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Lattice expansion and contraction in nanocrystalline yttria-stabilized zirconia powders

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Rietveld refinement of powder X-ray diffractograms from nanocrystalline yttria-stabilized zirconia (2, 3.5, 5.5 and 8 mol.% $YO_{1.5}$) shows two tetragonal lattices. Transmission electron microscopy on powder with 8 mol.% $YO_{1.5}$ reveals two types of particles: tetragonal phase agglomerates of crystallites up to 28 nm experience lattice expansion and unagglomerated primary particles of 6 ± 2 nm undergo lattice contraction. Lattice contraction is due to surface curvature. Expansion is due to grain boundary free volume and point defects.
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The phase stability of zirconia across length scales from <10 nm to bulk sizes continues to be of interest as it influences the performance of this material in most applications. The stabilization of the tetragonal phase over the monoclinic one in nanocrystalline pure zirconia is well known [1]. Such a crystallite size effect combined with the role of a stabilizer cation leads to interesting phase-selection scenarios in zirconia-based materials as far as the relative stability of tetragonal and monoclinic phases is concerned. To illustrate, ultrafine grain size in tetragonal zirconia polycrystal, with ~4–6 mol.% $YO_{1.5}$, enhances the tetragonal phase stability [2]. Even the high-temperature transformation of the metastable t' tetragonal phase in thermal barrier coatings (TBCs) shows interesting phase transformation pathways. The precipitation of the cubic zirconia phase during exposure to temperatures exceeding ~1200 °C exhibits characteristics of spinodal decomposition. Another feature of phase transformations in TBCs is the simultaneous presence of multiple tetragonal phases upon annealing at 1482 °C [3].

Considering the role of nanocrystallinity in yttria-stabilized zirconia (YSZ) powders, so far the focus has been on the relative stability of the tetragonal and the monoclinic phases. It has, however, become apparent that nanometric particle or grain size influences the lattice dimensions of the phases present. Nanoparticles of ceria exhibit lattice expansion due to the enhanced concentration of trivalent cerium cations and anion vacancies [4]. As particle size decreases towards 3 nm, Ce^{4+}, which is coordinated with eight oxygen ions in the fluorite structure, reduces to Ce^{3+} with a coordination of seven oxygen ions. This leads to the formation of oxygen vacancies. The 8-fold ionic radius of Ce^{3+} (1.143 Å) is higher than that of Ce^{4+} (0.97 Å) [5]. Because of the above reasons the lattice is distorted in nanometric particles. It has also been shown that ceria–zirconia nanoparticles contain nanoscale regions of cubic and monoclinic ordering in ceria-rich and zirconia-rich clusters, respectively [6]. In order to relieve the lattice distortions to some extent, lattice expansion occurs in pure nanocrystalline ceria with Ce^{3+} and Ce^{4+} cations [4]. The dissolution of $YO_{1.5}$ in ZrO_2 creates anion vacancies to compensate for the charge balance of the ionic crystal. The ionic radius of Y^{3+} is 1.019 Å and it prefers 8-fold coordination with O^{2-} ions. The 8-fold radius of Zr^{4+} is 0.84 Å and it prefers 7-fold coordination [7–8]. Therefore it is an interesting possibility that these point defects influence the lattice parameters of nanocrystalline YSZ.

Lattice expansion has also been reported in nanostructured metals formed by high-energy ball milling

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[9]. This latter observation is believed to originate from the presence of excess free volume at the grain boundaries [9–11]. This factor may also influence nanocrystalline YSZ lattice.

In contrast to the above, lattice contraction is expected in the presence of surface curvature pressure through the Gibbs–Thomson effect [9,12]. Lattice contraction occurs in isolated nanocrystalline particles due to surface stress, which induces more hydrostatic compression on the nanoparticle as compared to micron-size particles. Hence, the change in the unit cell volume can be expressed as:

$$\Delta V/V_0 = (-4\sigma)/(KD) \quad (1)$$

where V_0 is the coarse-grained unit cell volume, σ is the surface energy, K is the bulk modulus and D is the spherical particle diameter.

In the present investigation, the simultaneous presence of two tetragonal lattices of different unit cell volumes in YSZ nanocrystalline powders has been probed, primarily through Rietveld refinement of X-ray diffraction (XRD) data. The presence of two tetragonal lattices has been confirmed.

Powders of pure zirconia and YSZ were prepared by the reverse co-precipitation technique. The assayed yttrium (III) nitrate hexahydrate (Alfa Aesar, 99.9% purity) and zirconyl nitrate hydrate (Sigma Aldrich, 99.99% purity) were dissolved in deionized water, in ratios dictated by the compositional requirement, to obtain a 0.25 M precursor solution. This solution was added dropwise to an ammonium hydroxide solution (pH 9.5) with continuous stirring. The white precipitate that formed was filtered and washed repeatedly with deionized water and then dried at 120 °C for 8 h. Nanocrystalline powder particles were obtained by calcining the dry precipitates between 800 and 900 °C for 2 h. Infrared spectra (not shown here) confirmed complete calcination. The compositions studied and their nomenclature are presented in Table 1. Selected materials were annealed at 900 °C for up to 50 h. No grinding was carried out after the initial calcination of the powders.

X-ray diffraction using Cu K_α radiation was carried out on all the powders in Bragg–Brentano geometry with a step size of 0.01° and with a time per step of 100 s (X'Pert PRO, PANalytical). Rietveld refinement (FullProf Suite software) using a pseudo-Voigt profile with axial divergence asymmetry was performed on the powder XRD patterns to derive the lattice parameters and weight fraction of each phase. Space groups $P4_2/nmc$ [13] and $P2_1/c$ [14] were used to model the tetragonal and monoclinic phases, respectively. The Rietveld refinement fit was evaluated based on the agreement indices R_p and R_{wp}, as well as the goodness of fit χ^2.

The XRD patterns of the as-synthesized zirconia and YSZ samples are shown in Figure 1. Rietveld refinement performed on the XRD patterns from both the 8YSZ powders considering only one tetragonal phase (Table 1) led to unit cell parameters that are in close agreement with similar analysis in the literature [15]. The yttria content was calculated based on the formula proposed by Krogstad et al. [15]:

$$c/a = 1.02311 - 0.001498x \quad (2)$$

where the c/a ratio is based on the pseudocubic description of the tetragonal phase, and x is mol.% $YO_{1.5}$. Based on Eq. (2), the $YO_{1.5}$ concentration in 8YSZ powders was found to be in good agreement with the nominal composition. Table 1 shows that as the yttria content in zirconia increases, the c/a ratio decreases. This trend is also consistent with the data in Ref. [15]. However, in order to determine whether multiple tetragonal lattices exist in nanocrystalline YSZ, Rietveld refinement was carried out based on the simultaneous presence of two tetragonal lattices. The full pattern fitting along with difference plot is shown in Figure 2. The goodness of fit based on two tetragonal lattices fitting is better than for single lattice fitting.

The results of Rietveld analysis based on two tetragonal lattices for the various materials of this study are presented in Table 2. It can be seen that both 8YSZ-A and 8YSZ-B consist of two tetragonal lattices. The t_1 unit cell volumes in these two powders are larger than the t_2 unit cell volumes. The presence of two tetragonal lattices was detected in all YSZ compositions except pure zirconia powders. The 2YSZ-A as-calcined powder has t_1, t_2 and the monoclinic phase ($a = 5.15359$ Å, $b = 5.19089$ Å, $c = 5.31426$ Å, $\beta = 99.057°$, weight fraction of 9.91%). Only a 0.19% difference in unit cell volume between the tetragonal lattices is observed. On the other hand, a 0.51% difference in the unit cell volumes of t_1 and t_2 lattices of 2YSZ-B (calcined at 800 °C) is observed along with the presence of monoclinic phase ($a = 5.16097$ Å, $b = 5.21645$ Å, $c = 5.28250$ Å, $\beta = 98.863°$, weight fraction of 3.79%). There is a 0.74% and a 0.58% difference between the unit cell volumes of t_1 and t_2 in 3.5YSZ and 5.5YSZ, respectively. Pure zirconia powder contains tetragonal (weight fraction 29.45%) and monoclinic phases with lattice parameters $a = 5.14950$ Å, $b = 5.20212$ Å, $c = 5.31745$ Å and $\beta = 99.008°$ (Fig. 1 and Table 1).

Table 1. Rietveld results of pure zirconia (which also contains monoclinic phase) and YSZ powders, considering a single tetragonal phase only.

Sample ID	Mol.% $YO_{1.5}$	Calcination temperature (°C)	Tetragonal (t) phase parameters				R_p	R_{wp}	χ^2
			a (Å)	c (Å)	c/a (pseudo-cubic)	Unit cell volume (Å^3)			
Zirconia*	0	850	3.59554	5.18424	1.0195	134.043	8.4	7.4	3.4
2YSZ-A*	2	900	3.59980	5.18029	1.0176	134.258	13	9.9	6
2YSZ-B*	2	800	3.60006	5.17841	1.0171	134.228	13.8	10.6	6.1
3.5YSZ	3.5	850	3.60173	5.17572	1.0161	134.284	6.6	5.4	3.3
5.5YSZ	5.5	800	3.60708	5.16792	1.0131	134.479	10.4	7.8	5.1
8YSZ-A	8	900	3.61115	5.16426	1.0112	134.688	7.5	5.7	3.6
8YSZ-B	8	800	3.61246	5.15979	1.0099	134.669	5.4	4.7	4.8

* Monoclinic phase is also present.

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