Segregation aspects in the ZrO_2-Y_2O_3 ceramic system

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In solid solutions a difference is often present in chemical composition between bulk and interface of the materials. The difference frequently occurs because of segregation of impurities or main components to the interfaces. The composition of grain boundaries and of surfaces of ceramic materials often control fabrication behaviour such as sintering and grain growth [1]. Besides this, segregation of main components under the influence of water may also influence the thermal stability of tetragonal zirconia as was discussed by Winnubst and Burggraaf [2].

In most zirconia ceramics grain growth behaviour varies with composition. Different mechanisms have been proposed to explain this difference in grain growth. Lange [3] attributed this difference to the presence of different crystals phases in the ceramic (the cubic grains control the growth of the tetragonal ones). Jurado *et al.* [4] assumed that the larger grains in tetragonal zirconia had grown at the expense of the smaller ones. However, in our zirconia materials, with a bulk composition ranging from 4 to 8.9 mol % $YO_{1.5}$, no cubic phase or abnormal grain growth was observed. The mechanisms mentioned above therefore do not account for the differences observed [5].

Another phenomenon, which may explain the difference in grain growth rate is a decrease in grain boundary mobility through an "impurity" drag mechanism [1]. This implies the presence of a segregation layer at the surface, which consists of impurities or solute atoms.

In order to find an explanation for the difference in grain growth (and grain boundary conductivity) in zirconia materials doped with different amounts of yttria, the chemical composition of pure ultrafine grained $(ZrO_2)_{100-x}(YO_{1.5})_x$ ceramic interfaces was studied by means of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

As starting materials for the synthesis of the $(ZrO_2)_{100-x}(YO_{1.5})_x$ ceramics (sample code ZY*x*) ultrafine-grained powders were used. These powders were prepared by the alkoxide or chloride method [5, 6], which yields a pure and sinter-reactive powder. After isostatic pressing at 400 MPa and consequently sintering at temperatures from 1100 to 1400° C a relative density of more than 95% could be obtained. The resulting grain sizes range from 0.1 μm with low yttria content to 0.4 μm with high (> 13 mol % $YO_{1.5}$) yttria content.

Before the surface analysis experiments were carried out, the specimens were carefully polished with Al_2O_3 and ultrasonically cleaned in ethanol. These specimens were submitted to a temperature treatment in an oxygen atmosphere for 5 h at 600, 700 or 1000° C. As

a standard, rods were prepared which fractured transgranular under ultra-high vacuum. In this way surface contamination could be avoided and a fresh surface having the bulk composition is obtained.

The Auger analyses were performed with a cylindrical mirror analyser, type 10-155 (Physical Electronics). The analyses were performed using a primary beam current of 0.25 μA. No sample charging occurred under these conditions when clean specimens were used.

The XPS measurements were carried out on a Kratos ES 200B spectrometer, using Al-K_α radiation (1487 eV), in a vacuum chamber with a background pressure lower than 10^{-8} torr. Calibration of the XPS spectra was performed using the C_{1s} peak.

In case of AES the spectra were examined in a semi quantitative way using the equation of Palmberg *et al.* [7]:

$$C_x = (I_x/S_x)\Big/\sum_\alpha (I_\alpha/S_\alpha) \qquad (1)$$

where C_x is the concentration (in at %) of element x, and I_x and S_x are, respectively, the peak intensity and the relative elemental sensitivity factor of the Auger line of element x used for quantification. The yttrium and zirconium sensitivity factors are obtained from the standard spectra, the oxygen sensitivity was given a fixed value [7]. To quantify the XPS specta an equation similar to Equation 1 was used [8]. The method of analysis is described elsewhere [9].

To give a good interpretation of the Auger spectra, good knowledge of the correct position of the Auger peaks is necessary. Yttrium has an MNN Auger peak at 76 eV, zirconium an MNN peak at 147 eV and oxygen a KLL peak at 503 eV. In measuring the yttrium peak one has to be careful because of the presence of an LMM silicon peak on exactly the same position (76 eV). This is important because in some cases a small amount of silicon (which segregates quite easily) is present in the ceramic. Therefore, part of the peak intensity at 76 eV can be due to silicon. In order to eliminate the silicon part of the 76 eV peak a calculation has to be made. This can be done by deducing the silicon intensity at 76 eV from the intensity of the free KLL silicon peak at 1606 eV (oxide form; in elemental form the peak is situated at 1619 eV [7]).

By using the sensitivity factors as stated in Table I, the transformation is performed as follows:

$$I_{Si,76} = I_{Si,1606} S_{Si,76}/S_{Si,1606} \qquad (2)$$

The sensitivity factors of silicon at 76 and 1606 eV are obtained from a standard SiO_2 Auger spectrum [7]. In cases where silicon is found to be present, the yttrium

TABLE I Auger sensitivity factors (E_p = 3keV)

Element	Oxide form
Zr	0.10
Y	0.13
O	0.50
Si (1619 eV)	0.081
Si (76 eV)	0.373

intensity is obtained by subtracting the silicon intensity from the total intensity at 76 eV. Because only the upper part of the Auger peak at 76 eV has been taken into account, the calculated $I_{Si,76}$ has to be divided by a factor of 2 to obtain the yttrium intensity:

$$I_Y = I_{tot,76} - I_{Si,76}/2 \qquad (3)$$

in which $I_{tot,76}$ represents the measured peak height at 76 eV. However, in the XPS spectra a clear distinction can be made between the Y_{3d} and the Si_{2s} peak. The Y_{3d} peak has its maximum at 161.6 eV, Si_{2s} at 157.8 eV.

The Auger spectra of a polished surface of ZY17 heat treated at T = 873 and 1273 K, respectively are shown in Figs 1a and b. From this it can be seen that the Y/Zr peak intensity ratio of the high-temperature treated specimen (Fig. 1b) is higher than that of the bulk (Fig. 1a). The inaccuracy in the choice of the baseline is smaller than the observed differences in the peak intensity ratio between the two spectra. Therefore, it can be concluded that yttrium enrichment occurs at the surface of ZY17.

The yttrium enrichment at the surface is also indicated by a decrease of the yttrium signal as function of the Ar^+ ion-sputtering time. After 30 to 40 sec of ion sputtering the Y/Zr peak intensity ratio becomes constant (surface composition is then about ZY10). This
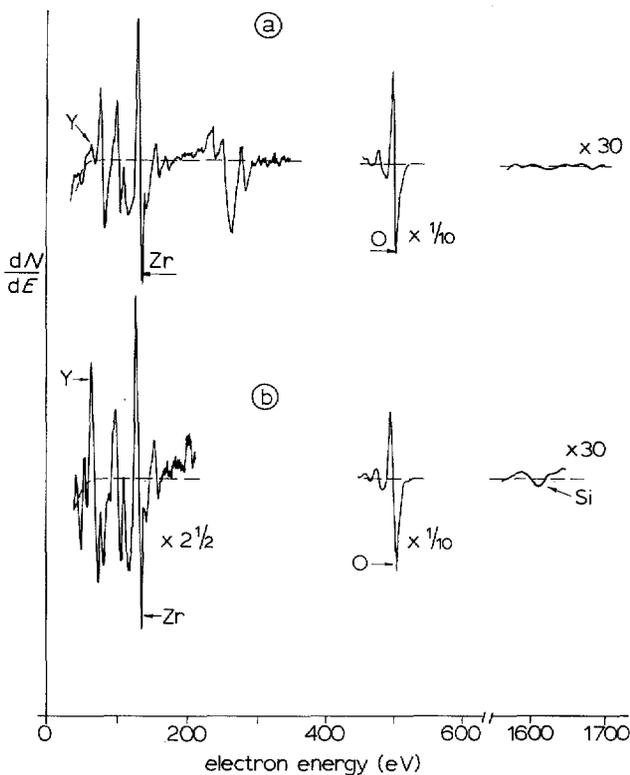
TABLE II Chemical surface composition Y_2O_3–ZrO_2 ceramics heat treated for 5h as determined by AES. (Materials with compositions between 4 and 9wt% $YO_{1.5}$ have a tetragonal structure, the others have a cubic fluorite structure)

Bulk composition of sample	Temperature treatment (K)	Surface composition x (from ZYx)
ZY4	873	5
ZY4	1273	31
ZY5*	873	6
ZY5*	1273	30
ZY6.1	873	6
ZY6.1	973	14
ZY6.1	1273	30
ZY8.9	1273	29
ZY13	873	11
ZY13	973	12
ZY13	1273	34
ZY17	873	17
ZY17	1273	35
ZY17*	1273	31
ZY26.4	873	28
ZY26.4	1273	34
ZY32	873	33

*Single crystals

quantitative result, obtained from the observed sputter profile, is not very reliable because of some reduction of Zr^{4+} to zirconium metal (the maximum of zirconum metal does not occur at the same energy as Zr^{4+} in oxides). Therefore, the thickness of the yttrium-segregation layer cannot be determined with any precision, but is estimated to be of the order of 2 to 4 nm [9].

The quantitative results of the measurements are given in Table II, using the sensitivity factors given in Table I. From this it can be seen that after temperature treatment a pronounced yttrium enrichment takes place up to a composition of about ZY30.

These results are already corrected for possible silicon contamination if this is present. That the larger Auger peaks at 76 eV are not due to silicon is shown in the XPS spectra of Fig. 2. In Fig. 2b no significant
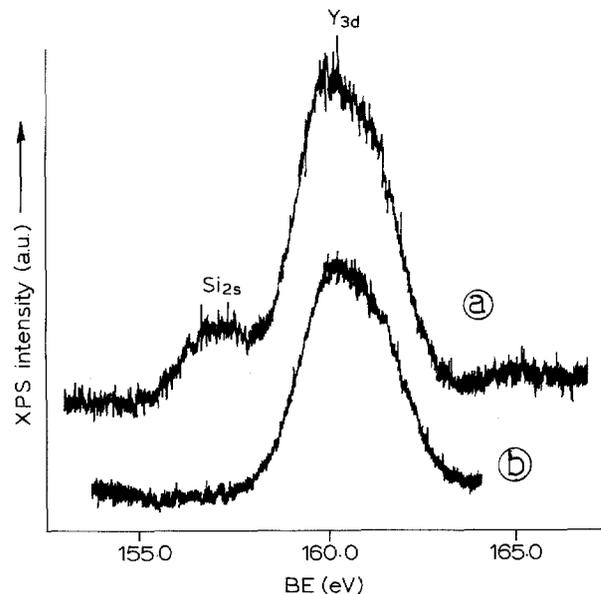

Figure 1 Auger spectra of a polished surface of ZY17 heat treated for (a) 5h at 873 K or (b) 5h at 1273 k.

Figure 2 XPS spectra of ZY specimen treated at 1237 K for 5h. (a) ZY4 with silicon contamination; (b) ZY6.1 without silicon contamination.

presence of silicon is shown (the detection limit is about 0.2 at %).

In AES (Fig. 1) the peak-to-peak height of silicon at 1606 eV (with a 30 × peak enlargement) should be at least 5 mm to be visible above the background level. In case of a peak height of 5 mm (1606 eV) a silicon intensity of less than 0.5 mm is calculated at 76 eV which, in general, causes a correction of only a few per cent in the total peak height at 76 eV (and therefore in the yttrium intensity).

The large influence of a possible silicon contamination is shown in the following example. A sample was deliberately contaminated with silicon. In this particular case the real peak intensity of yttrium was about 20% lower than for the case ignoring silicon, where the total 76 eV peak intensity was ascribed to yttrium. The composition was calculated to be ZY42 (ignoring silicon) and ZY34 with silicon taken into account. In this case the silicon concentration at the surface was found to be 3 at %.

All samples which received a temperature treatment of 1273 K showed an yttrium enrichment of about 30 at % to the surface (and probably also to the grain boundary [9–11]). This is independent of their crystal structure (both 100% tetragonal and 100% cubic materials show the same result) and bulk composition. This concentration therefore seems to be a saturation value. In the XPS spectrum yttrium enrichment is also observed. Using the sensitivity factors found by Wagner et al. [8], a surface composition of ZY20 is calculated (bulk composition ZY6.1). To calculate the exact composition, standards had to be made, which has not been done in this case. The AES results were confirmed by Steel and Butler [12], who found with SPS on the (0 0 1) surface of ZY15 a concentration of 33 at % yttrium. These results mean that the yttrium enrichment factor (defined as $C_{Y,surface}/C_{Y,bulk}$) for materials containing low amounts of yttria (i.e. tetragonal materials) is much larger than the (cubic) materials containing high percentages of yttria. A stronger segregation (higher enrichment factor) results in a steeper yttrium gradient between the surface and the bulk of the material, and therefore in a stronger "solute" drag. Probably a stronger "solute" drag results in a stronger retardation of the grain growth (which means a smaller grain size after sintering). This is what has been observed while sintering yttria-stabilized zirconia materials doped with various amounts of yttria. All of the materials started with the same initial crystallite size [5]. This might also explain why in PSZ ceramics containing both tetragonal and cubic phases the larger grains are cubic.

Because the as-prepared single crystals (by skull-melting) show the same segregation behaviour as the ceramical materials, a retardation in domain growth in single crystals may also be possible.

In conclusion:

1. After temperature treatment at 1273 K for 5 h $(ZrO_2)_{100-x}(YO_{1.5})_x$ ceramics show a surface com-

position of about 30 to 34 at % yttrium, regardless of the bulk composition of the ceramic. The segregation layer has a thickness of a few atom layers (~ 2 nm).

2. A similar surface composition of about 30 at % yttrium for ceramics containing low amounts of yttria (in the bulk) results in a larger yttrium enrichment factor than in ceramics containing larger amounts of yttria. The yttrium enrichment factor therefore increases from 1.5 to 7 with a bulk concentration of yttria decreasing from 26 to 4 at % $YO_{1.5}$.

3. Grain growth is dependent on the amount of yttria in the bulk, which results for tetragonal yttria-stabilized zirconia in a slower grain growth than the cubic ones.

4. To obtain reliable results, special attention has to be paid to the presence of silicon.

Acknowledgements

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