Improving Zirconia ceramics

through Thermoanalytical Characterization

Thermoanalytical
characterization of
zirconia ceramics during
binder burnout and sintering
can help manufacturers
optimize these processes
and improve the quality
of their finished products.

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Zirconium dioxide (ZrO_2), better known as zirconia, exists as a mono-clinic, tetragonal and cubic crystal modification. The most familiar and commonly used modification is the cubic form, which occurs for pure zirconia only at temperatures above 2950 K (4850°F). Other oxides such as yttrium oxide (Y_2O_3), magnesium oxide (MgO) or calcium oxide (CaO) are added to stabilize the cubic form at room temperature.

Zirconia offers high bending and tensile strengths, high fracture toughness, high abrasion and corrosion resistance, low thermal conductivity, a thermal expansion similar to cast iron and an elastic modulus similar to steel. Zirconia also possesses the ability to conduct oxygen ions at elevated temperatures—a phenomenon that enables it to be used in applications such as measuring the partial pressures of oxygen or developing solid oxide fuel cells.

In the production of oxide ceramics such as yttria-stabilized zirconia, a powder is mixed with additives and a binder. This formulation is pressed to form a green body and is then sintered at elevated temperatures. For many manufacturers, the binder burnout and sintering stage is where most quality problems are likely to occur. Optimum temperature profiles are required to allow binder burnout without damage to the green body and sintering with highest possible density. Thermoanalytical instruments can be used to provide detailed insights into the reactions that occur during binder burnout and sintering, thereby helping manufacturers optimize these processes.

Experiments

To demonstrate how thermoanalytical instruments can be used to measure properties such as thermal expansion and density change, a partially stabilized zirconia sample (green body) with a length of approximately 15 mm and a diameter of 6 mm was analyzed with a high-temperature dilatometer* in air (see Figure 1, p. 30). The sample composition is shown in Table 1 (p. 30).

The dilatometer system included a graphite furnace, an alumina protective tube and a sample holder, and it allowed measurements to be carried out between room temperature and 1975 K (2915°F) under oxidizing conditions.[1] Measurements were carried out at a heating rate of 5 K/min, and temperature measurements at the sample were obtained using a type S thermocouple. The system was calibrated using an alumina standard prior to the sample tests, and the measurements were conducted from room temperature to approximately 1875 K (2915°F).

Simultaneous thermal analysis (STA) measurements** were also carried out to characterize the mass change and transformation energetics of the sample during

*The NETZSCH model DIL 402 C, supplied by NETZSCH-Gerätebau GmbH, Selb/Bavaria, Germany.
**A NETZSCH model STA 409 PC Luxx® simultaneous thermal analyzer was used for this analysis.
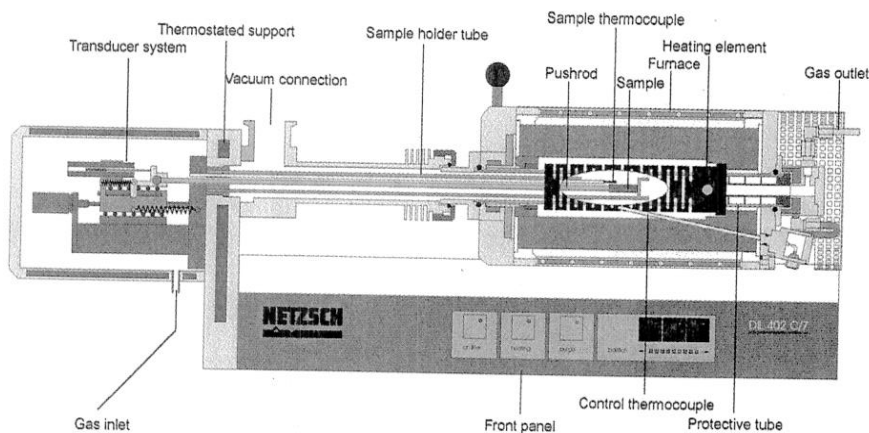
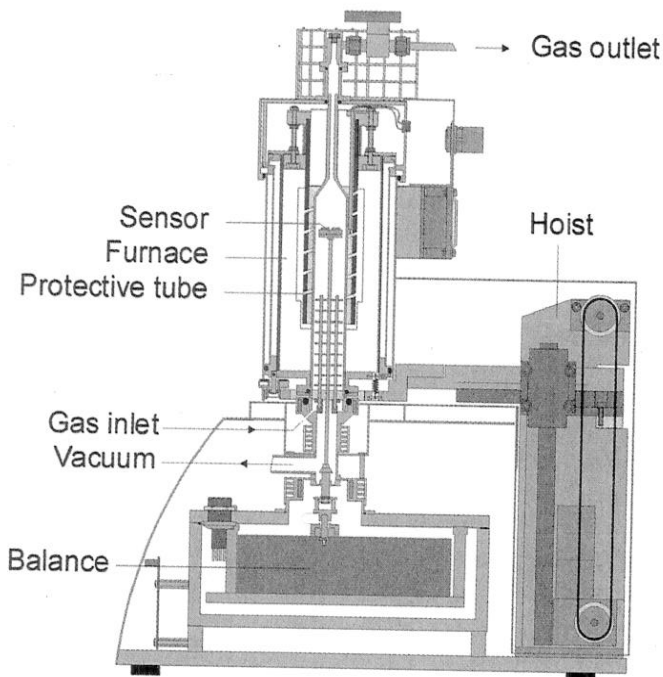Figure 1. Schematic of the NETZSCH dilatometer DIL 402 C/7.

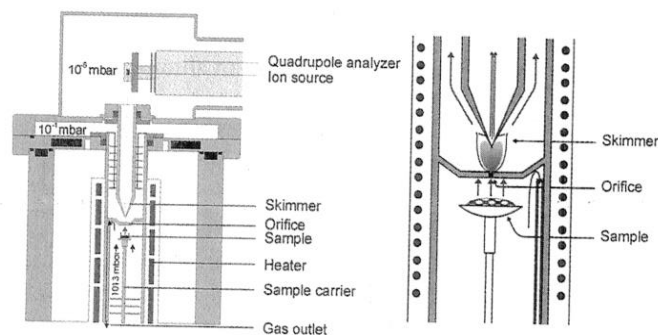Figure 2. Schematic of the NETZSCH STA 409 PC Luxx® simultaneous thermal analyzer.

Figure 3. Coupling of an STA to a quadruple mass spectrometer for gas analysis.

Table 1. Sample composition.
91.6 mass % zirconia
5.2 mass % yttrium oxide
3.2 mass % organic binder
<0.02 mass % inorganic contaminants
Average grain size: 0.3 mm
Average size of the microcrystallite: 24 nm

the binder burnout phase.[2] A schematic design of the STA instrument is shown in Figure 2. The system was equipped with a thermogravimetric-differential scanning calorimetry (TG-DSC) sensor, and the measurements were carried out between room temperature and 880 K in a dynamic air atmosphere at a heating rate of 10 K/minute. Platinum crucibles with lids were used for the tests.

Additional tests were carried out using an STA coupled to a quadruple mass spectrometer (QMS) system (see Figure 3).[†] The sample chamber of the STA was connected with the QMS analyzer to allow the evolved gases to be analyzed. The instrument used in this test features a two-stage orifice system for pressure reduction (required for the coupling between a QMS and STA system) directly installed in the STA furnace to heat the orifices and avoid condensation of the gases evolving from the sample. Due to the short gas paths, the system's measuring signals achieve a good signal-to-noise-ratio.[3]

Results and Discussion
Length, Volume and Density Changes

Figure 4 shows the length change and rate-of-length change of the zirconia green body at a heating rate of 5 K/minute. Between 400 and 800 K (260 and 980°F), small oscillations in the rate-of-length change can be seen. These effects can be explained by the burnout of the organic binder. Sintering of this material started at 1237 K (1766°F) (maximum in the thermal expansion). A length change of 20.63% was detected during sintering, and the maximum sintering rate occurred at 1666 K (2539°F). Only one shrinkage step was detected during the sintering between 1237 and 1875 K (1766 and 2915°F).

The volumetric expansion and density changes of the sample were determined from the measured length change and room-temperature bulk density of 3.089 g/cm³ (see Figure 5). For the density change, the mass change during binder burnout was also taken into consideration. (This effect is discussed in detail later in this article.) The influence of the binder burnout on both the density and volumetric change can again be seen between 400 and 800 K, and a volume change of approximately 50% can be seen during sintering. The density increased to approximately 5.8 g/cm³ between room temperature and the maximum measurement temperature of 1875 K.

Figure 6 (p. 32) shows the length change and mean coefficient of thermal expansion (using a reference temperature of 298 K) of

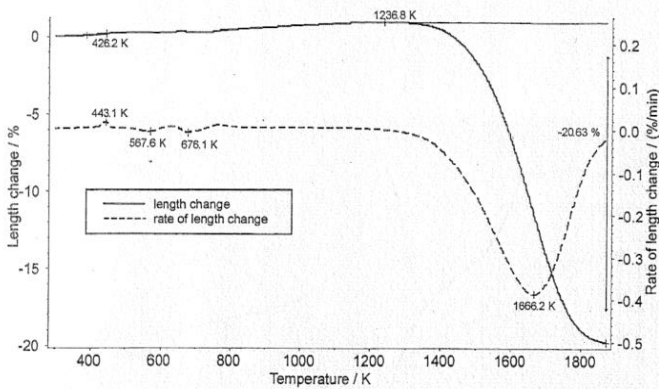[†]The NETZSCH model STA 409 C-QMS 403-Skimmer.

Figure 4. The length change and rate-of-length change of a zirconia green body at a heating rate of 5 K/minute, measured with the DIL 402 C/7.
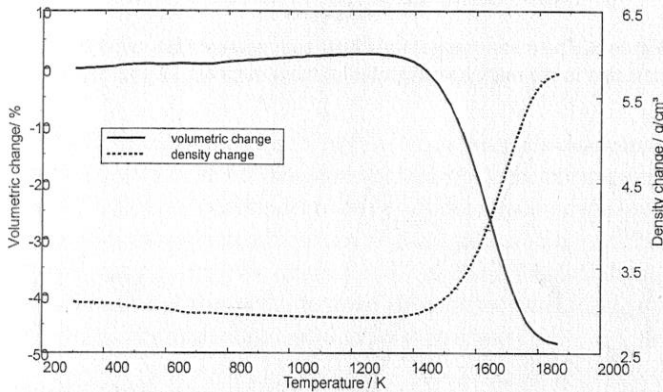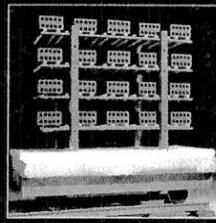

Figure 5. The volumetric change and density change of a zirconia green body at a heating rate of 5 K/minute (room-temperature density: 3.089 g/cm³).

the zirconia sample sintered at 1875 K (2915°F). The measurement was carried out in air between room temperature and 1700 K (2600°F). It can be seen that the ceramic expanded almost linearly with temperature; no overlapping steps in the length change were found. Of course, the mean coefficient of thermal expansion also increased with temperature. The expansion coefficient was in the typical range $(10\text{-}12)°10^{-6}$ 1/K.[4]

Mass Change and Transformation Energetics

The results of an STA measurement with an initial sample mass of 76.54 mg are shown in Figure 7 (p. 32). The system influences (i.e., buoyancy effects on the TG baseline) of the STA were corrected with a baseline measurement. The contribution of the specific heat of the material on the DSC curve (specific heat flow rate) was removed from the measured data by subtracting a curve obtained with a comparative measurement on a debinded material. This enabled a more precise analysis of the influences of the binder.
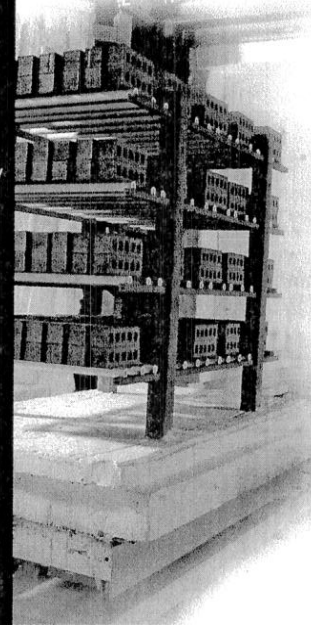
At 332 K (137°F) (extrapolated onset), an endothermal effect with an enthalpy of 1.54 J/g was found in the specific heat flow rate. The peak temperature was at 337 K (147°F). It can be concluded from the melting temperature that the binder was probably based on wax or paraffin, or a long-chain polyethylene glycol (PEG). At 445 K (341°F) (extrapolated onset), the decomposition or oxidation of the binder was recorded. This decomposition occurred in two steps, illustrated by the two characteristic temperatures (455 and 656 K [359 and 721°F]) seen in the specific heat flow rate. The exothermal reaction of the binder burnout is associated with an entire energy of -341 J/g, and the total mass decrease
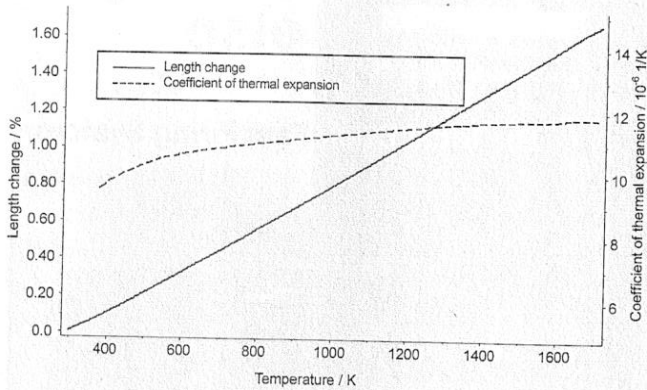
Figure 6. The length change and mean coefficient of thermal expansion (reference temperature: 298 K) of sintered zirconia at a heating rate of 5 K/minute.
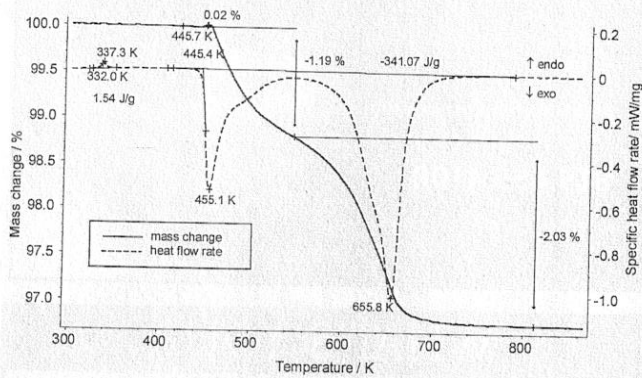

Figure 7. The mass change and specific heat flow rate of a zirconia green body at a heating rate of 10 K/min. For an easier evaluation, the contribution of the ceramic's specific heat to the heat flow rate was subtracted from the curve.
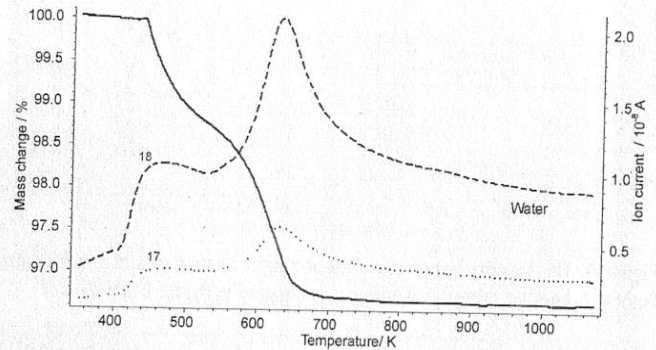

Figure 8. The mass change (solid line) and measured ion currents detected in the mass spectrometer for mass numbers 17 and 18.
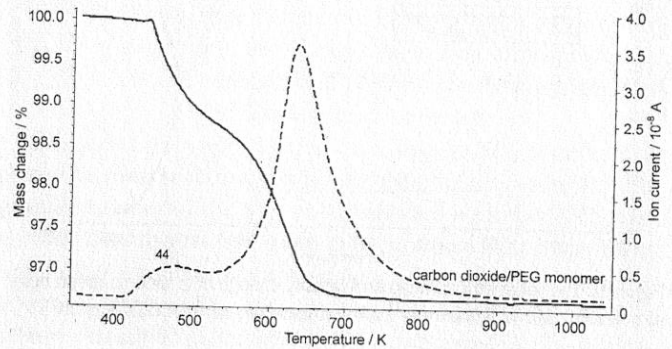

Figure 9. The mass change (solid line) and measured ion currents detected in the mass spectrometer for mass number 44.

of 3.22% over the investigated temperature range corresponds well to the manufacturer's information of an organic amount of 3.2%.[5] The mass change curve shows two separate mass-loss steps (1.19 and 2.03%), which correlate well with the two peaks measured in the specific heat flow rate. Additionally, a small mass increase of 0.02% was measured prior to the actual mass loss steps. This phenomenon can be explained by the adsorption of oxygen that occurred before the binder molecules decomposed.

To characterize the evolving gases, a mass spectrometer (MS) coupled to an STA was used. The initial sample mass was 123.87 mg. The measurement was conducted in synthetic air (80% nitrogen/20% oxygen) between room temperature and 1200 K (1700°F) at heating rate of 15 K/minute. The results for the different mass numbers detected are shown in Figures 8 through 10.

Figure 8 shows the ion currents of water, as well as the mass change detected in the mass spectrometer. The fragmentation of the molecules in the mass spectrometer allows both mass numbers 18 (H_2O) and 17 (OH) to be seen. It is evident that water has evolved in both mass-loss steps.

The results for mass number 44 (CO_2) are shown in Figure 9, along with the mass change. As expected for organic binders, the CO_2 evolved during decomposition/oxidation. However, mass number 44 is

also typical for other gases, such as a PEG (polyethylene glycol, C_2H_4O) monomer. Since CO_2 and water are also formed in the decomposition range during heating of PEG in air, clear proof of the binder composition could not be obtained through mass number 44. As a result, other mass numbers had to be evaluated.

Figure 10 shows that mass numbers 41 and 43 evolved during the two-step decomposition/oxidation of the binder material. These mass numbers, along with mass number 44, are a typical fragmentation pattern for PEG and cannot occur for CO_2. Taking the conditions in the sample into account, the PEG monomer also evolved in the sample due to the lack of oxygen. Since the time required for the binder to arrive from the sample surface to the mass spectrometer is not sufficient to completely finish the reaction with air, non-oxidized binder residuals can be detected directly.

Because of the binder's high melting point of 332 K (138°F) (Figure 7), it must be assumed that PEG did not occur in the binder as a monomer. If PEG were present, the melting point would have been around 273 K (32°F).[6] Long-chain molecules (chain number 150, with a molecular weight of approximately 6000), on the other hand, have a considerably higher melting point of approximately 333 K (138°F).[6] However, these long-chain compounds cannot be detected in the mass spectrometer since there is a reduction of long-chain molecules in the decomposition range and in the transition into the gas phase.
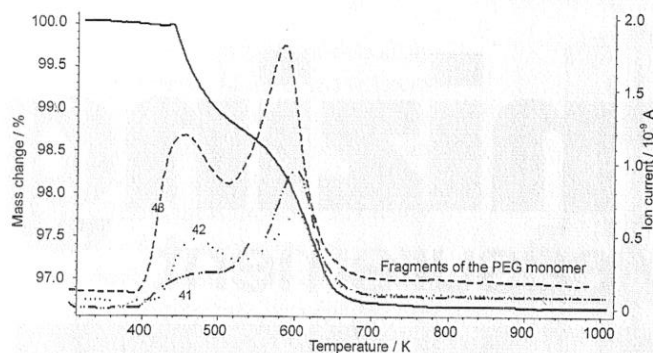
Figure 10. The mass change (solid line) and ion currents detected in the mass spectrometer for mass numbers 41, 42 and 43.

The DSC, TG and MS results highlighted in this study clearly indicate the presence of PET 6000 as an organic binder in the zirconia sample. PET 6000 is an ideal binder material as it decomposes completely under oxidizing or inert atmospheres; no residuals are left inside the ceramic material. However, careful furnace control is required during decomposition of the binder to avoid pressure increases inside the green body, which can cause cracks and part damage.

Optimized Sintering

These tests demonstrate how the binder burnout and sintering behavior of a green zirconia material can be analyzed using different thermoanalytical testing techniques. The resulting values for the mass change/transformation energetics during binder burnout and thermal expansion/ density change during sintering allow detailed insights into the processes that occur during the thermal treatment of the material. By understanding these processes, operators can make any necessary changes to the sintering profile to ensure complete binder burnout, efficient sintering—and high-quality finished products. ⊕

For more information about thermoanalytical characterization techniques, contact NETZSCH-Gerätebau GmbH, (49) 9287-881-49, e-mail j.blumm@ngb.netzsch.com or visit www.ngb.netzsch.com. (U.S. contact: NETZSCH Instruments, Inc., (781) 272-5353, e-mail info@netzsch.net, www.e-Thermal.com.)

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