MODELING OF BINDER BURNOUT AND SINTERING OF SOLID OXIDE ELECTROLYTE TAPES BY THERMOKINETIC ANALYSIS

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ABSTRACT

Burnout of organic binder and sintering behavior of YSZ electrolyte green tapes were investigated by thermogravimetry and dilatometry, respectively. With the help of thermokinetic analysis burnout and sintering were described by a mathematical model based on formal kinetics. Thus the measured data were reduced to a set of a few parameters which can be easily used to simulate the kinetic behavior for an arbitrary temperature profile. Good accordance between prediction and respective measurement was accomplished. Using rate controlled binder burnout and rate controlled sintering, optimization of the temperature profile was achieved with respect to time and energy saving.

INTRODUCTION

A lot of researches has been and is being done to look for alternative materials and production techniques to increase performance and long term stability and to decrease production costs of SOFC single cells. In this paper we will focus our attention on the sintering optimization of electrolytes which are made by tape casting and often used as the supporting element.

Usually a fine ceramic powder is mixed with an organic binder, and tape casting is used to form an electrolyte green body. In a subsequent process the binder is removed by a thermal treatment, and the green body is sintered at high temperatures to build a dense ceramic. For optimal properties low heating rates and high temperatures are preferable, but these conditions contradict industrial applications. A reasonable way to fulfill both requirements — high density and fast temperature profile — was introduced by Palmour (1,2) and is better known as rate controlled sintering (RCS).

Usually the transducer signal of a push-rod dilatometer is used to adjust the temperature profile in such a way that a constant shrinkage rate can be achieved. But it would be desirable to describe the sintering behavior with the help of a thermokinetic model, because in that way the shrinkage curve for an arbitrary temperature profile can be easily calculated and optimized by computer without resorting to further experiments. However, it would be nearly impossible to apply a scientific model which describes the individual steps of sintering by physical/chemical processes, because it is quite complex (3–5). Therefore we used another approach in this work.
A kinetic model based on a simple but in principle arbitrary mathematical model that reduces the measured data to a set of a few formal parameters was used. Sintering experiments with different heating rates were carried out in a push-rod dilatometer and analyzed with an advanced thermokinetic software tool (6, 7). Having used a combination of several reaction steps which were based on the technique of formal kinetics, a comprehensive model was built up. Different reaction types were used and their dependence on temperature was described by an Arrhenius term. The parameters of the model were obtained by multivariate nonlinear regression. Further details of the basic concepts of the software package can be found in (8).

Besides the applied sintering profile, the temperature profile used for burnout of the organic binder has a great impact on the sintering behavior of the green bodies. Therefore the binder burnout of the samples was first analyzed by the use of thermogravimetry (TG) and later evaluated by the above-mentioned thermokinetic software package. From the analysis of the data, a temperature profile for rate controlled mass loss (RCM) was evaluated and applied before the actual sintering.

The electrical conductivity of differently sintered specimens was determined and their microstructure was analyzed by electron microscopy. Based on these results, an optimal temperature profile for binder burnout and sintering was selected to decrease total sintering time and maximum sintering temperature.

**EXPERIMENTAL**

**Burnout of Organic Binder**

Zirconia green tapes with different types of dopant were investigated: 8 mol% yttria (8YSZ) and 8 mol% yttria with 1 mol% alumina (8Y1ASZ). The specimen had a thickness of about 200 μm (8YSZ, 8Y1ASZ). For the determination of the binder burnout kinetics, samples of about 25 mg were heated up in air from room temperature to 873 K in a NETZSCH TG209 thermogravity balance at heating rates of 2, 5 and 10 K/min.

The relative length change because of the sintering shrinkage was measured in air in a NETZSCH DIL402C push-rod dilatometer. To prevent the samples from adhesion with the measurement system, thin alumina disks were positioned on both sides of the sample. Influences caused by the measurement setup were corrected by previous calibration measurements with a 1 mm thick alumina disk (99.9 %) under the same conditions as the specimen.

For the determination of the influence of the binder burnout on sintering behavior, samples were heated up to 573 K in the dilatometer using different burnout profiles. Afterwards, a constant heating rate of 5 K/min up to 1473 K was applied.

**Sintering Behavior**

For the actual sintering experiments, the temperature profiles were divided into three segments. For the first segment – the binder burnout – an optimized RCM temperature profile obtained from the evaluation of the former thermogravity measurements was used. Afterwards, the samples were fired to 1673 K at different heating rates of 2, 5 and 10 K/min and then they were held at this temperature for 2-5 hours.

The microstructure of the samples after binder burnout and sintering was analyzed in a Leo 230.
Gemini 1530 electron microscope. The electrical conductivity of the sintered specimen was determined in the temperature range of 573 - 1223 K in air by four-point dc measurements. Thermokinetic analysis of the binder burnout and sintering were carried out with the help of the Thermokinetics software from NETZSCH (6).

RESULTS AND DISCUSSION

Burnout of Organic Binder

In fig.1 TG curves (symbols) for the mass change of the 8Y1ASZ samples during binder burnout are presented. The mass loss was subdivided into 4 single steps. For the TG curve with a heating rate of 2 K/min, binder burnout began at 383 K and ended at 643 K. For higher heating rates, onset and end of burnout were shifted to higher temperatures. The overall mass loss of about 18 % was the same for all heating rates. As the individual mass losses of the single steps were independent from the heating rate, a kinetic model with four consecutive steps was chosen (for a graphical representation see fig.1). Nonlinear multivariate regression was carried out to adjust the model parameters to the measured data. The simulated curves, which resulted from these parameters are shown in fig.1 as solid lines and are in good accordance with the measured data.

Because of the reduction of the kinetic data to a few formal parameters, it is now possible to easily calculate the mass loss for an arbitrary temperature profile. Therefore, the applied model and its parameters were verified by calculating a temperature profile for a rate controlled mass loss of 0.07 %/min (RCM-007) and by comparing it with an actual measurement based on this temperature profile. The heating rate was limited between 0.1 and 3 K/min. As shown in fig.2, the accordance of prediction and measurement is excellent. Thus, the proposed model is adequate to describe the binder burnout. But it should be remembered that the model is only a formal description of the binder burnout process, and that physical or chemical interpretation of the kinetic parameters should not be overstrained. Furthermore it should be emphasized that the obtained parameters are valid only for the examined type of specimen. If one uses, for example a different thickness or particle
size distribution, the results will be altered. To obtain the optimal burnout profile, the microstructure of samples exposed to different burnout profiles was analyzed by SEM and the influence on the sintering behavior was determined by dilatometry. SEM analysis indicated that high heating rates were accompanied by large pores and cracks due to the fast evaporation of the organic binder. But a uniform microstructure is important for an early sintering onset and high final density after sintering (9). Both the samples treated by a low constant heating rate of 2 K/min (CHRM-2) and the RCM samples revealed a homogeneous microstructure. However, great differences were visible in their sintering behavior. In table I, sintering onset and total shrinkage between sintering onset and 1473 K are given for various burnout profiles. It is obvious that sintering of the RCM samples began at lower temperatures in comparison with the CHRM samples. Furthermore it can be seen that the energy-conservative RCM profiles also lead to higher shrinkage in the same (RCM-007) or in even less time (RCM-01). It is assumed that the different sintering behavior is caused by small deviations in particle contacts which influence the diffusion processes during sintering and which cannot be resolved by SEM. Similar thermogravimetry investigations were carried out with the 8YSZ specimen and the same kinetic model was chosen as for the 8Y1ASZ specimen. The calculated model parameters were of course different. The excellent accordance between prediction and measured data is shown in fig.3. Based on these results, the RCM profiles listed in table II were selected for the subsequent sintering investigations.

Table I. Influence of different binder burnout profiles on sintering behavior of 8Y1ASZ. After binder burnout (573 K) the samples were fired with 5 K/min to 1473 K.

| burnout profile | burnout time | sintering onset | shrinkage at 1473 K |
|-----------------|--------------|-----------------|---------------------|
| 1 K/min (CHRM-1) | 285 min | 1282 K | 6.7 % |
| 0.1 %/min (RCM-01) | 210 min | 1279 K | 7.4 % |
| 0.07 %/min (RCM-007) | 285 min | 1275 K | 7.3 % |

Figure 2. Comparison between prediction (lines) and measurement (symbols) of 8Y1ASZ green tapes mass loss due to binder burnout for a RCM temperature profile (0.07 %/min).
Figure 3. Comparison between prediction (lines) and measurement (symbols) of 8YSZ (0.1 %/min) green tapes mass loss due to binder burnout for a RCM temperature profile.

Table II. RCM profiles selected for the subsequent sintering investigations

| sample    | profile            |
|-----------|--------------------|
| 8Y1ASZ    | 0.1 %/min (RCM-01) |
| 8YSZ      | 0.1 %/min (RCM-01) |

Sintering Behavior

The sintering curves obtained by dilatometry were divided into three segments. In the first segment the organic binder was burnt out according to the RCM profiles which were evaluated in the last paragraph. Only a small length change occurred in this segment. The actual shrinkage curves of the 8Y1ASZ specimen are presented in fig.4. For the better illustration only the sintering regime is shown and sintering onset of the different curves was set to time null. Sintering onset happened between 1251 and 1275 K and was shifted to higher temperatures for higher heating rates. Most of the shrinkage occurred during the dynamic heating whereby the samples in the isothermal segment shrunk only about 1 %. Values for sintering onset and shrinkage are given in table III. Densification of all samples was completed after the isothermal segment.

For the thermokinetic modeling, a four-step model was used as indicated in fig.4. As pro-

Table III. Dependence of sintering onset and total shrinkage on heating rate of the 8Y1ASZ specimen.

| heating rate | sintering onset | shrinkage at 1673 K | total shrinkage |
|--------------|----------------|---------------------|-----------------|
| 2 K/min      | 1251 K         | 21.6 %              | 22.3 %          |
| 5 K/min      | 1258 K         | 20.6 %              | 21.3 %          |
| 10 K/min     | 1275 K         | 20.7 %              | 21.9 %          |

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Figure 4. Sintering behavior of 8Y1ASZ green tapes for different heating rates as a function of time. The sintering onset is set to time null. A four-step model was used for the simulation (lines).

posed by Opfermann et al. (10, 11) the sintering process can be formally described by two consecutive reactions which are followed by two competitive reactions. Two competitive steps are absolutely necessary, because the total shrinkage depends on the heating rate, as shown in table III and in fig.4. Multiple processes, like surface, volume and grain-boundary diffusion, take place simultaneously. This behavior is well known from sintering theory (3). The results of the nonlinear multivariate regression are shown in fig.4 as solid lines. One can see that the contribution of the first two reaction steps to the overall shrinkage is small. They determine the sintering onset.

Based on this model and its parameters, a RCS temperature profile was calculated and an appropriate measurement was carried out. Comparison between prediction and actual measurement is shown in fig.5 and indicates a good agreement. Thus the applied model and its parameters can be seen as valid to describe the sintering behavior.

Comparable results were obtained for the 8YSZ specimen. A four-step model with two competitive reactions was also applied and the model parameters were determined by nonlinear multivariate regression. With the help of these parameters, temperature profiles for

Figure 5. Comparison between prediction (lines) and measurement (symbols) of 8Y1ASZ green tapes sintering behavior for a RCS temperature profile (0.05 %/min).
Figure 6. Comparison between prediction (lines) and measurement (symbols) of 8YSZ green tape sintering behavior for a RCS temperature profile (0.5 %/min).

A constant shrinkage rate (RCS) were calculated. As shown in fig.6, a good accordance between prediction and actual measurement was achieved.

With the help of the thermokinetic models, optimal temperature profiles for sintering were calculated for all types of specimen in compliance with the following constraints:

- maximal shrinkage to obtain dense electrolyte
- in best time
- lowest possible final temperature
- maximal heating rate of 3 K/min
- minimal heating rate of 0.1 K/min

Priority was set according to this list.

The optimal profiles for the various sample types are given in table IV. Thus, the total sintering time – including binder burnout and cooling down – for electrolyte tapes was reduced to less than 28 hours and a decrease of the final sintering temperature was also possible. This results in saving of time and energy.

All samples exhibited a homogeneous and dense microstructure (fig.7) and the final grain size distribution was narrower in comparison with samples sintered at a constant heating rate due to the uniform grain growth during sintering. This is in accordance with the results obtained by Palmour (1) and Abe (12). The electrical conductivity of the samples sintered according to the temperature profiles listed in table IV were comparable with the data given in the literature as can be seen in fig.8.

Table IV. Optimized sintering profiles

| sample  | profile    | final temperature | holding time | total time |
|---------|------------|-------------------|--------------|------------|
| 8Y1ASZ  | 0.05 %/min | 1673 K            | 3 h          | 27.5 h     |
| 8YSZ    | 0.1 %/min  | 1623 K            | 5 h          | 25.7 h     |
CONCLUSIONS

The burnout of the organic binder and sintering behavior of YSZ electrolyte green tapes were investigated by means of thermokinetic analysis. It was shown that the binder burnout which precedes the actual sintering, as well as the sintering itself, can be described by a mathematical model based on formal kinetics. Through multivariate regression, the measured data were reduced to a set of a few parameters which were used to easily simulate the kinetic behavior for an arbitrary temperature profile without knowledge of the physical nature of the underlying processes.

For the binder burnout, a model with four single consecutive steps was chosen and validated by comparison between prediction and respective measurement. Using a temperature pro-
file for a constant mass loss rate, a positive influence on the sintering behavior is observed. The sintering behavior was described by a four-step model with two competing reactions which led to a good accordance between prediction and measurement. Based on this model, temperature profiles for rate controlled sintering were evaluated. SEM analysis of the microstructure and determination of the electrical conductivity as a function of temperature revealed that by using rate controlled binder burnout and rate controlled sintering, optimization of the temperature profile can be achieved with regard to time and energy saving.

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