Nucleation of the Martensitic Transformation of ZrO_2 in the System Al_2O_3-ZrO_2

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Introduction

The nucleation of the martensitic transformation of ZrO_2 from the tetragonal (t) to the monoclinic (m) symmetry is utilized to increase the toughness of ZrO_2-toughened Al_2O_3 (ZTA), polycrystalline Y_2O_3-stabilized tetragonal ZrO_2 (Y-TZP) and other ceramics. This phenomenon is caused by a volume increase of the transforming particles of about 4.7% which opposes the opening of cracks and reduces the crack tip stresses.

In this paper, attention is focussed to the system ZTA where spherical and ellipsoidal ZrO_2-inclusions are embedded in Al_2O_3-grains while facetted ZrO_2-particles are located between Al_2O_3-grains (1). In contrast to bulk ZrO_2 with a martensite start temperature of M_s=950 °C, the transformation is suppressed by the constraint of the surrounding Al_2O_3-matrix in ZTA even at room temperature (RT). It is of great technological importance to control the M_s-temperature simply by changing the size of the ZrO_2-particles. The critical ZrO_2-grain size d_c is defined as that particle size where the transformation occurs at RT: d_c=d(M_s=RT) (2). A maximum toughness increase is obtained keeping the size of ZrO_2-particles slightly below d_c (d_c≈0.6 μm - 0.8 μm for ZTA (3)) in order to benefit from the transformation of a maximum number of grains. It has been realized that the incorporation of 15 vol.% of facetted ZrO_2-particles into Al_2O_3 leads to optimum toughness values (4). This is mainly attributed to the interaction of the particles in case of denser populations and to the fact that regularly shaped ellipsoidal particles of a size already critical for facetted grains are lacking in defects. The latter, however, is a second prerequisite to start the martensitic transformation.

Therefore, the main driving force for the nucleation of the martensitic transformation was soon identified with the thermal stresses in the system ZTA together with geometrical irregularities such as facetted phase boundaries. The martensitic t→m transformation is thus believed to nucleate heterogeneously at corners and edges of the ZrO_2-particles which are otherwise defect free and that shear components of the eigenstresses play a prominent role for the transformation (5). The results from the homogeneous nucleation theory suggest an oblate spheroidal shape of the nucleus (6) with a large volume of 30·30·5 nm^3 in Y-TZP and an experimentally observed growth direction of m-ZrO_2 from the grain boundary into the grain in Y-TZP (7).

The presence of stress singularities at grain edges has been confirmed by numerical and analytical means (8-10). Neither the preferred nucleation site at facetted interfaces nor the shape and the growth direction of the nucleus have been addressed theoretically in the frame of heterogeneous nucleation theory until now. However, this is necessary to understand the lack of experimental observations in the transmission electron microscope (TEM) with respect to nucleation strain precursors in the system ZTA.

Particle Shape and Elastic Fields

In this section literature data and own results are reported in order to understand the dependence of elastic stresses and strains on the particle shape. The general assumption in all referred calculations is the presence of a linear isotropic elastic continuum with a single isotropic ZrO_2-inclusion. This means that interactions between ZrO_2-grains are neglected in this study. Details about the model and the algorithms are given in ref. (13).

The shape of the inclusion is assumed to be either facetted, ellipsoidal or spherical. The actual shape of the facetted grains is considered two-(hexagon) and three-dimensionally (tetrahedron, cuboid). It was shown in ref. (11) that stresses due to thermal expansion anisotropy in a two-dimensional hexagonal array of grains obey a weak logarithmic singularity at the corners of the array. Otherwise, the stresses are finite at the edges of the hexagons.

In a three-dimensional analytical solution for the elastic fields in a cuboidal inclusion surrounded by an elastic identical matrix and undergoing transformation strains (inclusion problem) it was shown in ref. (12) that stresses and strains depict a logarithmic singularity at the cuboidal edges. The complicated formulae have been numerically evaluated (13). It was shown (8,10,13) that shear strains are concentrated at the grain edges. They have their maximum at the edge center with a slight decrease towards the corners of the cuboid. Therefore, every volume bounded by a constant stress value assumes the shape of a quarter of a prolate spheroid. According to the initial strains acting inside the inclusion, the volumes at the four types of edges may differ significantly.

In addition, only special shear components become singular at individual grain edges (Table 1).

Initial strain component	Singular elastic strain	At edges
ε^*_{11}	ε_{23} ε_{13} ε_{12}	E_1 E_2 E_3
ε^*_{11}	ε_{12} ε_{11}, ε_{33} ε_{23}	E_1 E_2 E_3

Table 1: Initial strains produce only special singular elastic strains at certain cuboidal edges (E_i=edge type with direction parallel to coordinate axis x_i, i=1,2,3).

Frequently, the lattice correspondence O1 in which the c-axes of Al_2O_3 and t-ZrO_2 coincide is present, and only normal initial strains are acting. It was shown that even for an orientation dependence, O2 (with coinciding a-axis and an angle of 45° between b-axis of ZrO_2 and c-axis of Al_2O_3) where large initial shear strains can be expected, the magnitude of initial shear strains remains below 16% of the minimum normal initial strain component (Table 2).

ZTA	ε^*_{11}	ε^*_{22}	ε^*_{33}	ε^*_{23}
O1	-0.0051	-0.0051	-0.0105	0
O2	-0.0051	-0.0044	-0.0112	-0.0007

Table 2: Thermal mismatch in ZTA for two different orientation relationships between inclusion and matrix.

Finite element (FE) calculations for a tetrahedral ZrO_2-inclusion in an Al_2O_3-matrix confirmed the overall picture of maximum shear strains at the center of inclusion edges (10,13). The asymmetry of these results for tetrahedral particles is mainly a consequence of a coarse FE-mesh according to the problem that arises when subdividing a tetrahedron and its surroundings by finite elements.

In his famous analysis, Eshelby (14) demonstrated that strains and stresses are constant in ellipsoidal inclusions and inhomogeneities. The stress values for the two above mentioned orientation relationships O1 and O2 for a sphere deforming into an ellipsoid are given in Table 3 assuming either a ZrO_2-matrix (homogeneous inclusions) or an Al_2O_3-matrix (inhomogeneity problem).

Problem	O1			O2			
	σ_{11},σ_{22}	σ_{33}	σ_{23}	σ_{11}	σ_{22}	σ_{33}	σ_{23}
Inclusion	1.13	1.59	0	1.11	1.07	1.59	0.054
Inhomogeneity	1.28	1.94	0	1.26	1.20	1.83	0.078

Table 3: Stresses (in GPa) in a spherical inclusion deforming into an ellipsoid in the presence of thermal initial strains as given in Table 2 for ZTA.

Discussion

The following procedure is used to interprete above results under the aspect of implications for heterogeneous nucleation theory: The solution for the cuboidal inclusion is adopted because of its analytical nature which makes it easy to apply it even at the singular edges of grains. It can be assumed that a cuboid is a reasonable representation of a facetted ZrO_2-inclusion and deviations of actual inclusions from the cuboidal shape should not affect the conclusions below to a large extent. The elastic fields of inclusions with another facetted shape depict the same characteristics, as for example in the case of tetrahedral inclusions (13).

The disadvantage of the solution for the cuboid is the assumption of homogeneity, i.e. that the matrix possesses the same elastic constants as the inclusion. In order to take into account the elastic fields in the inclusion according to the inhomogeneity problem the shear stresses are corrected by approximately 50% as necessary for spherical inhomogeneities (Table 4).

From the theory of stress-assisted nucleation it is well-known that one component of the elastic shear strain must reach ≈21% of the dominant component of the transformation shear strain $\epsilon^T_{13}\approx0.08$ to form a stable nucleus (8,15). This means that the elastic shear strain must reach a value of about 1.8% over the nucleus volume which corresponds to a critical shear stress of $\sigma^c_{13}=1330$ MPa according to the direct relation between shear stress and shear strain via the shear modulus. The size of the critical nucleus is obtained by calculating the volume at one edge of a cuboid of critical size $d_c=0.6\ \mu m$ (as known from the experiment) in which the stresses are critical over the volume of the nucleus. Furthermore, it is assumed that the nucleation process starts not along the whole edge but rather at the site where the critical volume has its maximum extension, i.e. at the center of the edge. A critical nucleus in ZTA with a height of 10% - 20% of the edge length comprises about 50-100 unit cells of t-ZrO_2 (for details see ref.(13)). From this point of view the shape of the critical nucleus is a quarter of a prolate spheroid or a fraction of the central part of a prolate spheroid with an approximate shape of a quarter of a cylinder.

Another interesting result from the analysis of the analytical solution for the cuboid is the observation that at any edge E_i of the cuboid only one of the elastic shear strains ϵ_{jk} ($i \neq j \neq k \neq i$) becomes singular (c.f. Table 1) which is the shear in the plane perpendicular to the edge. This result suggests that the nucleus of the martensitic transformation tends to grow into the ZrO_2-grain in a direction perpendicular to the cuboid edge.

The validity of this result is not restricted to the ZTA-system but more or less general as long as the initial strains are normal strains along the cuboid axes. Therefore, it is not surprising that this predicted growth direction was found experimentally in Y-TZP. In this system the nucleation site and the growth direction of martensite is observable (7) and in good agreement with our predictions (13). It has to be kept in mind that a direct comparison of theory and experiment is not allowed because of the two-dimensional stress-state in in-situ TEM-experiments.

Conclusions

The results of this study may be summarized as follows:

Shear stresses in ideally spherical ZrO_2-grains are constant and too small to drive the nucleation without any promoting influence from stress-assisting neighbouring defects.

In facetted grains of different shapes strain and stress distributions always show a singular behaviour at grain edges.

Stress and strain concentrations are stronger and the nucleation of the martensitic transformation is most probable at the center of the edges, in agreement with experimental observations in the system Y-TZP.

The regions in which critical shear components are present scale with the actual edge length. One consequence is the occurrence of a critical grain size.

In contrast to the results from homogeneous nucleation theory the shape of the critical nucleus in heterogeneous nucleation theory is described best as a quarter of a prolate ellipsoid or part of this volume.

The size of the critical nucleus is calculated to be about 50-100 t-ZrO_2 unit cells in ZTA. The lack of strain precursors prior to transformation is attributed to the extremely slender shape of the prolate ellipsoid.

The growth direction of the nucleus is predicted from the analytical solution for a cuboidal inclusion to be perpendicular to the edge of the grain in agreement with experimental observations in Y-TZP.

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SM Effect / Technology	One–way	Two–way	Pseudo–elasticity
connecting, fastening	couplings, pipe connections expanding rivets		seals, spectacle frames
control		valve control, temperature protection, greenhouse opener	
motor vehicle		opening of fog–lights gear adjustments	high noise absorption
data processing	plug connections for circuits	head/disc system magn. data memory colour changes for opt. storage	
engines/ power		rotating machines, solar battery control	
automation	manipulators	robot hands,	
medicine	implants (osteosynthesis)	endoscope control	dental braces
clothing	fabric reinforcement		rubber substitute

Table 2
Systematic survey of shape memory effects and applications in different fields of engineering