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Powder diffraction investigations of plasma sprayed zirconia

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The crystallographic and microstructural parameters of plasma sprayed pure zirconia powders were studied by X-ray and neutron powder diffraction. A significant influence of the flow rate of the quenching gas on the phase composition (the tetragonal to monoclinic ratio varied between 0.6 and 3.5) and on the micro-structure was observed, while structural parameters of both phases of all investigated samples remained essentially unchanged and were close to those reported in the literature. These results do not support the concept of a critical particle size effect as a stabilizing factor for the tetragonal phase. A transition from a tetragonal to a monoclinic phase was observed without any measurable change in the crystallite sizes by heating at 845 °C. A very high background on the neutron powder patterns may have been caused by the presence of pores in the samples.

1. Introduction

Pure bulk zirconia, ZrO_2, samples are monoclinic (m) at room temperature, tetragonal (t) between 1440 and 2640 K, and cubic up to the melting point at 2950 K. The tetragonal and cubic phases can be stabilized by the addition of suitable oxides, like MgO or CaO. The existence of the tetragonal phase at room temperature in fine pure zirconia powders is well established, but still the subject of controversial interpretation. Garvie [1] suggested that a lower surface free energy stabilizes the tetragonal form in very small crystals. This explanation was questioned by Srinivasan *et al.* [2], who observed the transition from a tetragonal to monoclinic phase at a rather low temperature, 500 °C, which was accompanied by a small decrease in particle size. Morgan [3] reported ca. 6 nm monoclinic particles and concluded that a small particle size was not necessarily the determining factor in stabilizing the tetragonal phase. Alternative explanations may be the presence of water vapour, structural similarities between amorphous precursor gels and the tetragonal structure, or the absence of defect arrangements in small particles which could be operational to trigger the t → m transformation. The role of domain boundaries, vacancies, stress-fields, nucleation and growth mechanisms (homogeneous, heterogeneous) are discussed, for example, in [4]. On the other hand, the crystal structures of, and the transformation mechanism between, the phases and their stabilization are of considerable technological interest with respect to optimized physical and chemical properties of zirconia.

Crystal structure determinations have been performed on tetragonal ZrO_2 using X-ray powder diffraction at elevated temperatures, 1470–2230 K [5]. The monoclinic structure of ZrO_2 has been studied at room temperature with X-ray single crystals [6, 7]. Stabilized tetragonal and pure monoclinic phase were re-examined by means of neutron powder diffraction [8], and the structure of the tetragonal phase in the status of fine pure powder also studied [9]. The m → t and t → m phase transformations in undoped zirconia were recently investigated *in situ* [10, 11], and a displacive character at the first stage of the m → t transformation was found. This study presents results of refinements of X-ray and neutron diffraction data of ultradispersed powders obtained by plasma spraying.

2. Experimental procedure

Ultrafine ZrO_2 powders were prepared in low temperature r.f. air–plasma by means of equipment described in [12]. A coarse grained commercially available ZrO_2 powder was used containing 0.0023% Hf. The amounts of other impurities were even smaller both in the starting powders and in the reaction products, except for nitrogen which was about 0.2–0.3% in all samples (determined by neutron activation analysis). The plasma apparatus operated with a main power supply of 105 kW, and an additional maximum power supply of 65 kW for regulation. The plasma gas was introduced tangentially using a flow rate of $8\ m^3\ h^{-1}$. The carrier gas and raw materials were introduced radially through four channels with flow rates of $1.2–2\ m^3\ h^{-1}$. The condensation and the subsequent growth process of the ZrO_2 particles was controlled by introducing cold air as a quenching gas, with flow rates between 1.6 and $5.8\ m^3\ h^{-1}$. Estimated

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TABLE I Characteristics of plasma syntheses products

Sample no.	Spec. surface ($m^2 g^{-1}$)	Size (nm)	Zr (wt %)
1	16 (2)	66.0	74.2 (4)
2	22 (2)	50.0	73.9 (4)
3	25 (2)	43.0	73.7 (4)
4	37 (2)	29.0	73.4 (4)

quenching rates were ca. 10^{-2} s. The characteristics of the final products are summarized in the Table I. The content of zirconium was determined by conventional chemical analysis with an error of 0.5% and particle sizes were calculated from measurements of specific surfaces carried out by the BET argon adsorption–desorption method (assuming a spherical particle shape) [13].

All X-ray experiments were carried out with a STOE X-ray transmission powder diffractometer: monochromatic $CuK_{\alpha1}$ radiation, cylindrical powder samples (diameter 0.2 mm), step scanning mode with step width of 0.02° between 10 and 126°. The neutron powder experiments were carried out at the FRM reactor facility in Garching (instrument MAN I): cylindrical powder samples (diameter 15 mm) step-scanning between 10° and 105° with $\Delta(2\theta) = 0.1°$, wavelength 0.1075 nm.

3. Data analysis and results

The data were analysed by means of the GSAS program package [14]. Very flexible profile shapes, which were directly interpretable in terms of particle sizes and strains, could be refined with this multiphase X-ray and neutron Rietveld program. As a good approximation to the Voigt profile function needed in particle size and strain analysis [15], the Thompson-Cox-Hastings pseudo-Voigt profile function [15, 16] was chosen for analysis:

$$\mathrm{pV}(\delta 2\theta) = \eta \cdot L(\delta 2\theta, \Gamma) + (1 - \eta) G(\delta 2\theta, \Gamma) \quad (1)$$

where $pV(\delta 2\theta)$ is the intensity of a data point displayed by $\delta 2\theta$ from the Bragg angle $2\theta_k$ of the kth line in the powder diagram. L and G are Lorentzian and Gaussian profile functions, respectively, and η is the mixing parameter. Γ is the full width at half maximum (FWHM) of the combined profile function pV. η and Γ can be expressed by series expansions of Γ_L and Γ_G, the respective individual FWHM of the Lorentz and Gauss profiles.

Neglecting anisotropic line broadening, the angular variation of these FWHMs are modelled in GSAS as:

$$\sigma^2 = 8 \ln 2 \Gamma_{G^2} = U \cdot \tan^2\theta + V \tan\theta + W + P/\cos^2\theta \quad (2)$$

$$\Gamma_L = L_x/\cos\theta + L_y \tan\theta + Z \quad (3)$$

where σ is the variance and U, V and W are the well-known Gaussian profile coefficients [17]. P allows for Gaussian–Scherrer broadening. L_x and L_y describe the Scherrer and strain broadening components of the Lorentzian profile, respectively. To cope with the information losses due to severe overlapping of diffraction peaks, it was assumed that particle size and strain broadening of line of profiles could be adequately described by Lorentzian and Gaussian functions, respectively. Thus, the same model as De Keijser *et al.* [18] was used for the physical broadening of line widths, which lead to $P = L_y = Z = 0$. The volume-weighted crystallite size $\langle D \rangle_V$ and some weighted average strain ε can then be written as:

$$\langle D \rangle_V = K\lambda/(\beta^S \cos\theta) \quad (4)$$

$$\varepsilon = \tfrac{1}{4}(\beta^D \cos\theta) \quad (5)$$

where β^S and β^D (taken on a 2θ scale) denote the integral breadths of the size and strain broadened profiles, respectively. K is the Scherrer constant and λ the wavelength. For a pure Gaussian strain profile ε is related to the mean square strain $\langle e^2 \rangle$ by $\varepsilon^2 = \pi/2 \langle e^2 \rangle$. Comparison with Equations 2 and 3, assuming $K = 1$, yields:

$$\langle D \rangle_V = \lambda \cdot K_d L_x^{-1} \quad (4a)$$

$$\varepsilon = 1/K_\varepsilon U^{-1/2} \quad (5a)$$

where the coefficients K_d, K_ε convert the FWHMs Γ_L, Γ_G of the Rietveld refinement to the integral breadths β^S, β^D needed for the size and strain analysis.

Correction for instrumental broadening was done via Rietveld refinement of profile parameters for reference substances. In the X-ray case a well-crystallized standard sample of LaB_6 powder was used. The refinement yielded $W_i = 6.0(1)$ [centidegree^2] and $L_y = 6.0(1)$ [centidegree], where the other profile parameters U, V and L_x were zero within one estimated standard deviation. In the neutron case, a Ni standard powder yielded pure Gaussian instrumental profiles and the following parameters were refined: $U = 2542(159)$, $V = -1640(116)$, $W = 442(25)$ [centidegree^2]. For the ZrO_2 samples the same Gaussian profile parameters and L_x were refined. The relatively large instrumental broadening yielded somewhat less precise (but more accurate, see below) results in the neutron case. Results of the refinements for four samples (see Table I for numbering of the samples) are summarized in Table II. Particle sizes are given in Table IV.

To investigate the origin of the stabilizing phenomena of the phases, further X-ray and neutron experiments were carried out. Sample 3 was studied again before and after annealing at $T = 845\,°C$. The results are given in Table III. The particle sizes and microstrains were analysed by the method described above and by the method of Langford [19] and Warren and Averbach [20] (Table V). As can be seen from this table there are some discrepancies between the different methods less severe for particle sizes than for strains.

4. Discussion

The observed values of atomic coordinates for the monoclinic phase are very close to those given in [10], whereas the values found for the tetragonal phase are somewhat closer to those reported in [9]. Although there are some differences for the different samples, no

TABLE II Refined parameters of X-ray (X) and neutron (n) powder data

Sample no.	2 (X)		1 (X)		1 (n)		3 (X)		4 (X)	
	Tet	Mon	Tet	Mon	Tet	Mon	Tet	Mon	Tet	Mon
R_{wp} (%)	3.8		3.6		3.5		4.6		4.2	
GoF	0.89		0.90		1.15		1.01		0.92	
a (nm)	0.35960 (1)	0.51482 (2)	0.35958 (1)	0.51484 (2)	0.35957 (8)	0.51495 (40)	0.35957 (1)	0.51496 (1)	0.35961 (1)	0.51491 (3)
b (nm)		0.52076 (2)		0.52067 (2)		0.52075 (40)		0.52076 (2)		0.52079 (3)
c (nm)	0.51841 (2)	0.53149 (2)	0.51844 (2)	0.53154 (2)	0.51844 (2)	0.53164 (40)	0.51845 (2)	0.53163 (2)	0.51843 (1)	0.53160 (3)
β (°)		99.232 (2)		99.229 (2)		99.23 (6)		99.225 (1)		99. 225 (2)
U (c.d.^{2})	9 (4)	8 (4)	0	9 (5)	2576 (77)	2875 (204)	22 (2)	126 (5)	61 (8)	221 (17)
L_x (c.d.)	20.9 (2)	12.2 (1)	16.8 (1)	10.0 (1)	11 (2)	7 (2)	18.2 (1)	10.7 (2)	25.0 (5)	13.4 (8)
Zr										
x		0.2756 (2)		0.2758 (3)		0.2747 (9)		0.2754 (2)		0.2748 (4)
y		0.0392 (2)		0.0391 (2)		0.0394 (9)		0.0391 (2)		0.0384 (3)
z		0.2092 (2)		0.2094 (2)		0.2090 (9)		0.2098 (2)		0.2093 (3)
B (nm^2)	4.8×10^{-3} (2)	4.4×10^{-3} (3)	9.3×10^{-3} (3)	9.6×10^{-3} (4)	3.5×10^{-3} (5)	5.9×10^{-3} (17)	5.2×10^{-3} (4)	6.1×10^{-3} (5)	1.75×10^{-2} (5)	1.56×10^{-2} (9)
O1										
x		0.070 (1)		0.063 (2)		0.070 (1)		0.065 (1)		0.067 (2)
y		0.331 (1)		0.328 (1)		0.332 (1)		0.326 (1)		0.326 (2)
z	0.4545 (1)	0.343 (1)	0.4510 (2)	0.343 (1)	0.4522 (4)	0.3464 (9)	0.4514 (6)	0.347 (1)	0.4537 (6)	0.348 (2)
B (nm^2)	3×10^{-3} (2)	4.1×10^{-3} (2)	1.8×10^{-2} (3)	2.6×10^{-2} (3)	4.2×10^{-3} (7)	3.2×10^{-3} (5)	2.0×10^{-2} (1)	3.1×10^{-2} (3)	3.2×10^{-2} (1)	2.5×10^{-2} (4)
O2										
x		0.453 (2)		0.450 (2)		0.451 (1)		0.461 (2)		0.464 (2)
y		0.760 (1)		0.758 (1)		0.758 (1)		0.757 (1)		0.760 (1)
z		0.477 (1)		0.474 (2)		0.478 (1)		0.479 (1)		0.476 (3)
B (nm^2)		4.1×10^{-3} (2)		2.6×10^{-2} (3)		3.5×10^{-3} (4)		3.1×10^{-2} (3)		2.5×10^{-2} (4)
phase ratio tetragonal: monoclinic	37.9 (1):62.1 (1)		36.3 (3):63.7 (3)		34 (1):66 (1)		58.2 (2):41.8 (2)		77.8 (4):22.2 (4)	

[a] c.d. = centidegree.

TABLE III Refined parameters of sample 3 before and after annealing

		X-rays	X-rays annealed	Neutrons	Neutrons annealed
R_{wp} (%)		5.8	5.5	2.9	3.3
GoF		0.92	1.05	1.31	1.10
Tetragonal					
	a (nm)	0.35958 (1)	0.35957 (2)	0.35936 (4)	0.35916 (8)
	c (nm)	0.51849 (2)	0.51850 (3)	0.51814 (6)	0.5179 (2)
Zr	B (nm^2)	5.9×10^{-3} (2)	9.5×10^{-3} (5)	3.0×10^{-3} (2)	5.5×10^{-3} (10)
O	z	0.4509 (7)	0.452 (2)	0.4524 (3)	0.454 (2)
	B (nm^2)	4.5×10^{-3} (8)	3.2×10^{-3} (21)	4.7×10^{-3} (2)	2.9×10^{-3} (13)
Monoclinic					
	a (nm)	0.51505 (2)	0.51481 (2)	0.5149 (1)	0.51423 (9)
	b (nm)	0.52077 (3)	0.52059 (2)	0.52026 (9)	0.52000 (1)
	c (nm)	0.53164 (3)	0.53209 (2)	0.5313 (1)	0.5311 (1)
	β (°)	99.223 (2)	99.216 (1)	99.23 (2)	99.205 (6)
Zr	x	0.2763 (4)	0.2750 (2)	0.276 (1)	0.2766 (6)
	y	0.0395 (3)	0.0399 (2)	0.0389 (9)	0.0394 (6)
	z	0.2084 (3)	0.2096 (2)	0.209 (1)	0.2098 (6)
	B (nm^2)	7.6×10^{-3} (5)	1.01×10^{-2} (2)	4.5×10^{-3} (8)	5.0×10^{-3} (2)
O1	x	0.066 (2)	0.067 (1)	0.069 (2)	0.0694 (8)
	y	0.327 (2)	0.330 (1)	0.331 (2)	0.3310 (7)
	z	0.338 (2)	0.344 (1)	0.343 (1)	0.3462 (6)
	B (nm^2)	1.18×10^{-2} (21)	6.6×10^{-3} (10)	3.2×10^{-3} (8)	5.3×10^{-3} (2)
O2	x	0.453 (3)	0.453 (1)	0.448 (2)	0.4495 (7)
	y	0.763 (2)	0.7538 (7)	0.758 (2)	0.7572 (7)
	z	0.479 (3)	0.479 (2)	0.480 (1)	0.4774 (7)
	B (nm^2)	0.0 (9)	6.8×10^{-3} (10)	2.1×10^{-3} (8)	3.2×10^{-3} (2)
Phase ratio tetragonal: monoclinic		63.9 (3):36.1 (3)	14.1(2):85.9 (2)	61 (1):39 (1)	13 (1):87 (1)

TABLE IV Particle sizes D (nm) and strain ε (%)

Sample	D		ε	
	Mon	Tet	Mon	Tet
1 (n)	89.0 (38)	49.7 (76)	0	0
(X)	56.2 (5)	34.4 (3)	12 (3)	0
2	46.1 (4)	26.9 (3)	12 (3)	12 (3)
3	52.5 (10)	30.8 (1)	46 (1)	19 (8)
4	42.0 (25)	22.5 (5)	61 (2)	32 (2)

TABLE V Particle sizes D (nm) and strains ε (%) of sample 3 before and after annealing; method 1 from profile parameters; method 2 from single reflexions (Langford [19]); method 3 from two reflexions (Warren and Averbach [20])

	D		ε	
	Before	After	Before	After
Tetragonal phase				
Method 1				
X-rays	31.2 (3)	29.5 (5)	0.20 (2)	0.35 (3)
neutrons	28.8 (11)	28.0 (64)	0.0 (3)	0.05 (5)
Method 2				
X-rays	37.0 (20)	38.0 (20)	0.4 (3)	0.4 (3)
Monoclinic phase				
Method 1				
X-rays	54.0 (10)	40.0 (4)	0.48 (2)	0.41 (3)
neutrons	49.7 (115)	33.0 (30)	0.8 (2)	0.3 (2)
Method 2				
X-rays	57.0 (20)	40.0 (20)	0.20 (5)	0.06 (3)
Method 3				
X-rays	30.0 (10)	21.0 (5)	0.62 (2)	0.61 (1)

clear tendency can be extracted which could be related to the production process. The behaviour of the atomic displacement parameters gives no clear picture. The thermal parameters of the monoclinic phase derived from the more reliable neutron data (uncertainties with absorption correction in the X-ray case) agree within the error limits with those reported in [8–11]. Considering the lattice constants there is poor consistency between literature values [8, 9, 21, 22]. We believe that our data are free from significant systematic errors. In the X-ray case this is proven by the results from the well-characterized LaB_6 standard sample; neutron and X-ray results agree within 1 e.s.d. (sample 1) and within 2 e.s.d.s for sample 3. There is close agreement for the monoclinic phase with the data given in references [8, 10, 11].

The c-lattice constants of the tetragonal phases for all investigated samples are very close to each other, but are significantly larger when compared with values given in [9]. According to the suggestion about the orientational relationship obtained in [10] from an extrapolation of the high temperature tetragonal lattice constant to room temperature, c_{tet} should correspond to b_{mon} and $a_{tet} \cdot \sqrt{2}$ to $a_{mon} \cdot \sin\beta$. Table II shows that both relations are indeed fairly well fulfilled, thus giving confirmation of the earlier assumption.

The particle sizes determined by X-ray powder pattern analysis are generally lower than those derived from specific surface measurements. However, the neutron results of samples 1 and 3 are close to the "specific surface value" when a weighted average of t and m size is compared. This is probably a consequence of the better description of the line shapes by the pV-functions in case of neutrons. In other words, the deconvolution procedure is more reliable. Comparing the different analytical methods in Table V it turns out that the results from profile parameters and from the Langford method are in good agreement with each other, while those from the Warren–Averbach method differ appreciably. In any case, without taking the absolute values too literally, the particle sizes for the tetragonal phase are generally lower than those of the monoclinic phase. The D_{tet}-values are below the values reported in [1] necessary for stabilizing the tetragonal phase. Moreover, more rapid quenching conditions resulted in smaller crystallite sizes with a significantly increased amount of t-phase. These facts are consistent with the so-called critical size effect. On the other hand, repeating the procedure suggested in [2], the results of these authors can be confirmed: the phase composition changed significantly in favour of the monoclinic phase content without any significant increase in particle sizes. On this basis, the assumption of a leading role of the surface energy among the stabilizing factors is rejected. Other effects related to the small particle size must play the decisive role. From these results it cannot, however, be decided whether or not anionic vacancies control the t → m transformation in plasma-sprayed zirconia, which was proposed for zirconia made by precipitation [23]. These conclusions are further supported by the results of sample 3 before and after annealing (cf. Table V). There is a clear tendency that the sizes of the surviving tetragonal particles remain almost unchanged, whereas the average size of the monoclinic particles were reduced after annealing. Together with the result that most of the tetragonal particles transform into the monoclinic phase this result may be understood by a transformation process t–m without any change, in particular, no increase in the size of the (transforming) particles.

The result of generally lower strains (Table IV) in the tetragonal particles is equivalent to that found in the m → t transformation regime [10]. Assuming the strained state of m-particles to be decisive for the transformation into the t-phase, a release of strains by temperature treatment without changing the size remarkably would prevent the transformation. The strains might be introduced by quenching, internal stresses due to defects, disorder, etc.

Considering the strain behaviour during annealing the figures (Table V) should not be taken too seriously due to the relatively large variations depending on the type of experiment (X-ray, neutrons) or the evaluation method. Nevertheless, there is some overall tendency for an increase of strains within the tetragonal particles after annealing and a decrease for the monoclinic particles. This increase in the tetragonal phase is similar to that observed for pure ZrO_2 within the tetragonal particles upon heating [10]. This strange behaviour might be discussed by a subgrain-domain structure where the transformation process proceeds inhomogeneously within one and the same grain.

A high and flat background was observed in the neutron diffraction powder patterns. In order to exclude water molecules adsorbed on the surface of the particles, which could cause large incoherent background scattering, the sample was heated to 300 °C and the neutron diffraction measurement repeated. No significant change was observed. Therefore, it is suggested that pores may be responsible. Such an assumption is justified because pores are considered to be an inherent property of such materials [24] and may cause such an effect [25]. A further indication that this explanation should be correct is given by the observation of a significantly reduced background in the annealed sample. Additional work, however, is necessary to prove this point (by small angle scattering).

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