
Precipitation and Ordering in Calcia- and Yttria-Stabilized Zirconia

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Abstract

Single crystals of ZrO$_2$–15 mol \% CaO and ZrO$_2$–9 mol \% Y$_2$O$_3$, annealed for either 400 h at 1273 K or 2.5 h at 1673 K and then quenched, were examined by electron diffraction and dark-field transmission electron microscopy. The thermal treatments duplicated those of diffraction and dark-field transmission electron microscopy. The thermal treatments duplicated those of previous authors have called the 'ordered' structure. The present results show that the extra reflections are due to precipitation of tetragonal ZrO$_2$ in both systems. Imaging with the diffuse-scattered intensity also present reveals small domains, presumably associated with oxygen-vacancy ordering, in the cubic solid-solution matrix. The diffuse intensity is observed whether or not tetragonal ZrO$_2$ precipitates are present.

I. Introduction

Solid solutions of ZrO$_2$ stabilized in the cubic fluorite structure (space group Fm3m) by additions of CaO and Y$_2$O$_3$ (respectively CSZ and YSZ) exhibit complex diffraction phenomena. These diffraction effects arise from several microstructural features related to phase separation and ordering of the anion vacancies present as charge-compensating defects for the aliovalent stabilizing cations. Carter & Roth (1968) observed diffuse neutron scattering from 'disordered' CSZ single crystals after aging at 1673 K; a decrease in the intensity of the diffuse maxima was observed upon 'ordering' at 1273 K. Extra reflections (hkl: odd, odd, even), forbidden for crystals with the fluorite structure, were also observed after the lower-temperature heat treatment. On the basis of their observations, these authors proposed a model for the 'ordered' structure in which the oxygen ions are displaced from their ideal fluorite unit-cell positions in a random manner at temperatures near 1673 K, giving rise to diffuse scattering, but occupy ordered anion sublattice positions different from the fluorite positions near 1273 K, giving rise to the fluorite-forbidden reflections. Allpress & Rossell (1975) used transmission electron microscopy (TEM) to study ordering in the HfO$_2$–CaO and ZrO$_2$–CaO systems; they found that the diffuse intensity in HfO$_2$–20 mol \% CaO and ZrO$_2$–20 mol \% CaO single crystals gradually evolved into discrete reflections, which they associated with precipitates, in several crystallographically equivalent orientations, of the intermediate phases CaHf$_4$O$_9$ and CaZr$_4$O$_9$. Morinaga, Cohen & Faber (1980) measured the diffuse intensity using X-rays; calculated intensities using Allpress & Rossell's model did not, however, agree with their experiments. Hudson & Moseley (1976) found that the fluorite-forbidden reflections and the diffuse intensity increased in 15 mol \% CSZ during aging at 1273 K, but the intensity of these diffraction phenomena varied in opposite senses upon changing the concentration of the stabilizing cations. They suggested that the fluorite-forbidden reflections were due to 'domains' of monoclinic ZrO$_2$, but they did not index the extra reflections. Faber, Mueller & Cooper (1978) investigated the fluorite-forbidden reflections by elastic neutron scattering and deduced a (010) tetragonal shear distortion on {100} planes of the oxygen sublattice, corresponding to what these authors called the 'ordered' structure. For reasons which are set out below, we argue that the terms 'ordered' and 'disordered' are inappropriate for describing these diffraction phenomena in stabilized zirconia. On the other hand, it is possible to interpret these phenomena in a straightforward manner in terms of microstructural evolution in accordance with published phase diagrams, although our work shows that some details of the ZrO$_2$–CaO diagram need modification.

II. Experimental technique and results

ZrO$_2$–15 mol \% CaO and ZrO$_2$–9 mol \% Y$_2$O$_3$ single crystals, generously supplied by Dr Faber, were 'ordered' by aging in air at 1273 K for 400 h or were 'disordered' by heating in air at 1673 K for 2.5 h, and the resulting microstructures investigated by TEM. For these investigations, the bulk samples (~1 × 1 × 3 mm) were removed as quickly as possible from the annealing furnace (consistent with avoiding fracture), sectioned mechanically and prepared as electron transparent foils using argon ion-beam thinning. The annealing treatments for CSZ should have yielded a single-phase material, according to the recent phase diagram of Stubican & Ray (1977). The YSZ, on the other hand, should have decomposed into a two-phase mixture of tetragonal and cubic phases according to the phase diagram of Stubican, Hink & Ray (1978).
Bright-field electron micrographs from both CSZ and YSZ revealed considerable strain contrast similar to that illustrated in Fig. 3 of Hudson & Moseley (1976), but little detailed structure information can be deduced from such images. Selected-area diffraction (SAD) patterns (CSZ, Fig. 1a; YSZ, Fig. 2a) show the expected fluorite reflections, as well as reflections forbidden by the fluorite structure, and the diffuse intensity. These are indexed for CSZ in Fig. 1(b). The diffuse intensity was more prominent in CSZ than in YSZ (cf. Figs. 1a and 2a), and lengthy exposures of SAD patterns are needed to reveal the diffuse intensity in YSZ. The spatial distribution of this diffuse scattering in reciprocal space is similar in CSZ and YSZ. The fluorite-forbidden reflections can be satisfactorily indexed as tetragonal ZrO$_2$ (space group $P4_{2}/nmc$, but see Appendix) and dark-field images (CSZ, Fig. 1c; YSZ, Fig. 2b) using these reflections reveal small precipitates in the cubic matrix. The orientation relationship applying to tetragonal ($t$) ZrO$_2$ precipitates in the cubic ($c$) matrix is particularly simple (Bansal & Heuer, 1975; Porter & Heuer, 1979), viz $\{100\}$, $\langle 110 \rangle$, and $[001]$, $\langle 100 \rangle$, and in a given region of cubic ZrO$_2$ can be formally described by a small shear distortion of the oxygen ions on neighboring $\{100\}$ planes of the oxygen sublattice along one of the equivalent $\langle 010 \rangle$ directions. Three
tetragonal precipitate variants should therefore be present, two of which can be imaged in dark field using a given fluorite-forbidden reflection. Splitting of the higher-order fluorite-forbidden reflections, as expected from the presence of three variants, was found for YSZ but not for CSZ. This implies that the \( c/a \) ratio of the tetragonal precipitates in CSZ differs from unity by less than \( 10^{-4} \). The spot splitting due to these precipitates in YSZ, shown arrowed in Fig. 2(a), implies a \( c/a \) ratio of \( \sim 1.002 \).

Dark-field images formed with the diffuse maxima (Fig. 3) reveal a very fine distribution of small scattering regions, which are quite distinct from the larger tetragonal precipitates. Different diffuse maxima produced noncoincident images, indicating that several variants are contributing to the diffusely-scattered intensity. Heating 'ordered' CSZ at 1673K caused elimination of the fluorite-forbidden reflections but not the diffuse intensity (Fig. 4), whereas diffraction patterns from 'ordered' YSZ were similar before and after the 1673K heat treatment, i.e. both the tetragonal \( \text{ZrO}_2 \) reflections and the diffuse intensity were present.

**III. Discussion**

3.1 Fluorite-forbidden reflections

It is clear from the results presented in Figs. 1–4 that the fluorite-forbidden reflections present in 'ordered' CSZ are not due to ordering in the conventional sense, but to precipitation of a tetragonal form of \( \text{ZrO}_2 \) from the stabilized cubic \( \text{ZrO}_2 \) solid solution, and that 'disordering' involves re-solution of the precipitates. Precipitates in CSZ and YSZ are similar; in both systems, they arise from annealing in a two-phase cubic + tetragonal phase field. Heat treatment of YSZ at both 1273 and 1673K produced the fluorite-forbidden reflections, which is expected since for the composition used both annealing temperatures should lead to two-phase microstructures. Our results for CSZ are not so consistent with phase equilibria considerations. Before discussing the CSZ in more detail, however, we note that a quite different description of 'ordered' CSZ and YSZ was presented by Faber, Mueller & Cooper (1978) based on their neutron diffraction study; our results, however, are entirely compatible with theirs except for a small discrepancy in the \( c/a \) value for the tetragonal precipitates in YSZ. Our interpretation of the results of Faber, Mueller & Cooper implies \( c/a \) ratios of 1 and 1.014 for the precipitates in CSZ and YSZ. By way of comparison, Hannink (1978), studying relatively large tetragonal precipitates in polycrystalline CSZ and YSZ by TEM, found \( c/a = 1.017 \) and 1.008, respectively. We believe that the difference in \( c/a \) ratios for small and large precipitates in CSZ and YSZ is real and arises because solute content (and hence lattice parameter) of these coherent particles is a function of particle size.

Our observation of tetragonal precipitates in \( \text{ZrO}_2-15 \text{ mol}  \% \text{CaO} \) aged at 1273K provides evidence that the eutectoid temperature of 1023 ± 100K proposed by Stubican & Ray (1977) is too low. This conclusion requires that the CaO content be known to within \( \pm 1 \% \). The crystals we used were supplied by Dr Faber, and we are relying on his initial chemical analysis. However, a precision lattice-parameter measurement of our CSZ crystal annealed at 1673K yielded a CaO content of 15.5 ± 0.75 mol % by making comparison with published curves (Stubican & Ray 1977) of lattice parameters vs CaO content. Furthermore, Hudson & Moseley (1976) also reported fluorite-forbidden reflections for their \( \text{ZrO}_2-15 \text{ mol}  \% \text{CaO} \) sample similarly aged at 1273K.

Several alternative constructions of the phase diagram and microstructural evolution sequences are conceivable. It is possible, for example, that a eutectoid reaction of the type

\[
\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-x} \text{ cubic solid solution} \rightarrow \text{tetragonal ZrO}_2 + \text{CaZr}_4\text{O}_9
\]

(1)

has occurred at 1273K (but of course has not gone to completion), the reaction products giving rise, respectively, to the extra reflections and the diffuse intensity. In this case, however, we would expect the reflections...
from tetragonal ZrO$_2$ and CaZr$_4$O$_9$ to be coupled, because the invariant nature of the eutectoid reaction requires that these reaction products form in a coupled manner. The persistence of the diffuse intensity in CSZ during the 1673 K annealing, during which treatment the tetragonal reflections disappear, makes this possibility unlikely.

Alternatively, the invariant temperature for the eutectoid reaction could be below 1273 K but at a higher CaO content so that the precipitation of tetragonal ZrO$_2$ that occurred during annealing took place in the (thus-expanded) two-phase field of tetragonal ZrO$_2$ + cubic ZrO$_2$ solid solutions. It is also possible that the eutectoid temperature is above 1273 K but because of the sluggishness of the eutectoid reaction precipitation is occurring according to the metastable extension of the solvuses separating the two-phase region from the single-phase regions adjacent to it. The phase diagram of Stubican & Ray has also been called into question recently by Hellman & Stubican (1979), and it is clear that further phase equilibrium studies of the ZrO$_2$–CaO binary system are called for.

Finally, we note that, as the two-phase mixture of tetragonal and cubic ZrO$_2$ solid solutions is cooled to room temperature, both phases become unstable – the tetragonal precipitates should transform martensitically to monoclinic symmetry (Bansal & Heuer, 1972, 1974), and the cubic matrix should decompose eutectoidally to CaZr$_4$O$_9$ and either tetragonal or monoclinic ZrO$_2$. It is now well known (Porter, Evans & Heuer, 1979) that small tetragonal ZrO$_2$ precipitates in a cubic solid-solution matrix will not transform under normal cooling conditions, and that the eutectoid decomposition is rather sluggish (Porter & Heuer, 1979). Thus, the phase assemblage formed at 1273 K is retained metastably.

3.2 Diffuse intensity

It is clear that the diffuse intensity shown in Fig. 1(a), which arises from discrete regions in the cubic matrix as shown in Fig. 3, is unrelated to the presence or absence of tetragonal ZrO$_2$ precipitates, since heating CSZ at 1673 K removes the fluorite-forbidden reflections but not the diffuse scattering. Allpress & Rossell (1975) concluded that the diffuse intensity observed for ZrO$_2$–20% CaO and HfO$_2$–20% CaO was due to the precipitation of 12 crystallographically distinct variants of CaZrO$_4$ and CaHf$_4$O$_9$, respectively. These compounds possess a defect fluorite structure and differ from fluorite in that the vacancies are ordered and small cation displacements from the ideal cation positions in fluorite are present. However, similar diffuse intensity was found by Porter (1977) in MgO-stabilized cubic ZrO$_2$ (MSZ) solid solutions, despite the fact that no ordered compounds corresponding to CaZr$_4$O$_9$ or Y$_4$Zr$_3$O$_{12}$ are known in the MgO–ZrO$_2$ binary system.

We take the presence of distinct scattering regions in Fig. 3 as evidence for the existence of 'domains' which, below some critical temperature, have undergone an increase in order. The diffuseness of the diffracted intensity could be due to the small domain size or to imperfect long-range ordering, but this cannot be decided using electron diffraction data alone. Whether appearance of these ordered domains involves passing through a solvus below which CaZr$_4$O$_9$ in CSZ or Y$_4$Zr$_3$O$_{12}$ in YSZ becomes stable, or whether a vacancy order–disorder reaction occurs, as suggested by the MSZ result, is not known. In either case, differences in diffusion kinetics between CSZ and YSZ can explain the different intensities of diffuse scattering, since neither solid solution is initially at the composition of the ordered phase.

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Fig. 5. SAD (zone axis=[001]$_{\text{ubi}}$) from thin region of CSZ foil, showing reflections forbidden for both cubic and tetragonal ZrO$_2$. (Tetragonal reflections, if present, would superimpose with those of the cubic matrix for this zone-axis orientation.) 125 keV.

Fig. 6. Dark-field micrograph formed using circled monoclinic reflection of Fig. 5. 125 keV.
APPENDIX

On numerous occasions, still other reflections, forbidden for both cubic and tetragonal ZrO$_2$ and not attributable to double diffraction, were observed (arrowed in Fig. 5). Investigation revealed that such diffraction patterns invariably come from thin edges of the foil; the extra reflections arise from transformation of the tetragonal precipitates to monoclinic symmetry. While we have not investigated this aspect of the microstructural evolution in detail, we know from other work on MgO-stabilized ZrO$_2$ (Porter & Heuer, 1979; Heuer & Mitchell, 1979) that small particles can transform during foil preparation as the matrix constraints preventing the martensitic transformation are removed by ion thinning. A dark-field image formed from one of the monoclinic reflections is shown in Fig. 6.

References