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Instability of As-Sprayed Yttria-Stabilized Zirconia†

Yukio MAKINO* and Nobuya IWAMOTO**

Abstract

Instability of as-sprayed yttria-stabilized zirconia (YSZ) coating was investigated using x-ray photoelectron spectroscopy (XPS), combined with Ar⁺ ion sputtering. Sputter-induced reduction in the deeply sputtered regions was indicated from the broadening of Zr_{4p} peak and the appearance of second shoulder in the Y_{3d} spectrum. The reduction gives a proof of the existence of instable region in the as-sprayed YSZ coating. In the deeply sputtered regions, two O_{1s} peaks were observed and the O_{1s} peak in the lower energy position (second O_{1s} peak near 526-528 eV) decreased with increasing the leaving time in a high vacuum. Reasonable interpretation for the appearance of the second O_{1s} peak could not be shown in this study. However, it is suggested from the time-dependence and energy position of the second O_{1s} peak that the origin of the second O_{1s} peak is not attributed to the sputter-induced reduction.

KEY WORDS : (YSZ) (Plasma Spraying) (XPS) (Sputtering) (Reduction)

1. Introduction

Extensive application of yttria-zirconia ceramics has been performed in many fields and various compositions containing from 3 wt% to 20 wt% yttria are available. Various usages such as oxygen sensor, thermal barrier coatings, high-strength and wear resistant ceramics and optical coatings are found on account of the excellent properties of these ceramics¹.

Zirconia coatings for thermal barrier, in most cases, have been produced using plasma-spraying technique. However, several problems such as structural instability, poor adhesion and a low thermal fatigue life have been encountered in plasma-spraying ceramic coatings². Few investigation on structural instability, however, has been made irrespective of the importance for degradation of the coatings during high temperature usages.

Another interest on zirconia is the reduction phenomenon due to ion sputtering. Some investigators indicated the possibility of sputter-induced reduction of zirconia³, while the congruent sputtering in zirconia was suggested from thermodynamical model⁴. However, no clear conclusion has been obtained for the reduction of zirconia by ion sputtering.

In the oxidized surface of zirconium and some alloys containing zirconium in an ultra high vacuum, the existence of ZrO or Zr₂O and Zr₂O₃ has been suggested by XPS measurements^{5,6}. On the other hand, no formation of zirconium suboxides has been suggested in the binary and ternary zirconias^{7,8} which were ion-sputtered in

usual conditions.

In the present study, instability of as-sprayed YSZ coating was investigated with XPS, combined with Ar⁺ ion sputtering. Further, relation between sputter-induced instability and inhomogeneity of inner region within sub-micron depth was discussed, based on the results of depth profiles of oxygen and yttrium which were determined using relative intensity to zirconium.

2. Experimental Procedures

Yttria-stabilized zirconia coatings were prepared by spraying commercial powder of zirconium oxide composite (METCO 202, 20 wt% yttria) on SUS 316 stainless steel plates. Details on the experimental conditions of XPS measurement are shown in the previous paper⁹. Depth profile analysis was performed using the relative intensity ratio. The relative ratios of oxygen and yttrium (R(O) and R(Y)) to zirconium were determined by dividing the intensities of O_{1s} and Y_{3d(5/2)} peaks by the intensity of Zr_{3p(1/2)} peak, which measured at every sputtering step. The precise peak positions of O_{1s}, Y_{3d} and Zr_{4p} were measured when quite different R(O) was obtained in depth profile analysis.

3. Results

Depth profiles of oxygen and yttrium in the as-sprayed YSZ coatings is shown in **Fig. 1**. In the depth profile of oxygen, a few hollow regions were found in the profile of as-sprayed YSZ coating and two O_{1s} peaks appeared in

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these regions (see Figs. 2 and 5.) . Except outermost surface, R(Y) values in both zirconia coatings are nearly constant ones. Slight enrichment of yttrium was observed and the enrichment seems to correspond to the appearance of the hollow region in the oxygen depth profile.

Figure 2 shows the photoelectron spectra of O_{1s} , Y_{3d} and Zr_{4p} in the selected sputtering step with different R(O) values. In the as-sprayed YSZ coating, the position of O_{1s} binding energy shifted to lower energy with decreasing R(O) value as shown in **Fig. 3**. Similar behaviors were observed in the spectra of Y_{3d} and Zr_{4p} photoelectrons (see fig. 3) . Correlations among O_{1s} , $Y_{3d(5/2)}$ and Zr_{4p} binding energies are given in **Fig. 4**. The energies of $Y_{3d(5/2)}$ and Zr_{4p} decrease as the energy of O_{1s} decreases. Strong linearity is shown in each correlation but the slope is clearly different with each other.

Figure 5 shows the photoelectron spectra of O_{1s} , Y_{3d} and Zr_{4p} which were obtained at the sputtering time of 27 ks and afterward left in a high vacuum below 1×10^{-7} Pa. Two peaks were observed in the spectra of O_{1s} photoelectron and the intensity of second peak in lower energy side decreased with increasing the leaving time in the high vacuum. The spectra of Y_{3d} and Zr_{4p} photoelectrons be-

came narrower and the shoulder in the lower energy position of Y_{3d} spectrum gradually disappeared with increasing the leaving time in the high vacuum.

4. Discussions

In the previous paper⁹⁾, the inhomogeneous distribution of yttrium in the as-sprayed YSZ coating has been suggested from the observation of XRD peak due to yttria because the starting powder consists of the mixture of monoclinic zirconia and yttria (20 wt%).

Depth profile of oxygen measured with XPS demonstrates the inhomogeneity of oxygen in the inner region of the as-sprayed YSZ coating. On the other hand, the inhomogeneity of yttrium is not so remarkable even in the as-sprayed YSZ coating. The slightly enriched region of yttrium in the as-sprayed coating fairly corresponds to the remarkably oxygen-deficient region.

In the above discussion, the distribution means the average planar one because x-ray is radiated onto the total area of the specimen and the peak intensity of a characteristic photoelectron of a noticed atom reflects the total number of the atom in the total volume within escape

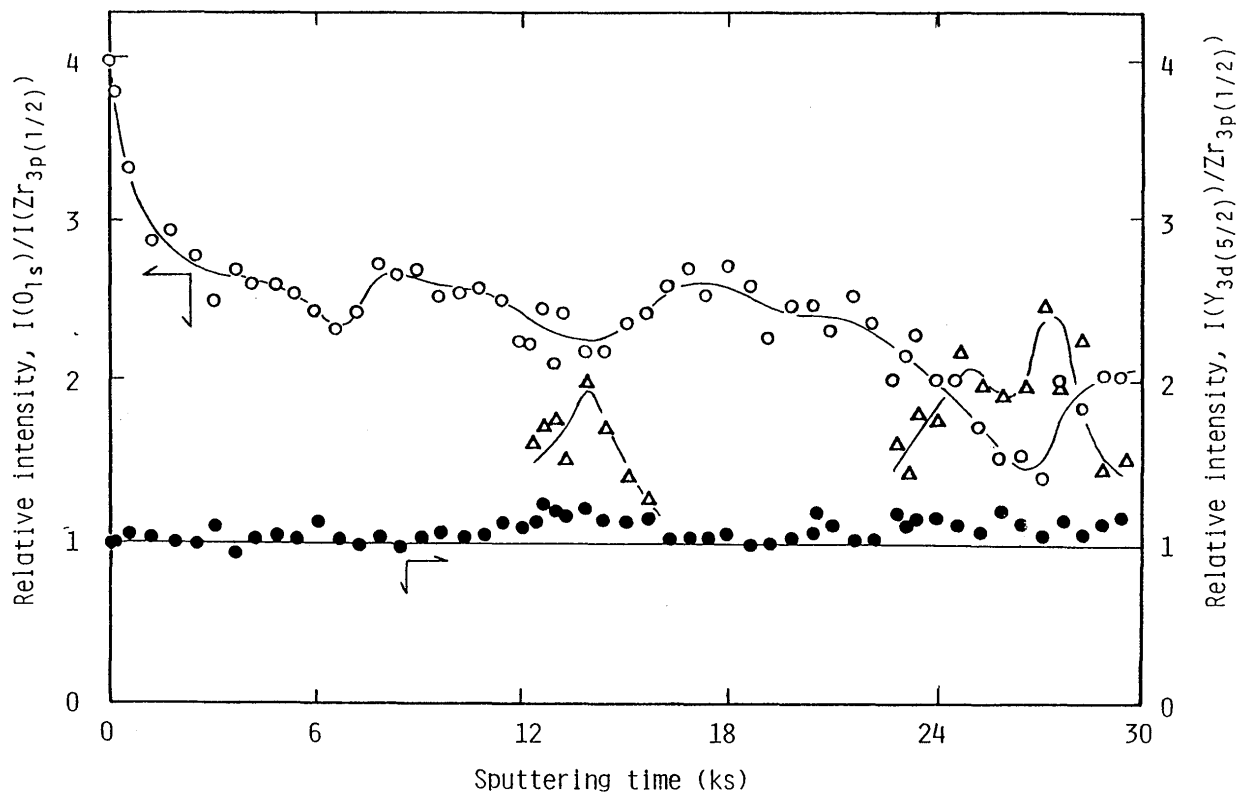


Fig. 1 Depth profiles of oxygen and yttrium in the as-sprayed YSZ coating. (Triangular plots show the data of relative intensities of second O_{1s} peaks. Sputtering rate is about 1 nm per min.)

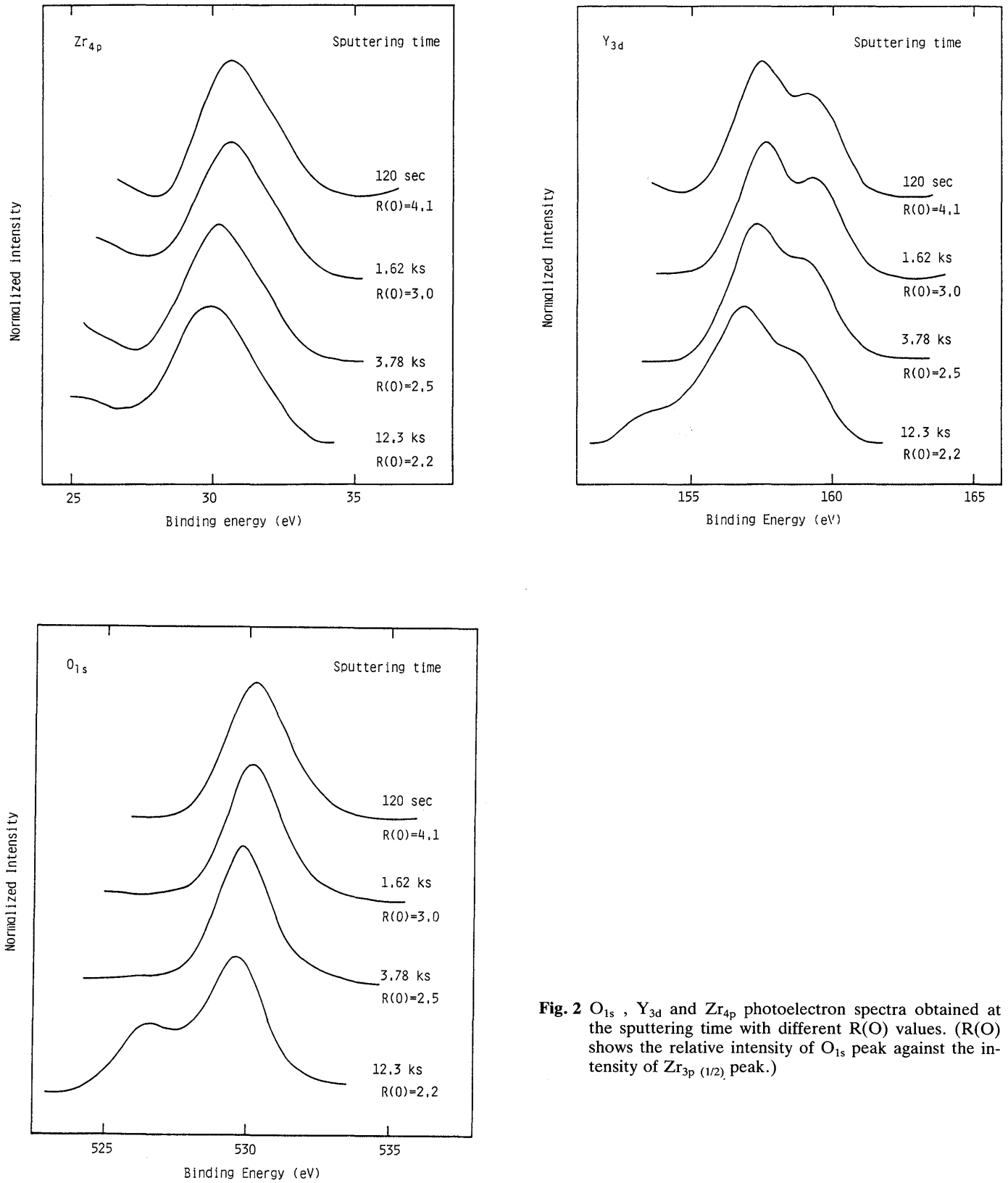


Fig. 2 O_{1s} , Y_{3d} and Zr_{4p} photoelectron spectra obtained at the sputtering time with different $R(O)$ values. ($R(O)$ shows the relative intensity of O_{1s} peak against the intensity of $Zr_{3p(1/2)}$ peak.)

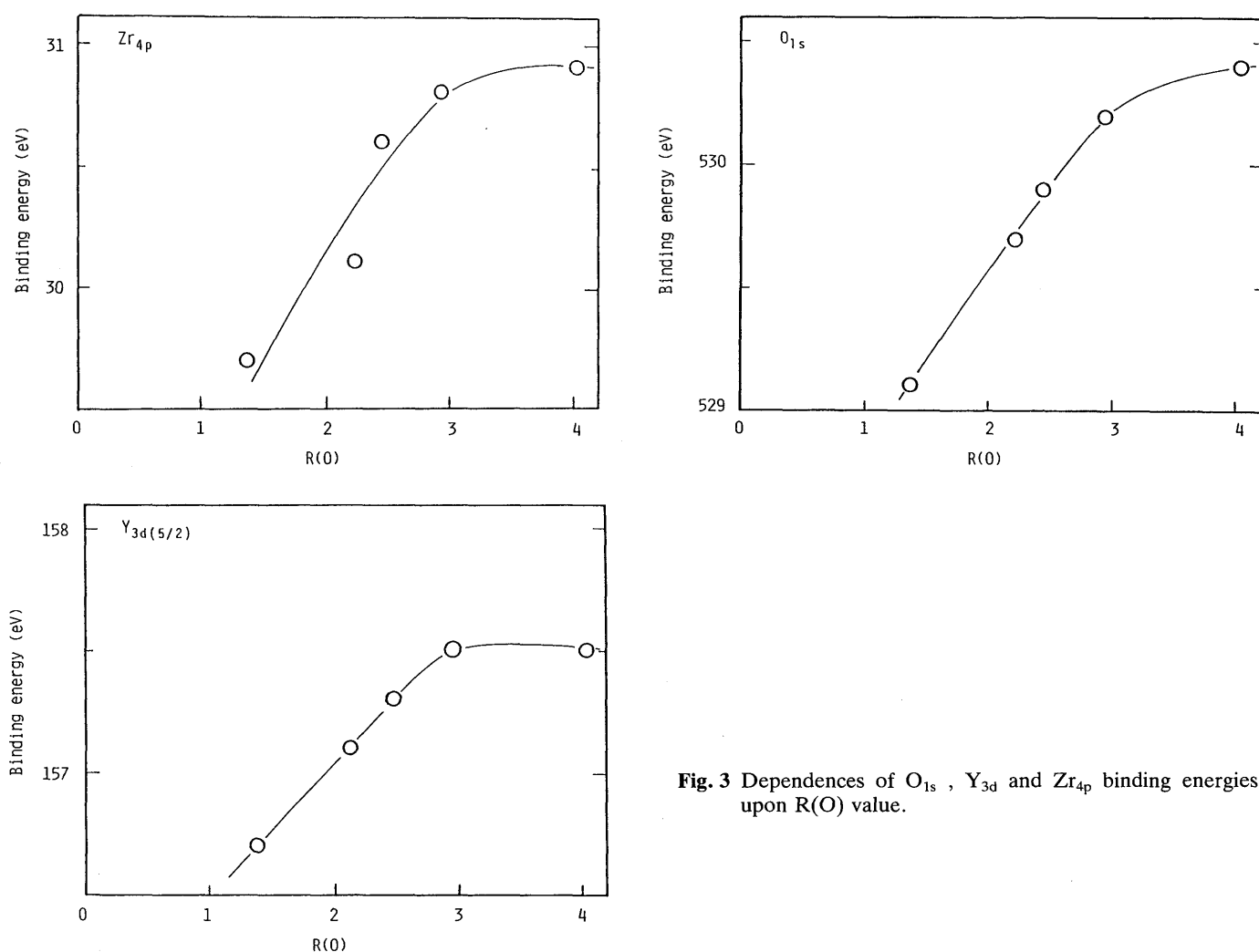


Fig. 3 Dependences of O_{1s}, Y_{3d} and Zr_{4p} binding energies upon R(O) value.

depth of the photoelectron. Therefore, it should be noted that it can be detected in this study whether average planar distribution at every sputtering step is homogeneous or not.

As shown in Fig. 2, energy decreases are observed in the photoelectron spectra of O_{1s}, Y_{3d} and Zr_{4p} in the as-sprayed YSZ coating as R(O) value decreases. Lowering of R(O) value means the low oxygen content due to non-stoichiometry of as-sprayed YSZ or the decrease of oxygen content attributed to sputter-induced reduction. The appearance of shoulder (second shoulder) in the lower energy position in Y_{3d} spectra and the obvious broadening of Zr_{4p} spectra, as shown in Figs. 2 and 5, give a clear evidence for the partial reduction of Zr⁴⁺ and Y³⁺ ions. Therefore, the lowering of R(O) value is attributed partly to sputter-induced reduction and partly to oxygen deficiency due to non-stoichiometry in the as-sprayed YSZ coating.

Dependence of O_{1s} spectra in the as-sprayed YSZ coating upon R(O) value is quite difficult to interpret by

only sputter-induced reduction. The observation of the second peak in O_{1s} spectra corresponds to the reduction of zirconium and yttrium as shown in Fig. 5. With increasing the leaving time in a high vacuum after ion sputtering, the energy positions of Zr_{4p} and Y_{3d(5/2)} photoelectrons shifted to the higher energies and are very close to the energies in ZrO₂ and Y₂O₃, respectively and therewith the intensity of the second O_{1s} peak decreased. Accordingly, the second O_{1s} peak seems to be connected with the reduced states of zirconium and yttrium.

The oxygen state in metallic zirconium has been extensively investigated by XPS and AES methods^{10,11}. However, the accurate chemical shift of O_{1s} photoelectron in the oxygen-dissolved zirconium have been scarcely reported. According to the result by Tapping¹², the binding energy of oxygen 1s electron in the oxygen-saturated Zr (0001) is 529.7 eV and the chemical shift is about 0.4 eV at most during oxygen exposure within 60 L. On the other hand, the binding energies of O_{1s} photoelectrons obtained from zirconia-alumina films containing yttria⁸

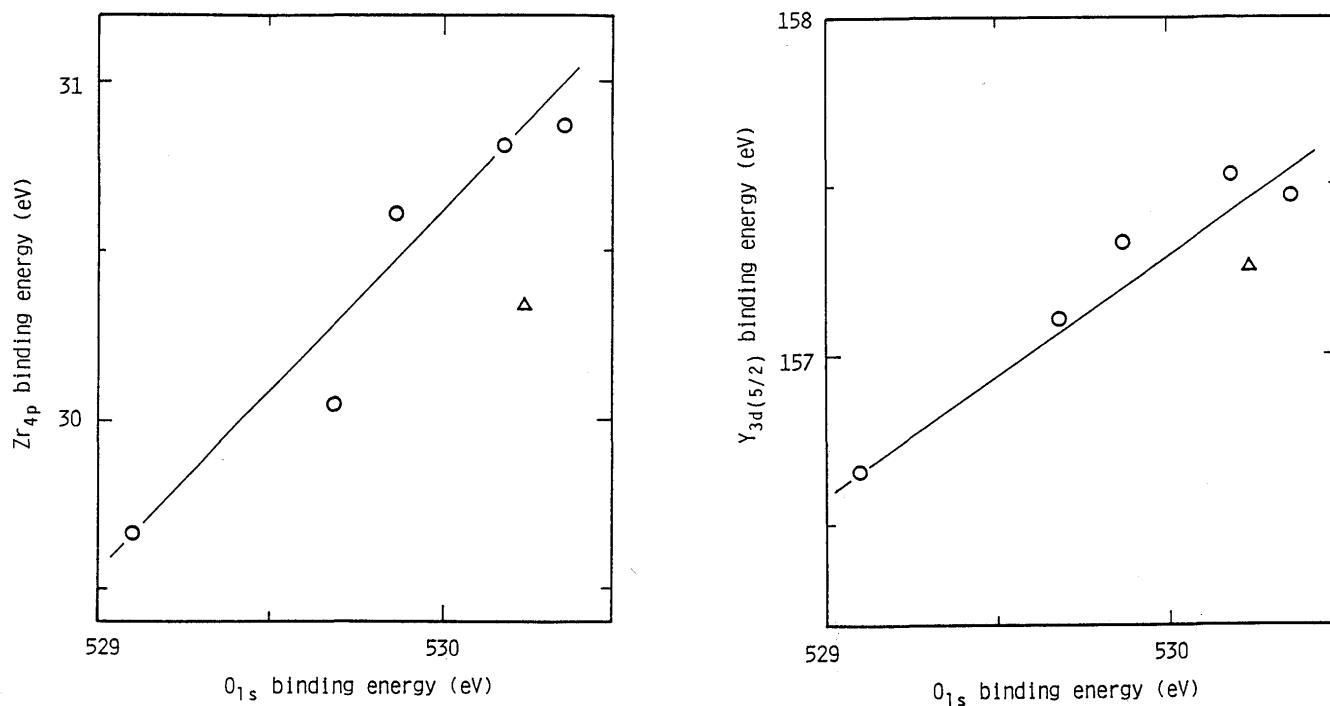


Fig. 4 Relations among O_{1s} , Y_{3d} and Zr_{4p} binding energies. (Triangular plots show the data obtained from outermost surface.)

and ZrO_2 with 8mol% Y_2O_3 ⁷⁾ are found between 530 and 532 eV. Therefore, the second O_{1s} peaks in Figs. 2 and 5 can not be attributed to oxygens in both zirconium dioxide and α -zirconium.

In the XPS measurement of insulators, charging effect causes a large shift, in most cases, to a higher energy position. When the charging effect depends upon the position of the specimen surface, the energy shift of photoelectron must be affected by the position and therefore the spectrum of the photoelectron will be broader if charging effect is continuously changeable. When charging phenomenon occurs discretely in the surface of specimen, a few peaks of a noticed photoelectron, for example O_{1s} , may be observed with a separation of several electron volts. Such discrete charging phenomenon may be possible to arise from inhomogeneous reduction in the as-sprayed YSZ coating.

Energy positions of the O_{1s} second peak, Y_{3d} second shoulder and Zr_{4p} peak are somewhat different with each other, though these positions could not be precisely estimated except O_{1s} second peak. Further, no broadening of Zr_{4p} peak obtained after sputtering for 12.3 ks observed as shown in Fig. 2 whereas two O_{1s} peaks appeared clearly. Therefore, the broadening of Zr_{4p} peak can not connect with the appearance of two O_{1s} peaks. In other words, the broadening of Zr_{4p} peak is not attributed to the inhomogeneous charging phenomenon. The appear-

ance of the second shoulder in Y_{3d} spectrum after deeply sputtering probably arises from the sputter-induced reduction in the as-sprayed YSZ coating. Further, the sputter-induced reduction indicates the existence of unstable region in the as-sprayed YSZ coating.

It is difficult to interpret the appearance of the two O_{1s} peaks from only XPS results. If the second O_{1s} peak is believable, the partial charge of oxygen related to the O_{1s} peak is estimated to be a value between -0.74 and -0.86 , which is calculated by modified Sanderson method¹³⁾. Assuming that partial charge is proportional to the valency of oxygen, the valency of oxygen ion related to the second O_{1s} peak takes a value between -2.7 and -3.2 . The estimation is not believable, when taking into account valence states of oxygens in various compounds.

Possible reasons for the appearance of two O_{1s} peaks are (1) the charging effect between reduced and non-reduced regions, or between particles, (2) inhomogeneous distribution of Y_2O_3 , (3) difference of work function between reduced and non-reduced regions, or between YSZ and residual Y_2O_3 , and (4) abnormal oxygens at the outermost surface of reduced YSZ.

When the reason (1) should be acceptable, two C_{1s} peaks should be observed. However, no evidence for the appearance of two C_{1s} peaks was obtained. The reason (2) is not acceptable because difference between the energy positions of O_{1s} peaks between ZrO_2 and Y_2O_3 probably

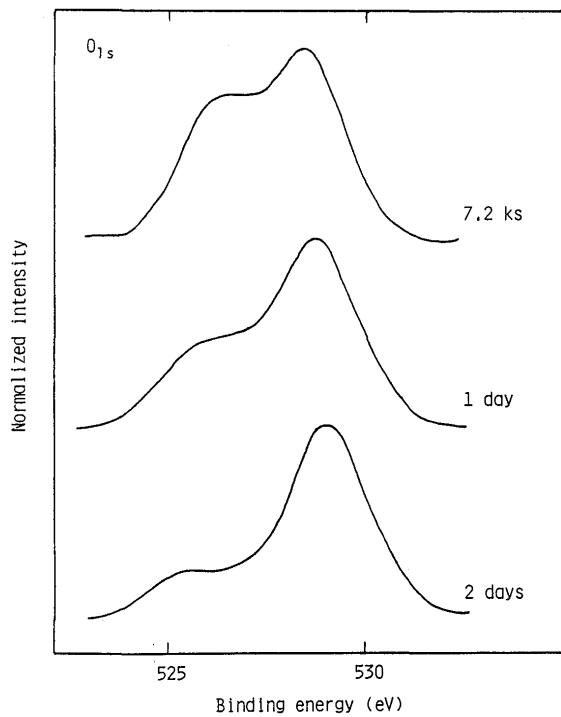
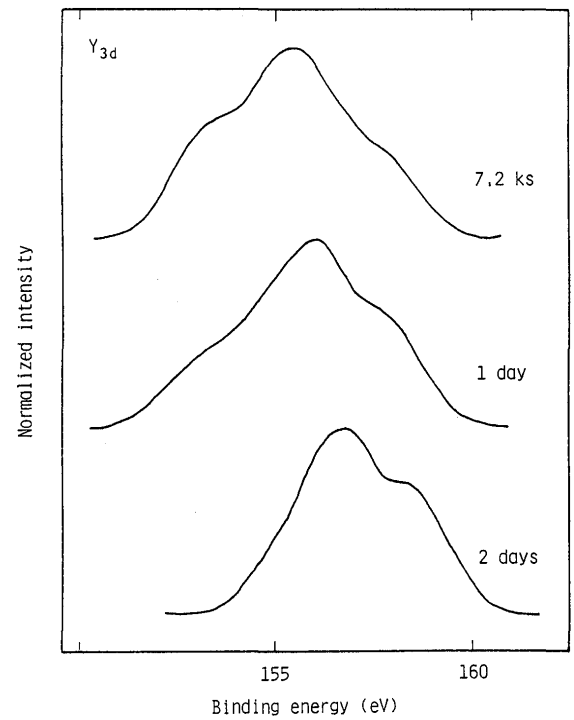
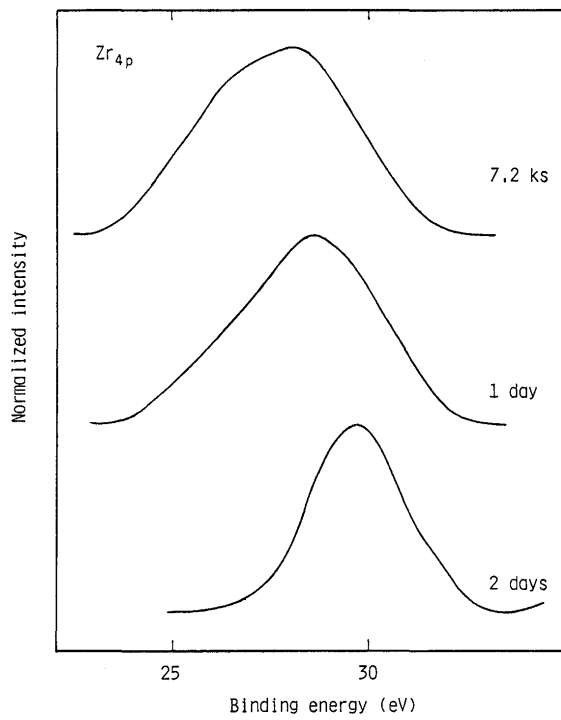


Fig. 5 Photoelectron spectra of O_{1s}, Y_{3d} and Zr_{4p} obtained after sputtering for 27 ks. (The times in each figure show the leaving times in a high vacuum below 1×10^{-7} Pa respectively)

is within about 1 eV. Subsequently, it is not easy to say whether or not the reason (3) is acceptable because work function is affected by surface state and practically data of work functions in Zr, ZrO₂, Y and Y₂O₃ depend on the method of measurement and investigator¹⁴). Lastly, as indicated before, it is difficult to accept the reason (4) on account of requiring the existence of oxygen higher than divalent. Conclusively, the observation of two O_{1s} peaks remains unclear, though it is easily acceptable that charging degree of oxygen is different from those of yttrium and zirconium.

5. Summary

Sputter-induced instability of as-sprayed YSZ coating and chemical states of constituent atoms in the coating are investigated with XPS method, combined with Ar⁺-ion sputtering.

The reduction was observed in the deeply sputtered regions. The chemical state of zirconium after reducing by Ar⁺-ion sputtering is in a mixed state of metallic zirconium and zirconium ions less than tetravalent. The chemical state of zirconium gradually changed into tetravalent zirconium with increasing the leaving time in a vacuum below 1×10^{-7} Pa.

The change of chemical state of yttrium after the sputter-induced reduction seems to be similar to zirconium though no clear change was observed.

Two O_{1s} peaks were observed after deeply sputtering and the reason for the appearance of two O_{1s} peaks could not be clearly interpreted.

The existence of unstable regions in the as-sprayed

YSZ was confirmed by the sputter-induced reduction. Further, it is suggested that sputter-induced reduction of zirconia delicately depends upon the crystalline state connected with production method.

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