Dedicated to Professor Dr. Roger Blachnik on the occasion of his 60th birthday

THERMAL STABILITY OF THE β″ PHASE IN THE ZrO₂-Zr₃N₄ SYSTEM

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Abstract

Annealing of ZrO_2 in a nitrogen atmosphere leads to a nitrogen containing phase called β″ phase having a trigonally distorted fluorite structure with ordered anion vacancies. DTA/TG investigations indicated that the β″ phase decomposes into m-ZrO_2 above 500°C releasing nitrogen during the reaction with oxygen. Prevention of oxygen uptake by use of closed tantalum tubes instead of open platinum crucibles enabled the detection of a new reversible phase transition at ~965°C. The thermoanalytical results have been confirmed by high temperature-X-ray investigation.

Introduction

Zirconia based ceramics are of huge interest in materials sciences. Thus ZrO_2 is used in a wide field of construction ceramics because of its extraordinary mechanical properties, and its high ionic conductivity at elevated temperatures makes it suitable as a solid state electrolyte in oxygen sensors.

At atmospheric pressure ZrO_2 exists in three polymorphs. At ambient temperatures it has a monoclinic structure, between ~1175°C and ~2400°C its structure is tetragonal, and up to the melting point at nearly 2700°C it exists in the cubic form (fluorite-type structure). The high temperature polymorphs of zirconia can be stabilized at ambient temperatures by doping with aliovalent oxides, e.g. CaO, Y_2O_3, or MgO. Systems like ZrO_2-CaO, ZrO_2-Y_2O_3, and ZrO_2-MgO have been investigated by many authors and the phase relationships are well established. Doping with aliovalent oxides leads to the formation of oxygen vacancies, which in turn are responsible for the outstanding ionic conductivity of zirconia ceramics.

A new approach to enhance the oxygen conductivity is doping with aliovalent anions such as nitrogen. Studies on the ZrO_2-Zr_3N_4 system were first performed by Gilles *et al.* [1–3], who investigated the ammonolysis and nitridation of ZrO_2/ZrN

mixtures. The first detailed studies of direct nitridation of pure ZrO_2 (N_2 atmosphere, graphite heated furnace, $T = 1400–2000°C$) [4, 5] revealed the formation of β''/m-ZrO_2 mixtures, the amount of the β'' phase increasis with increasing total nitrogen content of the sample. By use of a combination of chemical analysis (hot gas extraction) and quantitative XRD-phase analysis, the composition of the β'' phase was determined to $\sim Zr_7O_{9.5}N_3$ [6]. Its crystal structure can be described as a trigonally distorted fluorite structure with an ordered arrangement of anion vacancies [7]. Very little is known about the high temperature stability of the β'' phase against oxygen.

This behaviour has been investigated using thermoanalytical and high-temperature-XRD methods, and the results are described below.

Experimental

Nitrogen-doped zirconia was prepared from commercial ZrO_2 (99.9%; Alfa, Karlsruhe, Germany). The powder was pressed isostatically (530 MPa) into pellets (diameter: 8 mm; thickness: 10 mm), which were annealed in 1 bar-N_2 atmosphere at 1600°C for 2 h. After slowly cooling the pellets were powdered.

To investigate the thermal stability of nitrogen doped zirconia the simultaneous DTA/thermobalance L81 (Linseis, Selb, Germany) was used.

For determining the exact composition of the β'' phase TG measurements were carried out making use of commercial corundum crucibles. The DTA investigations were performed in air, flowing nitrogen ($pO_2 = 10^{-3}$ bar), and flowing argon ($pO_2 = 10^{-4}$ bar) using commercially available platinum crucibles. The oxygen partial pressure of the gases was controlled via solid state oxygen sensors.

To prevent thermal decomposition of the β'' phase, it was necessary to avoid the uptake of oxygen by means of oxygen getters like graphite or tantalum [6]. However, the best way to exclude oxygen is the use of closed tantalum capsules. Such capsules (Fig. 1) were manufactured from a 7 mm tantalum rod (99.99%, Heraeus, Hanau, Germany) by lathe manchining, a very difficult and time-consuming task
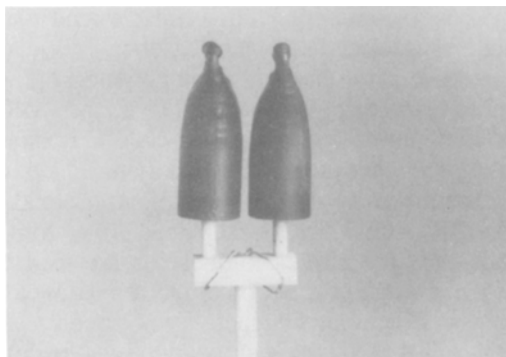

Fig. 1 View of self-manufactured sealed tantalum crucibles for DTA measurements

because of the brittleness of tantalum. The top of the rod was hollowed out by turning to a wall thickness of 1.5 mm. A second hole was drilled into the bottom, so that the crucibles could be fixed at the bead of the thermocouple. The remaining wall thickness between both the upper and lower hole amounted to 3 mm.

The tantalum crucible was filled with the β''/m-ZrO_2 sample and welded by special welding equipment in a nitrogen atmosphere. A tantalum crucible manufactured as described was filled with corundum as reference material.

To protect the tantalum crucibles against corrosion by oxygen, the measurements were carried out in an argon ($pO_2 = 10^{-12}$ bar) atmosphere. The heating and cooling rates were 5°C min^{-1} between room temperature and 1300°C.
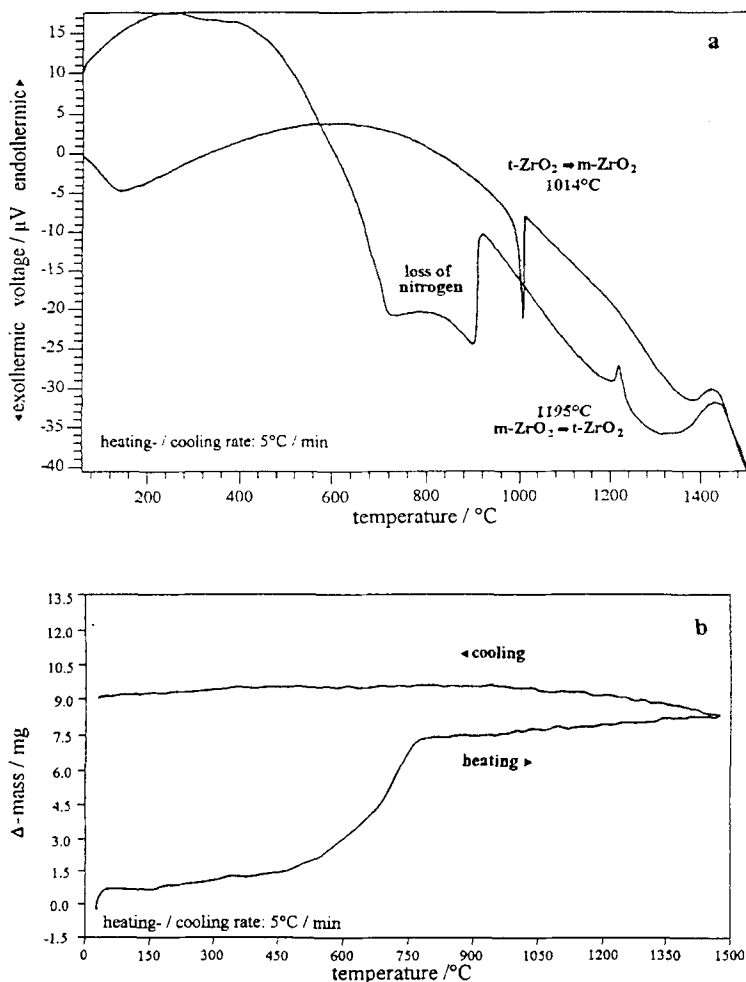

Fig. 2 a) DTA-curve of a β''/m-ZrO_2 sample in air; b) TG-curve of a β''/m-ZrO_2 sample in air

High-temperature-X-ray powder investigations between room temperature and 1150°C were carried out using a Stoe-STADIP diffractometer (Debye-Scherrer geometry, CuK$_{\alpha_1}$ radiation, $\lambda = 1.5406$ Å, position sensitive detector). Graphite heating elements were used to establish high temperatures. Because of the poor resistance against oxidation at temperatures above 500°C, the powders were investigated under nitrogen in sealed silica capillaries. The heating rate was 20°C min^{-1}. After establishing each relevant temperature, diffraction data were collected for 15 min after the samples had been hold for another 15 min at the respective temperatures. No significantly differing results could be obtained by prolonged annealing times.

Results and discussion

High temperature behaviour in air, nitrogen, and argon atmosphere

At temperatures above 500°C the β″ phase decomposes into monoclinic ZrO_2 according to the equation

$$ZrO_{2-2x}N_{4x/3} + xO_2 = ZrO_2 + 2x/3N_2 \qquad (1)$$
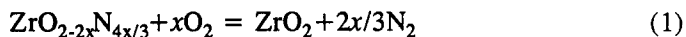
the loss of nitrogen being an exothermic process (Fig. 2) accompanied by an uptake of oxygen: hence, the mass of the sample increases. With regard to the results of a quantitative XRD-phase analysis, the composition of the β″ phase was calculated from our TG results to be $Zr_7O_{9.2}N_{3.2}$. This is in excellent agreement with the results given by the hot-gas-extraction method ($Zr_7O_{9.5}N_3$ [6]).

A point of interest is the wide temperature range the decomposition proceeds in. Presumably due to kinetic effects, the loss of nitrogen covers a range of about 300°C. This result was verified by high temperature-XRD experiments (Fig. 3). The intensities of reflections of the β″ phase decrease in the 400–600°C temperature range. At higher temperatures the well established martensitic transition mono-
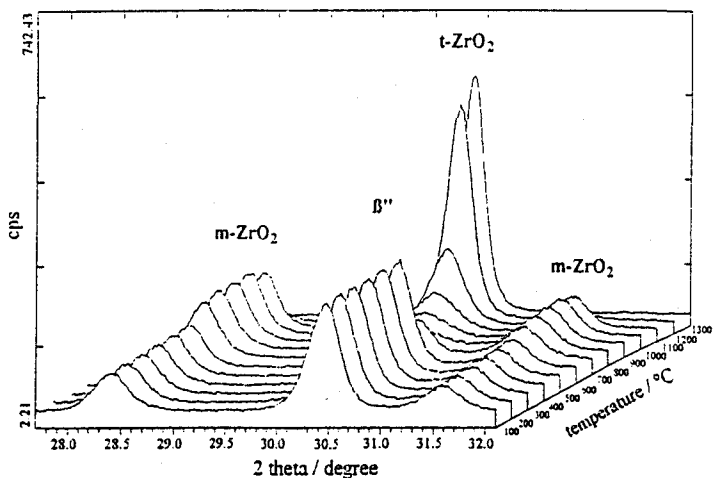

Fig. 3 High-temperature-X-ray-powder diagrams of a β″/m-ZrO_2 sample in air

clinic-tetragonal is observed. This transition can also be seen on the DTA curve (Fig. 2). As described in the literature, a large hysteresis effect exists, which amounts to ~180°C. It should be emphasized that the β'' phase has a very poor thermal stability, even if only small amounts of oxygen are present. This turns out from our investigations using gases (Ar or N_2) of technical grade ($pO_2 = 10^{-4}$ bar) instead of air. As shown in Fig. 4 an oxygen pressure of $pO_2 = 10^{-4}$ bar is sufficient to initiate the decomposition reaction.
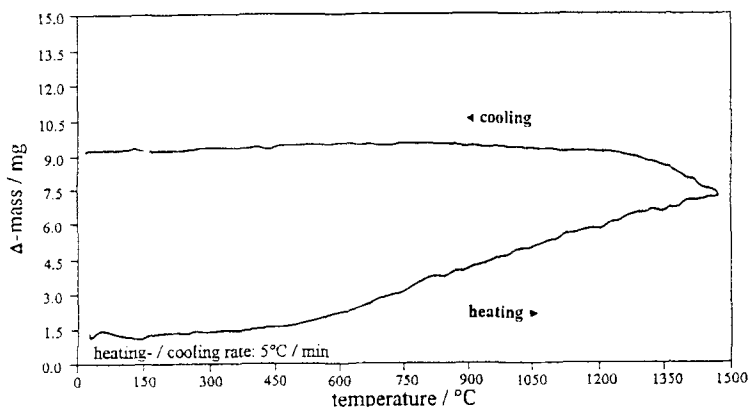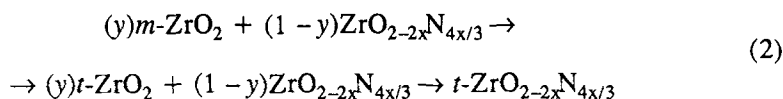

Fig. 4 TG-curve of a β''/m-ZrO_2 sample in a nitrogen atmosphere

High temperature behaviour in a closed inert gas atmosphere

For investigating the high temperature behaviour of the β'' phase in a non-oxidizing atmosphere, oxygen must be excluded carefully. Hence, the β''/m-ZrO_2 samples were incapsulated into nitrogen filled tantalum capsules as described above. Such incapsulated samples endure heating cycles between room temperature and 1300°C without any evidence of decomposition.

Figure 5 represents a DTA-curve of such an experiment. In contrast to pure ZrO_2, a second endothermic peak exists at ~965°C. At higher temperatures (~1115°C in Fig. 5) the well established transition m-$ZrO_2 \rightarrow t$-ZrO_2 takes place. Detailed data of the individual phase transition from the β'' phase with ordered anion vacancies to tetragonal $ZrO_{2-2x}N_{4x/3}$ (distorted fluorite-type structure) with randomly distributed vacancies at ~1000°C are presented in Fig. 6. This process is responsible for the first endothermic DTA-peak at ~965°C. The reaction product above 1115°C is single-phased and consists of t-$ZrO_{2-2x}N_{4x/3}$.

A tentative reaction path (y: mol fraction) could be

$$(y)m\text{-}ZrO_2 + (1-y)ZrO_{2-2x}N_{4x/3} \rightarrow$$

$$\rightarrow (y)t\text{-}ZrO_2 + (1-y)ZrO_{2-2x}N_{4x/3} \rightarrow t\text{-}ZrO_{2-2x}N_{4x/3}$$

(2)

The complete transition process is reversible (~949°C during cooling, Fig. 5) and independent of the N_2-pressure within the closed tantalum capsules because gaseous N_2 is not involved according to Eq. (2). The hysteresis effect of the transi-

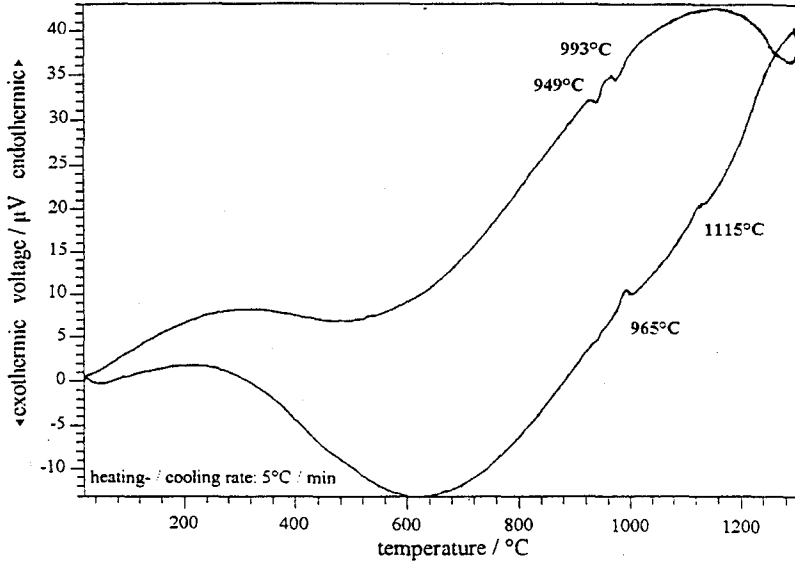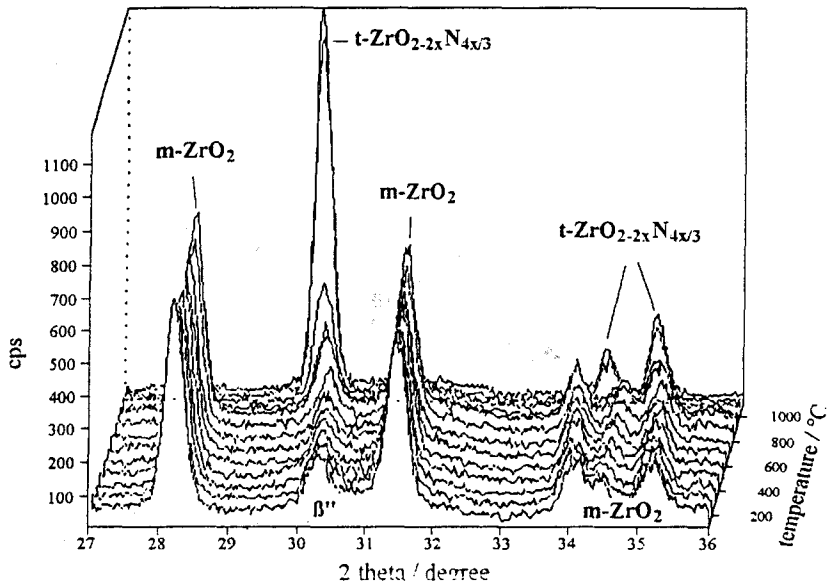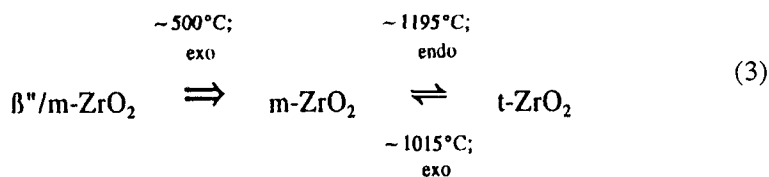Fig. 5 DTA-curve of a β''/m-ZrO_2 sample in a closed tantalum crucible

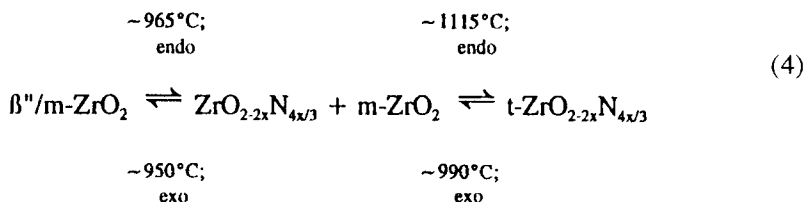Fig. 6 High-temperature-X-ray-powder diagrams of a β''/m-ZrO_2 sample in a nitrogen atmosphere

tion from the β'' phase to tetragonal $ZrO_{2-2x}N_{4x/3}$, which can be described as an order-disorder transition, is very small (~16°C). This behaviour is quite usual for order-disorder transitions, which are not kinetically controlled. The transition monoclinic-tetragonal ZrO_2 according to Eq. (2) shows a larger hysteresis effect covering a range of ~120°C. Compared to the value of ~180°C for pure ZrO_2, the hysteresis effect is smaller although the experimental parameters are the same. The strong decrease of the transition temperature detected in our DTA experiments points out, that a small amount of nitrogen is soluble in monoclinic ZrO_2 at elevated temperatures. This solubility in turn influences the transition mentioned above. At ambient temperatures, no nitrogen could be found in the monoclinic phase of a β''/m-ZrO_2 sample (see EELS results described in [6]).

The results of combined DTA/TG measurements can be summarized as follows:

a) Behaviour of $ZrO_{2-2x}N_{4x/3}$ in air (open platinum crucible)

$$\underset{\substack{\sim 500°C;\\ exo}}{} \quad \underset{\substack{\sim 1195°C;\\ endo}}{}$$
$$\beta''/m\text{-}ZrO_2 \quad \Longrightarrow \quad m\text{-}ZrO_2 \quad \rightleftharpoons \quad t\text{-}ZrO_2 \tag{3}$$
$$\underset{\substack{\sim 1015°C;\\ exo}}{}$$

b) behaviour of $ZrO_{2-2x}N_{4x/3}$ in nitrogen (tantalum incapsulated)

$$\underset{\substack{\sim 965°C;\\ endo}}{} \quad \underset{\substack{\sim 1115°C;\\ endo}}{}$$
$$\beta''/m\text{-}ZrO_2 \quad \rightleftharpoons \quad ZrO_{2-2x}N_{4x/3} + m\text{-}ZrO_2 \quad \rightleftharpoons \quad t\text{-}ZrO_{2-2x}N_{4x/3} \tag{4}$$
$$\underset{\substack{\sim 950°C;\\ exo}}{} \quad \underset{\substack{\sim 990°C;\\ exo}}{}$$

Conclusion

Direct nitridation of ZrO_2 in nitrogen (T>1400°C) leads to the formation of the β'' phase ~$Zr_7O_{9.2}N_{3.2}$. The β'' phase is instable against oxygen at temperatures above ~500°C. Even the small oxygen amount in gases of technical grade as argon or nitrogen (pO_2~10^{-4} bar) is sufficient to oxidize the β'' phase completely to monoclinic ZrO_2. Because of the incorporation of nitrogen into ZrO_2, anion vacancies are formed, which are randomly distributed in the crystal lattice at temperatures above 1000°C. Therefore, the high temperature phase could be of some interest as an anion conducting material. However, in view of the results described above, the main problem for a possible application of nitrogen containing zirconia materials is their instability against oxygen.

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