Sintering doped Ceria in air

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Abstract
Thermo kinetic software was used to evaluate the sintering mechanisms when Gadolinium-doped and Samaria-doped ceria powders (Rhodia, HSA and Fuel Cell Materials, SDC-TC, respectively) were sintered with two additives, Manganese oxide and Copper oxide, to control densification behaviour, i.e. promoting densification and grain growth during earlier stages of sintering as compared to sintering powders with no additives. Results indicate that grain boundary mobility was activated by the added promoters and that sintering mechanisms depend on the grain boundary chemistry, i.e. the sintering aid.

Introduction
Analysis of the sintering kinetics through the thermokinetic software “Kinetic3” may have both technical purposes, e.g. for data reduction and to predict sintering behaviour, and be used for more in-depth analysis of the individual mechanisms of the overall process. The conversion function, Ui(T, a(r), x(p)), is modeled through approximating and separating the conversion in to separate functions: Ui(T, a(r), x(p)) = f(T(i)) g(x(p)), which are dependent on temperature profile, f(T(i)), and degree of conversion, respectively. The conversion dependency may be modeled through a range of well established reaction mechanisms, of which the simplest is a first-order reaction, and the temperature dependent term is described by the well known Arrhenius equation, f(T) = A exp(-E/RT). Additionally, a model-free approximation of the activation energy may be derived, e.g. using the Friedman analysis (Friedman (1965)) including evaluation of the pre-exponential factor, A, assuming a first-order reaction.

Experimental
Powders CGO10, (Sv= 23 m²/g, dp=0.45μm), SDC-TC (Sv=7m²/g, dp=0.4μm) or SDC-HP (Sv=12 m²/g, dp=0.38μm) were mixed in ethanol with sintering aids (MnO₃ or CuO) in a ball mill for ~18 hours, dried and pressed both uniaxially and isostatically into samples with TD=0.6 and lengths of approximately 7.5 mm, which fitted into the double pushrod dilatometer, NETZSCH model 402 CD. Sintering in duplex was performed in flowing air at heating rates relevant for later processing (1, 5, 10 °C/min) and in cases also at 0.33 °C/min and 20 °C/min. Powders without sintering aids were heated from room temperature to ~1500 °C and powders with sintering aids to 1300 °C or 1400 °C.

Results and Discussion
Figure 1 illustrates the marked impact from sintering aids on both the sintering rates and on the temperature of maximum sintering rate. In Figures 3-4 are shown the results from a model-free calculation of the kinetic field, Friedman (1935), for which the primary results, the activation energy plot, has been exemplified in Figure 2. Sintering CGO10 at 1-10 °C/min CGO to final densities between 89%±1% and 98%±1% only shows very low activation energies, much like shown in Figure 4 for SDC-HP, but if lower heating rates (i.e. 0.33 °C/min) a marked change is seen, which is shown in uppermost part of Figure 3 indicating that lattice diffusion with high activation energy becomes an important densification mechanism towards the end of densification. A similar trend, but at a lower level of activation energies, is observed for the sintering of CGO10 with Cu-addition. In contrast, activation energy stays at a constant high level almost throughout the densification of CGO10 with Mn-addition, which also reaches the highest level of density, ~96%TD. In general, both SDC-HP and CGO10 powders reaches final densities, which depend on sintering aid but only little on the applied heating rates in the interval 1-10 °C/min. In contrast, sintering the SDC-TC powder is sensitive heating rates, cf. figure 4 bottom, and seems controlled by at least two parallel mechanisms. Further, the trend of the activation energy for SDC-HP powder shows relative low levels towards the end of densification, which is in contrast to CGO10, and may be attributed to the somewhat lower densities (~97%±1%) reached for this powder. Various levels of Mn-additions (%0, 0.5, 1%, 2%) were tried on SDC-powders (not shown here) and resulted in significantly higher density to be reached for addition of 0.5%Mn than any of the others, why only these results are shown here. Other investigations (Mr. N, this conference) showed activation energy Ea = 450-480 kJ/mol throughout sintering CGO10 powders could be attributed to the grain growth, but more than one mechanism is obviously responsible for the overall densification process, as indicated by the non-constant levels of activation energies generally observed for samples.

Conclusion and outlook
Analysis of the kinetic field was able to reveal qualitatively, differences in the sintering mechanisms and through further modeling work it is the aim to reach an even better understanding of the densification mechanisms, grain boundary chemistry and possibly also define optimum firing profiles for sintering the multi-layered cells

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