that partial charges of constituent ions show a higher value than those in the corresponding oxides. An investigator indicated the unusual coordination of platinum with oxygen in Pt$_3$O$_4$, that is, the eight coordination of platinum with oxygen. The indication agree with the XPS results because partial charge of platinum increases with increasing the number of oxygen which coordinates with platinum. However, structure of the compound formed in the interlayer was not identified in the present study. The formation of Pt-Zr-O bond can also change the partial charges of Zr, Pt and oxygen, respectively. Compound formation in Pt-Zr-O system is unclear and only Zr$_6$Pt$_2$O phase was suggested by Nevitt et al. Further, change of partial charges of these constituent ions can not simply calculated on account of no data on stability ratios of Pt and Zr and nearest neighbor structure.

Conclusively, Pt-Zr-O compound containing yttrium was formed in the interlayer of YTZ/Pt/YTZ joint and constituent ions are in such nearest neighbor environment as to raise partial charges of these constituent ions. Further, formation of the Pt-Zr-O compound is responsible for high fracture shear strength of YTZ/Pt/YTZ joint. In further investigation, identification of Pt-Zr-O compound and the effect of experimental conditions such as thickness of platinum film on fracture shear strength should be clarified.

5. Summary

Joining of zirconias using platinum films was performed in oxygen atmosphere. Fracture shear strength over 100 MPa was obtained in ZrO$_2$ (YTZ)/Pt/ZrO$_2$ (YTZ) joint. However, no good fracture shear strength was obtained from ZrO$_2$ (Zr-11)/Pt/ZrO$_2$ (Zr-11) joint. Excellent fracture shear strength of YTZ/Pt/YTZ joint is attributed to the formation of Pt-Zr-O compound in the interlayer of the joint. However, detailed structure of the Pt-Zr-O compound remains unclear. Enrichment of impure or alloying element such as silicon, aluminum or calcium causes to no good fracture shear strength of ZrO$_2$ (ZR-11)/Pt/ZrO$_2$ (ZR-11). Further, low strength of ZR-11 zirconia produces no good fracture shear strength of the joint.

References


