Appendix A

Segregation of Yttrium Ions to the Surfaces of t-ZrO_2

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A.1 Abstract

Atomistic simulation has been used to predict the segregation of defect clusters containing two substitutional Y^{3+} ions and one charge compensating oxygen vacancy to the (100) and (101) surfaces of t-ZrO_2. The most stable orientation of the defect cluster depends on its distance from the surface. Significantly, segregation energies vary greatly between surfaces. For example, the defect cluster is equally stable up to a depth of 8Å from the (100) surface but only to a depth of 4Å below the (101) surface. In both cases, segregation energies are negligible 14Å beneath the surface.

A.2 Introduction

At temperatures below ≈1000°C the crystal structure of zirconia is monoclinic. Above this temperature it transforms to a structure with tetragonal symmetry. However, a suitable combination of small grain size and the addition of an appropriate amount of a stabilising oxide, e.g. 3mol% yttria (Y_2O_3), results in a metastable tetragonal structure (t-ZrO_2) even at room temperature. This metastable material is commonly known as tetragonal zirconia polycrystalline ceramic (TZP) and has excellent mechanical properties. Unfortunately a complication arises at moderate temperatures (typically 60-200°C), when the presence of moisture causes the tetragonal phase to uncontrollably transform into the more stable monoclinic phase, thus degrading the mechanical performance [260,261]. Microstructural studies have shown that the reaction is nucleated at the surface and that the nuclei grow to form a monoclinic surface layer, which increases in thickness with time [262–264]. Unfortunately, the nucleation mechanism is not well understood.

One suggestion for the origin of monoclinic nucleation is the preferential dissolution of yttria due to the presence of water [265]; this leaching causes a local reduction in yttria content, which may lead to the transformation. As part of this mechanism, it is proposed that yttrium ions segregate to surfaces of t-ZrO_2 grains. Furthermore this segregation, and hence the leaching rate, is orientation dependent. The atomic simulation work reported here was designed to investigate this hypothesis under dry conditions by modelling the surface orientation dependence of the driving force for segregation.

There have been a number of previous experimental studies concerning segregation effects in TZP. For example, yttrium ions have been explicitly shown to segregate to grain boundaries [266] and to domain boundaries [267]. In addition, the segregation of Sr and Bi to surfaces of polycrystalline TZP has been studied using angular-resolved X-ray photoelectron spectroscopy [268,269]. Within the resolution limits of this technique, the results were consistent with there having been an increase in concentration of Bi in the top five atomic layers [269] whereas for Sb results were consistent with segregation to the top fifteen layers [268].

A.3 Methodology

The methodology used in these calculations is based on a pair potential description of forces between charged ions, as described in Chapter 2. Surfaces are modelled using a 2D repeat unit (the simulation block) whose thickness is in excess of 40Å. Final ion positions are determined through energy minimisation techniques. Using the tetragonal unit cell index, the (100) and (101) surfaces of t-ZrO_2 are studied; these are type I and II respectively [182]. Details of the computational technique and the model parameters are available in previous publications [77,259,270,271].

In the model presented here, trivalent Y^{3+} cations substitute for Zr^{4+}, and thereby form charged defects. Two such substitutional defects are compensated by an oxygen vacancy to form, in Kroger-Vink notation, the defect cluster $\{(\mathrm{Y}_{\mathrm{Zr}})':(\mathrm{V}_{\mathrm{O}})^{\cdot\cdot}:(\mathrm{Y}_{\mathrm{Zr}})'\}$. The most stable geometric configuration for this cluster is when both cations are in second neighbour positions with respect to the oxygen vacancy. The same result was found previously in studies of yttria doped cubic zirconia [272].

Segregation trends have been modelled by calculating the total internal energy of the simulation block as the cluster was moved from the bulk stepwise to the surface. The depth of the cluster from the surface is defined with respect to the position of the oxygen vacancy. This is the same approach used to investigate the segregation of fission products in UO_2 as reported in Chapter 4 and [273]. However, this technique was developed earlier to model impurities in other ceramic systems [274–276].

In a bulk crystal all orientations of a fixed geometry defect cluster are equivalent.

Conversely, when a surface is introduced, there is an inherent directionality; that is, the cluster has several non-equivalent orientations with respect to the surface. Thus, when the cluster is deep within the simulation block the differences in energy between different orientations becomes small. However, as the cluster approaches the surface different cluster orientations result in different total energies. In the present study, this meant that below 14Å all cluster orientations had practically the same energy. However, as the cluster approaches the (100) and (101) surfaces, there are four unique orientations of the second neighbour yttrium ions for each fixed position of the oxygen vacancy. All four possibilities were investigated at each position of the oxygen vacancy as it moved from the surface into the bulk. Table A.1 provides the coordinates for each of these defect cluster orientations, including those with respect to the (110) surface, although the results for that surface are not discussed.

(100)	x_1	y_1	z_1	x_2	y_2	z_2
A	x+3.59	y-1.45	z+1.80	x	y+3.67	z+1.80
B	x-1.80	y+3.67	z	x-1.80	y-1.45	z-3.59
C	x+3.59	y-1.45	z-1.80	x	y+3.67	z-1.80
D	x-1.80	y+3.67	z	x-1.80	y-1.45	z+3.59
(101)						
A	x-1.80	y-3.25	z±2.11	x-1.80	y+3.01	z±2.11
B	x-1.80	y+3.01	z±2.11	x-1.80	y+0.88	z±3.77
C	x-3.59	y+0.16	z±2.30	x	y-4.04	z±0.67
D	x-3.59	y+2.22	z±0.64	x	y+1.97	z±3.59
(110)						
A	x+1.27	y-1.11	z+3.81	x-1.27	y+3.67	z+1.27
B	x-1.27	y+3.67	z+1.27	x-3.81	y-1.11	z-1.27
C	x+3.81	y-1.11	z+1.27	x+1.27	y+3.67	z-1.27
D	x+1.27	y+3.67	z-1.27	x-1.27	y-1.45	z-3.81

Table A.1: Coordinates of $(Y_{Zr})'$ sites with respect to the oxygen vacancy (at (x,y,z)), where the notation A,B,C and D is used in the results. The Z direction is perpendicular to the surface plane and therefore denotes depth below surface.

Finally, for the (101) surface, symmetry results in there being an inversion in the (101) plane of the positions of the second neighbour zirconium lattice sites with respect to an oxygen site in each successive oxygen layer. That is, the zirconium sites are above the oxygen vacancy with respect to the (101) surface in one layer and below in the next layer (this is because the (101) surface is type II). Thus, the four configurations in successive layers are related by this symmetry operation, see Figure A.1.

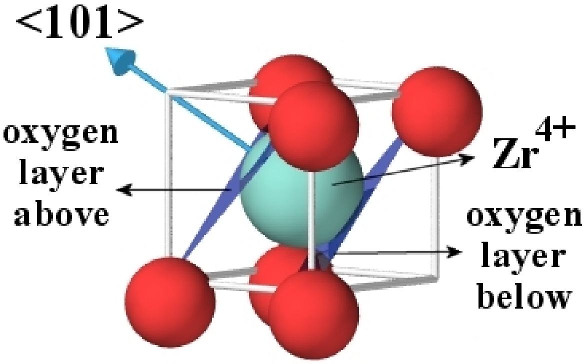

Figure A.1: The <101> surface of t-ZrO_2, denoting the oxygen layers above and below the Zr^{4+} ion.

A.4 Results

Let us define the energy E_S as the difference between the defect cluster in the bulk crystal (defined as the zero of energy) and at the surface (which may be negative i.e. more stable or positive i.e. less stable). (Note: E_S is not the same as the experimental enthalpy for segregation [189]). In addition, let us define E_T as the difference between the energy of the defect cluster at the surface and in the lowest energy trap site. It is these values which will be used to describe segregation trends. It should be noted that 0Åcorresponds to the cleavage plane which is equidistant between the top atomic layer and the next layer in a bulk material.

A.4.1 The (101) surface: Type II Surface

The (101) surface has been shown to be the most stable of the three perfect surfaces studied under dry conditions [270]. The energetics associated with the segregation process are shown in Figure A.2. It is clear that the cluster is more stable at the surface than in the bulk. The value calculated for E_S = -2.5eV, so that the driving force for segregation is strong. However, the stability of the cluster within the first three layers beneath the surface is constant. In fact, there may even be a very shallow trap site (E_T = 0.13eV) at a distance of 4Å from the surface plane. It is therefore expected that yttrium will segregate towards the (101) surface forming a higher concentration layer extending over 4Å (i.e. three or perhaps even four layers from the top). This result is consistent with the experimental observations on Bi segregation to the top five atomic layers in polycrystalline TZP [269]. It is also clear from Figure A.2 there is some smaller driving force for segregation ($E_S \gg$ 0.6eV) from the interior (bulk) to a region between 6 and 14Å. It seems likely that this is a consequence of the (101) surface being Type II. This is supported by the small energy differences between cluster orientations in this depth region, where the cluster dipole is interacting with the local dipole. Furthermore, analysis of ion displacements shows almost no movement for ions in layers beneath 8Å.

A.4.2 The (100) surface: Type I Surface

The energy associated with segregation of the cluster to the (100) surface is shown in Figure A.3. At distances of 9Å or more from the surface, the total energy no longer depends significantly on cluster orientation. However, similarly to the (101) surface, as the cluster approaches the surface, a strong configurational dependence is apparent. Interestingly the segregation energy, E_S, is larger than for the (101) surface, with a value of -3.29eV. This indicates that the (100) surface could be

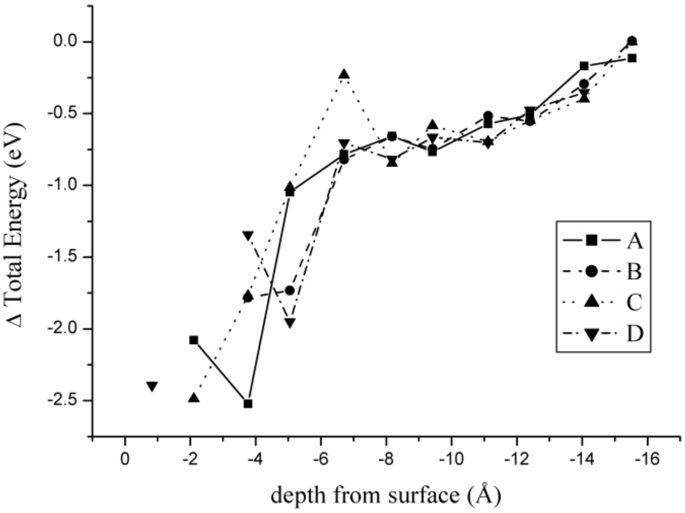

Figure A.2: Segregation of (Y_{Zr})' to the (101) surface of t-ZrO2.

stabilised with respect to the (101) surface through the addition of yttria. However, the extent to which this surface is stabilised will be concentration dependent. In this context, it may also be significant that the (100) surface shows this greater cluster stability within the top five layers compared to only three or four layers with the (101) surface.

An interesting feature of the (100) surface is the lack of stability of most configurations in the second and third layers beneath the surface. Clearly the distribution of yttria in surface layers may be quite complex. Nevertheless, this Type I surface seems well behaved in that values for E_S drop to zero very clearly below 10Å. This is the depth below which there are no significant displacements of ions from their bulk lattice positions.

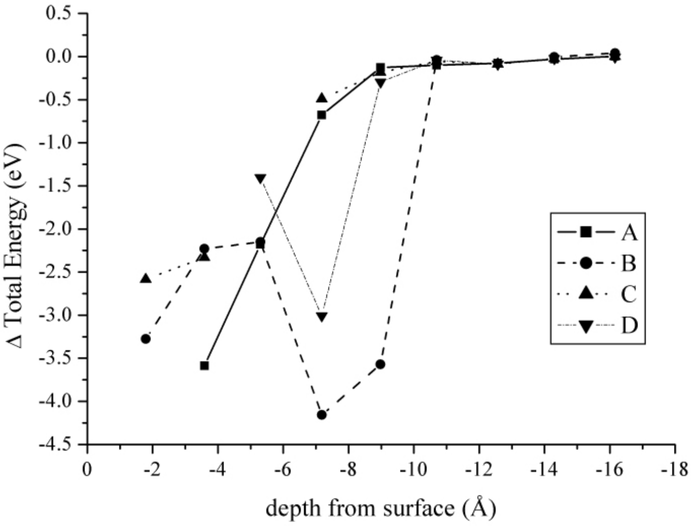

Figure A.3: Segregation of $(Y_{Zr})'$ to the (100) surface of t-ZrO2.

A.5 Conclusions

Y^{3+} ions as part of neutral clusters are more stable in layers beneath the (101) and (100) surfaces than in the interior bulk crystal. This provides a driving force for segregation.

The segregation energy is greater for the (100) surface compared to the (101).

There is a correlation between the extent of surface relaxation and segregation effects. However, for Type II surfaces, cluster orientation effects persist at greater depths.

It has been calculated in a previous study [270] that under dry conditions, the morphology of a single crystal of tetragonal zirconia is dominated by the (101) face, with the (100) surface not present and the Type III (110)A present to a minor degree. The present results imply that segregation of yttria to the crystal surfaces could be significant in promoting the amount of (100) surface present by lowering its energy with respect to the (101) surface.

A.6 Acknowledgements

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