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THERMOANALYTICAL INVESTIGATIONS ON HYDROUS ZIRCONIA

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The variations in the thermoanalytical curves for three differently produced powders of hydrous zirconia are discussed in connection with X-ray measurements and powder-metallurgical characterization. They were shown to characterize the ZrO_2—H_2O bonding and the thermal treatment for the calcination of hydrous zirconia. They allowed selection of the product with the most favourable microstructure for a high sinter activity, an explanation of the phase formation and phase transformations, and estimations of the energy content of the amorphous material and the thermal stability of the tetragonal phase. It was shown that thermal analysis is an appropriate method for the optimizing of ZrO_2-powder production.

Fine ZrO_2 powders with high sinter activity are prepared by precipitation from an aqueous solution e.g. according to

$$ZrOCl_2 + 2\,NH_4OH + H_2O \rightarrow Zr(OH)_4 + 2\,NH_4Cl \qquad (1)$$

followed by a drying process. Previous studies have shown that the conditions of precipitation (pH, concentrations, and temperature) do not significantly influence the sintering properties of the product. Rather the drying parameters predominantly control these properties, thereby providing a possibility for avoidance of the formation of hard agglomerates that are difficult to densify. The shifting of the critical steps to the thermal processes enables one to use thermoanalytical techniques for optimization of the production method and the properties of the ZrO_2 powder.

In this paper we study the three thermoanalytically detectable transformations of hydrous zirconia [1] (Table 1), with regard to how far they exhibit peculiarities suitable for characterizing the microstructure, the phase composition and the sinter activity of ZrO_2 powder, either pure or with admixtures of the stabilizers MgO, CaO or Y_2O_3.

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Table 1 Thermal effects of hydrous zirconia

Reaction		DTA		TG
		T_p, K	ΔT, K	Δm, %
1		389	−2.2	−29.4
2		687	+5.3	0
3a	(a)	1237	+0.2	0
3b	(b)	1449	−0.16	0

(a) = in the cooling step; (b) = in the heating step

Experimental

The following variants were applied to dry the hydrous zirconia precipitates:

A) Freezing of the $Zr(OH)_4$ precipitate, and thawing followed by:
- — Drying* = variant 1
- — Washing with acetone-toluene and drying = variant 2
- — Freeze-drying = variant 3

B) Direct treatment of the precipitate:
- — Freeze-drying = variant 4
- — Washing with acetone-toluene and drying = variant 5
- — Drying, crushing and milling = variant 6

The resulting powder properties are listed in Table 2.

Thermoanalytical investigations were performed on the most active powders

Table 2 Examined drying-modes and resulting powder properties

Drying variant	Powder density (a), g/cm³	Spec. surface area (b), m²/g	Green-density (c), g/cm³	Sinter-density (d), g/cm³
1	1.05	13	3.26	4.61
2	0.77	11	2.91	5.4
3	0.96	3	3.42	4.5
4	0.2	12	2.72	5.6
5	1.13	4	2.97	5.11
6	1.31	2	3.75	4.49

(a) = calcined at 1000°; (b) = dried at 120°; (c) = pressed at 200 MPa; (d) = sintered at 1700°. 2 h. H_2

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* Always at 20° for 24 h, then at 120° for 4 h.

(variants 2 and 4 in Table 1) in comparison with the normally dried powder (variant 6). The powder variants 2 and 6 were air-dried for 75 h at 20°.

Simultaneous DTA–TG and DTG measurements were carried out under dynamic conditions with a Mettler TA 1 instrument:

Sample holder: Pt/Rh–Pt type DTA 20; crucible: Al_2O_3 (vol. 0.9 cm^3); sample mass: 0.1 g; atmosphere: flowing nitrogen (5 l/h); heating rate: 6 deg/min.

Results and discussion

Reaction 1: drying, calcination:

$$ZrO_2 \cdot xH_2O \rightarrow ZrO_2 + xH_2O - Q_1 \qquad (2)$$

Beginning at room temperature, there is a broad endothermic DTA peak and an exponentially decreasing TG effect, obviously connected with the drying and calcination. Figure 1 and Table 3 show that these curves are quite different for the three powder variants. The following information can be derived from them:

The values of the activation energies demonstrate that the strength of the bonding between ZrO_2 and H_2O is very weak, indicating physical adsorption.

The continuous shape of the curves shows that definite hydrates do not occur, and thus it is correct to call the material "hydrous zirconia" [2].

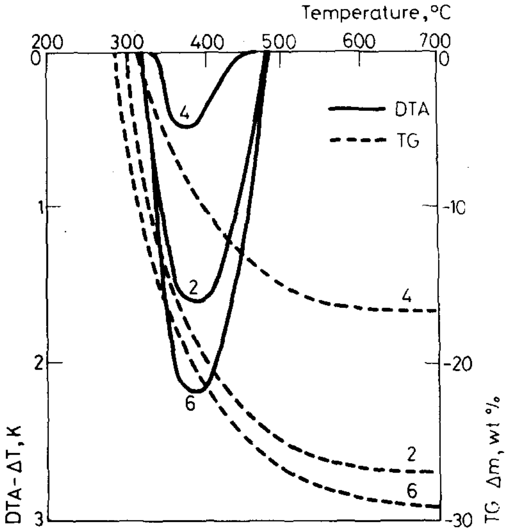

Fig. 1 DTA and TG curves of the hydrous zirconia powder variants
2 = freezed, 4 = freeze dried, 6 = directly dried

Table 3 Evaluation of TG and DTA results of reaction 1

Powder variant	Peak area F μV.s	Mass loss, Δm %	F_m mass loss, μV.s/g	E, kJ/mol
2	8190	27.2	3022	40
4	2435	16.7	1458	26
6	11845	29.4	4029	42

The mass loss of nearly 30 wt.% for normally dried powder (variant 6) is in agreement with a water content of three molecules per molecule of ZrO_2, so that $x = 3$ in Eq. (2). The water content depends on the drying treatment of the powder.

The quotient of the DTA peak area divided by the mass loss is proportional to the amount of energy necessary for the evaporation of the water from the solid. The small values for powder variants 2 and 4 (Table 3) reveal that they have a very loose and open microstructure, while the high value for variant 6 shows that is has a more strongly agglomerated, closed microstructure. Both accord with the values for the activation energy and the sinter densities obtained on these powders (Tables 1 and 3).

Reaction 2: formation of crystalline phases:

$$ZrO_{2(X-\mathrm{ray\,amorph.})} \rightarrow ZrO_{2(\mathrm{cryst.})} + Q_2 \tag{3}$$

Directly after the conclusion of reaction (1), a sharp exothermic peak appears, not connected with any loss of mass. The X-ray diffraction patterns show that this is caused by the formation of the crystalline phases from the X-ray amorphous product of the precipitation.

Since the peak area of this curve is proportional to the difference in energy content of the amorphous and crystalline states, it is surprising that the most sinter-active powder (variant 4) gives the smallest peak area (in Fig. 2). From the X-ray diffraction patterns, however, it can be seen that this, and also the other active powder (variant 2) exhibit an elevation of the background near the main reflex of the tetragonal structure, before reaction (2) indicating that these powders are preorientated towards the tetragonal structure. This preorientation is connected with the freezing process, probably due to the high pressure arising in the material. It diminishes the energy content to the crystalline state. This demonstrates once more that an excellent sinter activity requires not only a high energy content, but also a favourable agglomerate structure, like that existing in powder variants 2 and 4.

The addition of stabilizers changes (i) the temperature position and (ii) the

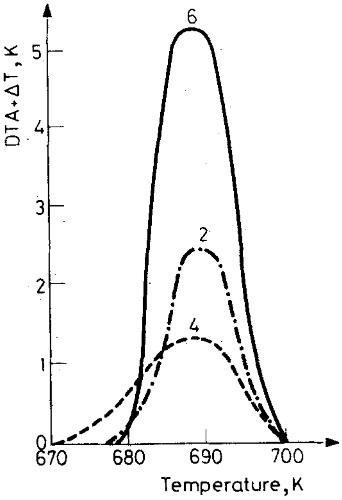

Fig 2 DTA curves for the formation of crystalline phases of the powder-variants 2, 4, 6

shapes of the DTA peaks (Fig. 3) and (iii) the structure of the crystalline product. Pure ZrO_2 and ZrO_2/MgO yield the tetragonal phase at relatively low temperature with a high transformation rate. From mixtures containing the bigger Ca^{2+} and Y^3 ions, the cubic phase is formed at higher temperatures and with a smaller rate.

The curves in Fig. 3 allow the further conclusion that the mixtures of the components, produced by adsorption (Ca^{2+}, Mg^{2+}) and coprecipitation (Y^{3+}) are microdisperse homogeneously, because they show only the peak of the solid solution.

Reaction 3: phase transformation:

$$ZrO_{2,\mathrm{monoclinic}} \rightleftharpoons ZrO_{2,\mathrm{tetragonal}} + Q_3$$

Beginning with the first cooling in the temperature cycles between 800 and 1500 K, pure and partially stabilized zirconia shows a very weak reversible DTA peak with considerable hysteresis. It is exothermic in the cooling, and endothermic in the heating run, and is caused by the transformation from the monoclinic to the tetragonal phase (Fig. 4). For the thermal processes of powder production, it gives the following information:

The lack of the peak in the first heating of ZrO_2 demonstrates that the tetragonal phase is formed directly in reaction (2).

The lack of the effect for stabilized ZrO_2 shows that the cubic phase is formed, which exists down to room temperature.

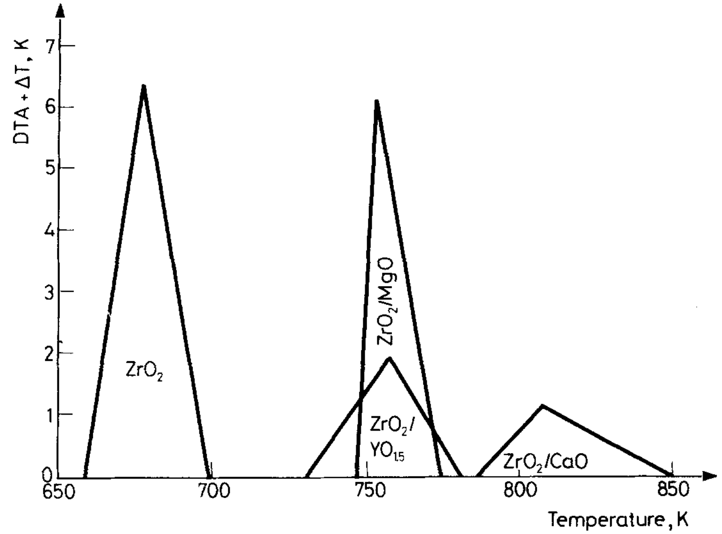

Fig. 3 DTA curves for the formation of crystalline phases in pure and stabilized zirconia (powder var. 2)
$ZrO_2 + 9.4$ mol% MgO
$ZrO_2 + 18$ mol% CaO
$ZrO_2 + 8.7$ mol% $YO_{1.5}$

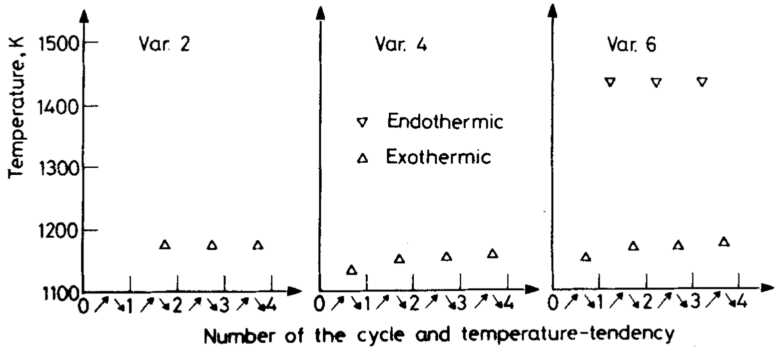

Fig. 4 Phase-transformation monoclinic → tetragonal for the powder variants 2, 4, 6 in temperature cycles. Peak heights ≈1 μV

Only the active powder variants 2 and 4, with a loose and soft microstructure, show the exothermic peaks clearly, but the reverse transformations take place without a visible peak in the curve.

The compact-structured variant 6 powder exhibits the reversible peaks (Fig. 4) both on heating and on cooling. Samples with a small content of stabilizers (for example 2.4 mol % MgO) display a wide region of metastability of the tetragonal phase, which diminishes in subsquent cycles as manifested by an increase in the T_p of the exothermic peak. This behaviour can be used for control of the stability of tetragonal ZrO_2 on thermal treatment.

References

1 H. Th. Rijnten, Zirconia, Proefschrift, TH Delft, 1971.

2 G. A. Gimbleth, A. A. Rahmann and K. S. W. Sing, J. Chem. Technol. Biotechnol., 30 (1980) 51–64.

Zusammenfassung — Die Unterschiede der thermoanalytischen Effekte für drei verschieden hergestellte wasserhaltige ZrO_2-Pulver wurden in Verbindung mit Röntgenuntersuchungen und der pulvermetallurgischen Charakterisierung diskutiert. Es zeigte sich, daß man mit ihrer Hilfe die ZrO_2—H_2O-Bindung und die thermische Behandlung bei der Kalzinierung des wasserhaltigen ZrO_2 formulieren kann. Sie erlauben, das Produkt mit der günstigsten Mikrostruktur für eine hohe Sinteraktivität auszuwählen, die Phasenbildung un Phasenumwandlungen zu erklären, den Energieinhalt des amorphen Materials und die thermische Stabilität der tetragonalen Phase abzuschätzen. Es erwies sich, daß die Thermoanalyse eine geeignete Methode zur Optimierung der ZrO_2-Pulver-Herstellung ist.

Резюме — Обсуждены различия термоаналитических кривых для трех порошковых образцов безводной двуокиси циркония, охарактеризованных порошковой металлургией и рентгенофазовым анализом. Тераналитические кривые представили возможность оценить связь ZrO_2—H_2O и термическую обработку безводной двуокиси циркония. Кривые также позволили отобрать продукт с наиболее благоприятной микроструктурой для высокоактивного спекания, объяснить фазовые образования и фазовые превращения, а также установить энергию образования аморфного материала и термоустойчивость тетрагональной фазы. Показано, что термический анализ является подходящим методом оптимизации получения порошкообразной двуокиси циркония.