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Synthesis and structural characterization of calcia-stabilized tetragonal zirconia

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Synthesis of calcia-stabilized tetragonal zirconia by the reaction of precipitated zirconium hydroxide with calcium oxide at ~1400 K is described. The unit cell parameters of the oxide $a_0 = b_0 = 0.3644$ nm, $c_0 = 0.5092$ nm and $Z = 2$ are in good agreement with the high-temperature tetragonal crystallographic modification of pure zirconia.

1. Introduction

Owing to its excellent mechanical properties such as flexural strength and fracture toughness, stabilized tetragonal zirconia (TZ) has attracted wide attention as an engineering ceramic. Yttria-stabilized TZ was first reported by Gupta *et al.* [1]. Tsukuma and Shimada [2] later described the synthesis of TZ stabilized with ceria. A review of these oxides has been given recently by Nettleship and Stevens [3]. Nevertheless, calcia-stabilized TZ has not as yet been reported in the literature.

During our investigations on the reaction of precipitated zirconium hydroxide with calcium carbonate, oxalate and oxide, it was found that the reaction with calcia under certain conditions yielded calcia-stabilized TZ [4, 5]. This was further investigated and the results are discussed here.

2. Experimental procedure

TZ was synthesized by the precipitation technique using high-purity zirconyl nitrate (containing ~ 1.8% hafnium oxide) and GR grade calcium oxide. The following procedure was employed: zirconium hydroxide was precipitated at ~ 355 K by slow addition of ammonia to the required quantity of standard zirconyl nitrate solution with constant stirring. A small quantity of excess ammonia was added to the precipitate to ensure the basicity of the slurry to which the necessary amount of freshly calcined calcium oxide was added. The slurry was left to stand for some time with stirring. It was then filtered and dried at ~ 375 K. The TZ was obtained by heating the dried material to a temperature of ~ 1400 K. The reaction leading to the formation of the tetragonal oxide can be represented as

$$(1 - x)\mathrm{ZrO_2} + x\mathrm{CaO} \longrightarrow \mathrm{Ca}_x\mathrm{Zr}_{1-x}\mathrm{O}_{2-x} \quad (1)$$

which was employed for calculating the molar quantities of the reactants. However, it was noted that the stabilized tetragonal phase only formed in the range $0.07 < x < 0.09$; the reason for this limitation of the reaction is not yet understood. Thermogravimetry (TG) and differential thermal analysis (DTA) of the samples were done using an Ulvac Sinku-Riko TGD 5000 RH simultaneous analyser, while characterization of the TZ was carried out by XRD using CuK_α radiation on a Philips wide-angle goniometer. The formation of TZ was monitored by the characteristic doublets of the tetragonal phase at ~ 35° and 60° 2θ. The course of the reaction was studied by X-ray analysis of the samples immediately before and after the exothermic DTA peak and after heating at 1400 K. The density of the samples was determined by noting weight losses in deaerated water and benzene. The measured density of 5.684 g cm^{-3} for the sample with $x = 0.07$ was found to be within 3% of the calculated density from X-ray data.

3. Results and discussion

As mentioned above, the reaction of calcium oxide with zirconium hydroxide is found to be totally different from the widely investigated reaction of calcium carbonate with the hydroxide [4–6], when either partially stabilized (cubic + monoclinic) or fully stabilized (cubic) zirconia are obtained depending on the amount of calcia. TG analysis shows that the reaction is continuous and involves a single step; DTA gives a large endothermic peak around 385 K corresponding to the loss of water associated with the hydroxide and a sharp exothermic peak at 780 K corresponding to the amorphous–crystalline transformation of zirconia [6, 7]. Typical TG and DTA plots of a sample with $x = 0.09$ are shown in Fig. 1. It is observed that the exothermic peak, however, has shifted to higher temperature by 40 K with respect to pure zirconia, which clearly indicates that the reaction is concurrent with the amorphous–crystalline transformation. This was confirmed by XRD: the diffraction patterns before transformation showed the amorphous nature of the samples, while those after the transformation revealed samples to be crystalline and tetragonal, though the

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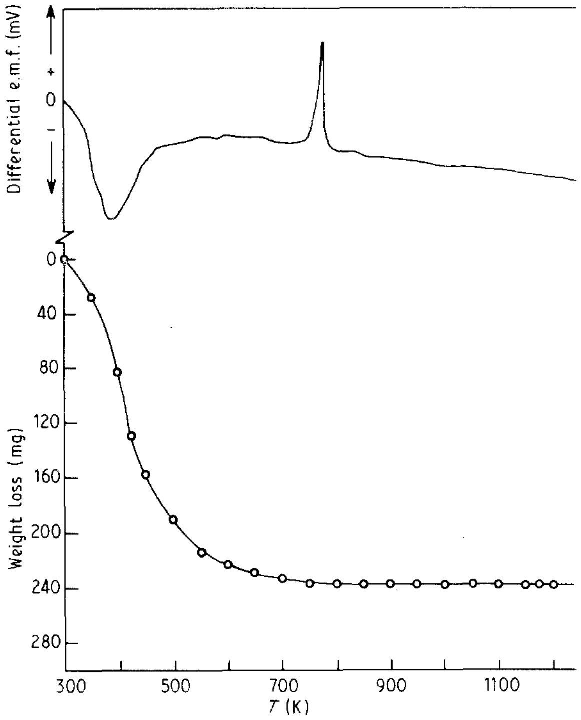

Figure 1 TG and DTA plots of the reaction of zirconium hydroxide with calcia.

lines were not as sharp as those of samples heated up to 1400 K.

The observed XRD reflections were indexed on the basis of a tetragonal unit cell; details for a sample of $x = 0.07$ prepared at 1375 K are given in Table I. The variations in cell constants due to changes in x between 0.07 and 0.09 were insignificant. The calculated cell constants $a_0 = b_0 = 0.3644$ nm and $c_0 = 0.5092$ nm are in close agreement with those of the high-temperature tetragonal modification of pure zirconia [8]. Nevertheless, it should be noted that the observed cell parameters are significantly different from those reported by Clark and Reynolds [9] for metastable pure tetragonal zirconia.

TABLE I Observed and calculated d-spacings and crystallographic data for calcia-stabilized tetragonal zirconia of $x = 0.07$

d_{obs} (nm)	I/I_0	hkl	d_{cal}(nm)
0.2950	100	101	0.2960
0.2582	8	110	0.2574
0.2548	18	002	0.2548
0.1810	39	112	0.1810
0.1554	13	211	0.1552
0.1539	24	103	0.1536
0.1481	7	202	0.1481
0.1175	8	213	0.1175

$a_0 = b_0 = 0.3644$ nm, $c_0 = 0.5092$ nm. $Z = 2$, $d_{\mathrm{obs}} = 0.5684$ nm, $d_x = 0.5838$ nm.

4. Conclusion

The preparation of calcia-stabilized tetragonal zirconia has been reported for the first time. The material was obtained by the precipitation method and heating at temperatures ~ 1400 K. Its unit cell parameters are in close agreement with the high-temperature tetragonal form of pure ZrO_2.

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