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Osaka University
Instability of As-Sprayed Yttria-Stabilized Zirconia†

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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 ZrO₂ peak and the appearance of second shoulder in the Y₃d spectrum. The reduction gives a proof of the existence of instable region in the as-sprayed YSZ coating. In the deeply sputtered regions, two O₁s peak were observed and the O₁s peak in the lower energy position (second O₁s peak near 526-528 eV) decreased with increasing the leaving time in a high vacuum. Reasonable interpretation for the appearance of the second O₁s peak could not be shown in this study. However, it is suggested from the time-dependence and energy position of the second O₁s peak that the origin of the second O₁s 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 ceramics. 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 coatings. Few investigation on structural instability, however, has been made irrespective of the importance for degradation of the coatings during high temperature usages.

Another interest of zirconia is the reduction phenomenon due to ion sputtering. Some investigators indicated the possibility of sputter-induced reduction of zirconia, while the congruent sputtering in zirconia was suggested from thermodynamical model. 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 Zr₃O or Zr₃O and Zr₂O₃ has been suggested by XPS measurements. On the other hand, no formation of zirconium suboxides has been suggested in the binary and ternary zirconias 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 paper. 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 O₁s and Y₃d(552) peaks by the intensity of Zr₃p(12) peak, which measured at every sputtering step. The precise peak positions of O₁s, Y₃d and Zr₄p 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 O₁s peaks appeared in...
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 became 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 paper$^a$, 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. 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 $Zr_{3p}$ ($3d$) peak.)
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\textsubscript{1s}, Y\textsubscript{3d} and Zr\textsubscript{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\textsubscript{3d} spectra and the obvious broadening of Zr\textsubscript{4p} spectra, as shown in Figs. 2 and 5, give a clear evidence for the partial reduction of Zr\textsuperscript{4+} and Y\textsuperscript{3+} 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\textsubscript{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\textsubscript{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\textsubscript{4p} and Y\textsuperscript{3d(5/2)} photoelectron shifted to the higher energies and are very close to the energies in ZrO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3}, respectively and therewith the intensity of the second O\textsubscript{1s} peak decreased. Accordingly, the second O\textsubscript{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\textsuperscript{10,11}. However, the accurate chemical shift of O\textsubscript{1s} photoelectron in the oxygen-dissolved zirconium have been scarcely reported. According to the result by Tapping\textsuperscript{12}, 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\textsubscript{1s} photoelectrons obtained from zirconia-alumina films containing yttria\textsuperscript{8}...
and ZrO₂ with 8mol% Y₂O₃ are found between 530 and 532 eV. Therefore, the second O₁s 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 O₁s, 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 O₁s second peak, Y₃d second shoulder and Zr₄p peak are somewhat different with each other, though these positions could not be precisely estimated except O₁s second peak. Further, no broadening of Zr₄p peak obtained after sputtering for 12.3 ks observed as shown in Fig. 2 whereas two O₁s peaks appeared clearly. Therefore, the broadening of Zr₄p peak can not connect with the appearance of two O₁s peaks. In other words, the broadening of Zr₄p peak is not attributed to the inhomogeneous charging phenomenon. The appearance of the second shoulder in Y₃d 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 O₁s peaks from only XPS results. If the second O₁s peak is believable, the partial charge of oxygen related to the O₁s peak is estimated to be a value between −0.74 and −0.86, which is calculated by modified Sanderson 'method(3). Assuming that partial charge is proportional to the valency of oxygen, the valency of oxygen ion related to the second O₁s 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 O₁s peaks are (1) the charging effect between reduced and non-reduced regions, or between particles, (2) inhomogeneous distribution of Y₂O₃, (3) difference of work function between reduced and non-reduced regions, or between YSZ and residual Y₂O₃, and (4) abnormal oxygens at the outermost surface of reduced YSZ.

When the reason (1) should be acceptable, two C₁s peaks should be observed. However, no evidence for the appearance of two C₁s peaks was obtained. The reason (2) is not acceptable because difference between the energy positions of O₁s peaks between ZrO₂ and Y₂O₃ 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 \( 1 \times 10^{-7} \) Pa respectively)
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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 investigator. 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 O₁s 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 O₁s peaks were observed after deeply sputtering and the reason for the appearance of two O₁s 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.

References