# Joning of Zirconia Using Platinum Film and Characterization of Its Interface

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**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. Experimentals

Two sorts of zirconias (ZR-11 (CaO-stabilized) and YTZ (3 mol%$Y_2O_3$), Nihon Kagaku Togyo Co.) and pure platinum films with 20$\mu$m and 50$\mu$m 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 (50$\mu$m)/Pt/YTZ (50$\mu$m) 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

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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.

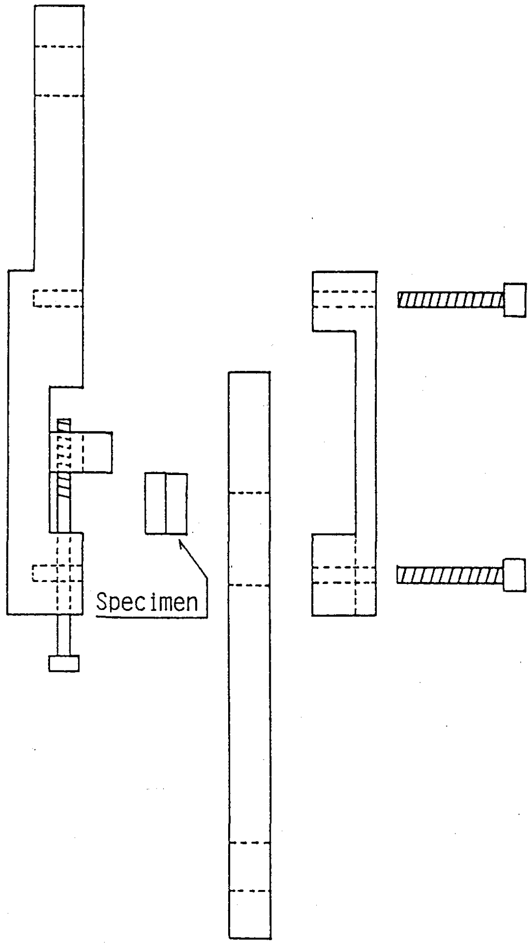


**Fig. 1** Schematic picture of self-produced jig for shear strength test.

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 prastically. **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 $\alpha$-$Al_2O_3$, 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-

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

| Specimen | Thichness of platinum film | Atmosphere (1 atm) | Pretreatment | Fracture shear strength | Fracture position |
|---|---|---|---|---|---|
| ZR-I | 1 μm | air | (zirconia) wasn in acetone | 5.9 MPa | zirconia & interface |
| ZR-II | 20 μm | $O_2$ | (zirconia) & (Pt) wash in trichlene 10%nital(15 min), 1000°C(heating) in $O_2$ | —— | zirconia & interface |
| YSZ-I | 20 μm | $O_2$ | same conditions as ZR-II | 105.9 MPa | interface |
| YSZ-II | 20 μm | $O_2$ | same conditions as ZR-II | 134.4 MPa | interface |
| YSZ-III | 20 μm | $O_2$ | same conditions as ZR-II | 102.0 MPa | interface |
| YSZ-IV | 50 μm | $O_2$ | same conditions as ZR-II | 104.9 MPa | interface |
| YSZ-V | 50 μm | $O_2$ | same conditions as ZR-II | 143.2 MPa | interface |

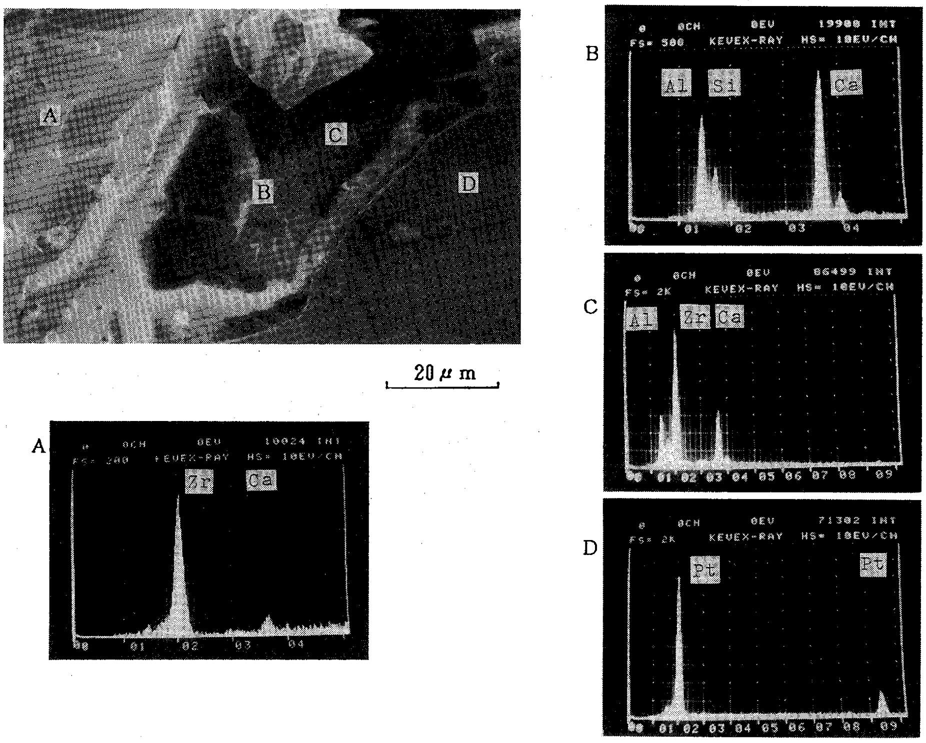


**Fig. 2** SEM image and EDX spectra obtained from the interface of $ZrO_2$ (ZR-11)/Pt/$ZrO_2$ (ZR-11) joint.

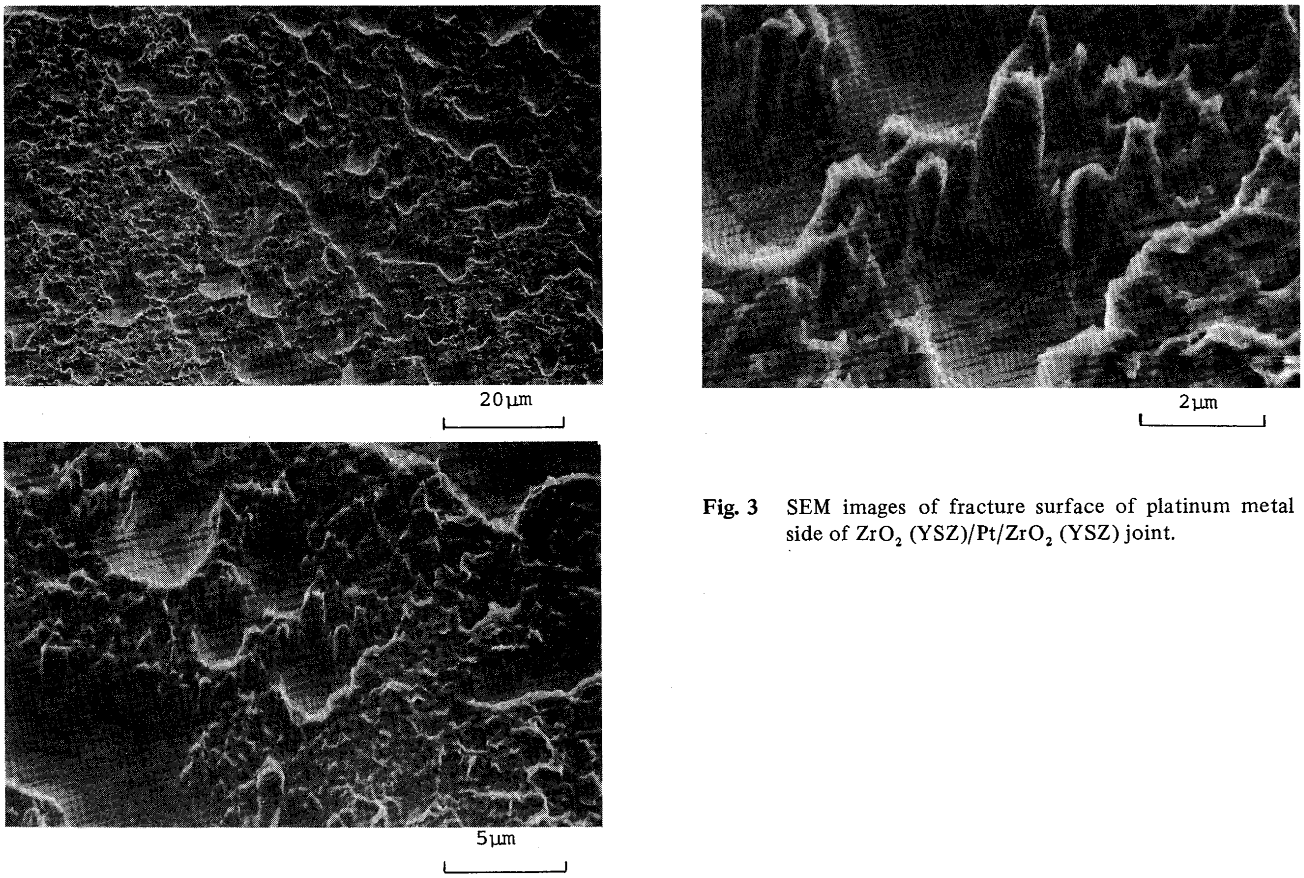


**Fig. 3** SEM images of fracture surface of platinum metal side of $ZrO_2$ (YSZ)/Pt/$ZrO_2$ (YSZ) joint.

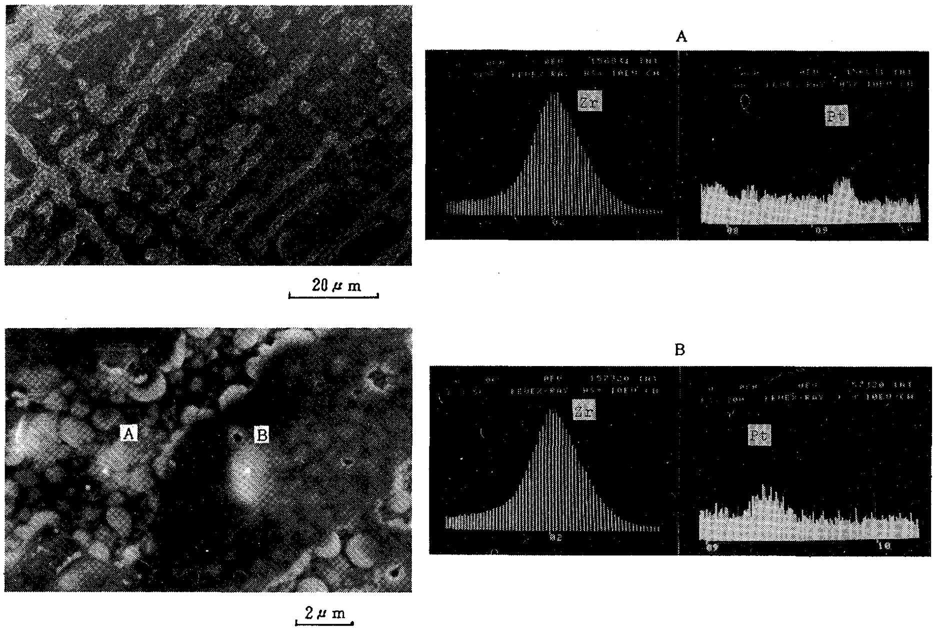


**Fig. 4** SEM images and EDX spectra obtained from fracture surface of zirconia side of $ZrO_2$ (YTZ)/Pt/$ZrO_2$ (YTZ) joint.

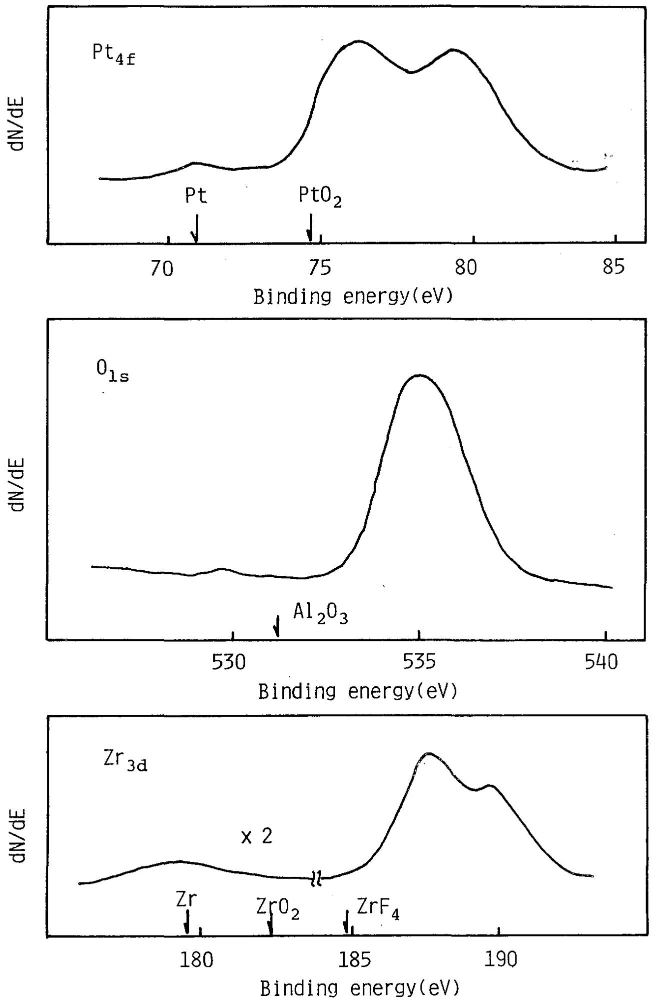


**Fig. 5** X-ray photoelectron specta of $O_{1s}$, $Pt_{4f}$ and $Zr_{3d}$ obtained from fracture surface of zirconia side of $ZrO_2$ (YTZ)/Pt/$ZrO_2$ (YTZ) joint (after $Ar^+$ ion sputtering for 120 min.).

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

| Sputtering Time | $O_{1s}$ | $Zr_{3d(5/2)}$ | $Pt_{4f(7/2)}$ |
|---|---|---|---|
| 5 min | 530.29 eV | 189.49 eV | 78.17 eV |
| 30 | 539.98 | 188.98 | 3 peaks* |
| 60 | 529.97 | 187.81 | 3 peaks* |
| 90 | 529.92 | 187.70 | 3 peaks* |
| 120 | 535.72 | 187.38<br>179.22 | 77.99<br>71.78 |
| 150 | 535.03 | 187.44<br>178.34 | 76.16<br>70.82 |

* see fig.6.

tributed 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 $Y_2O_3$ 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 $Y_2O_3$ 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

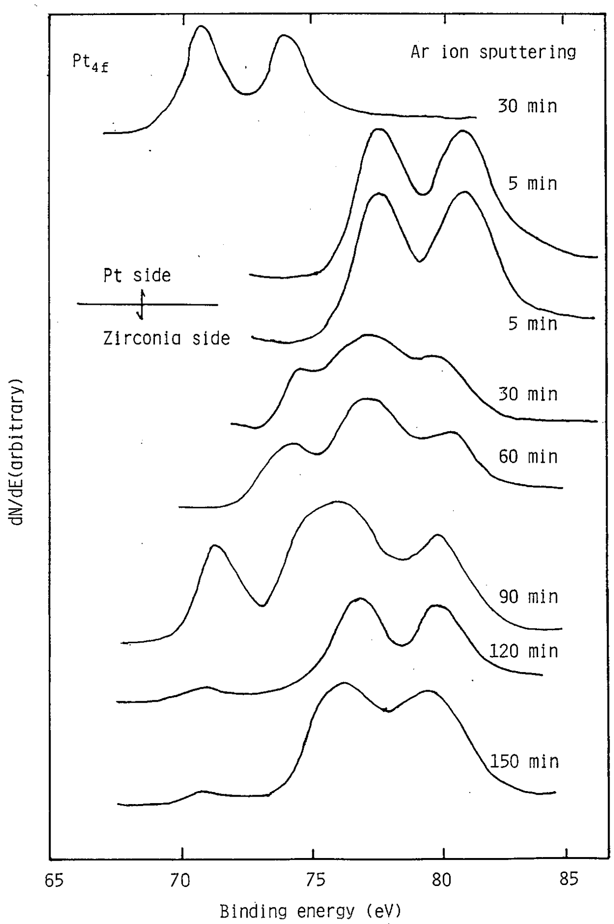


**Fig. 6** Dependence of $Pt_{4f}$ photoelectron spectrum upon $Ar^{+}$ ion sputtering in the fracture surface of zirconia side of $ZrO_2$ (YTZ)/Pt/$ZrO_2$ (YTZ).

upon thickness of platinum film was not investigated, so that higher fracture shear strength may be expected. Platinum metal with 1$\mu$m 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 $Pt_3O_4$,[6] 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 $Zr_6Pt_3O$ phase was suggested by Nevit et al.[7] 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.

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