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This issue of the Ceramic Transactions compiles a number of papers presented at the International Conference Sintering 2008, which was held in San Diego, USA on November 16-20, 2008. The meeting was chaired by Professors Rajendra Bordia and Eugene Olevsky and was organized under the auspices of The American Ceramic Society.

This was the fifth meeting in a series that started in 1995 as a continuation of a famous cycle of conferences on Sintering and Related Phenomena organized by G. Kuczynski in the period from 1967 till 1983. The first three meetings in the newly re-established series of conferences have been held at Pennsylvania State University in 1995, 1999, 2003, and the fourth has been held in Grenoble, France in 2005.

In parallel to the US-based cycle of conferences on sintering, from 1969 till 2002 another important series of conferences named Round Tables on Sintering have been held in Eastern Europe and have been attended by many sintering professionals from that geographical area as well as by scientists from Western Europe and Asia. In general, over the past 50 years, there has been a series of important conferences aimed at documenting the status of sintering theory and practice. Previous meetings were also organized by the Tokyo Institute of Technology, University of Notre Dame, and the University of British Columbia.

Sintering 2008 became the largest specialized sintering forum in history by bringing together more than 200 registered participants of various research communities, which fostered the high level of scientific interaction and created atmosphere of broader international collaboration. The meeting included participants from North and Central America, Europe (both Eastern and Western), Asia, Australia and Africa.

The technical program at this meeting included 203 presentations from 30 countries, which addressed the latest advances achieved in the sintering processes for the fabrication of powder-based materials in terms of fundamental understanding, technological issues and industrial applications. The conference has demonstrated a significant progress that has been made in multi-scale modeling of densification and microstructure development, better understanding of the processing of complex systems (multi-layered, composites and reactive systems). In sintering technology, innovative approaches like Field Assisted Sintering (also known as Spark Plasma Sintering) gain more attention of the materials processing community. Another very
timely and well represented topic was sintering and microstructure development in nanostructured materials. Papers were also presented on the sintering of bio- and energy applications-related materials. To augment the traditional technical presentations, a Plenary Round Table Discussion on the “Challenges and Opportunities in Sintering Science and Technology” identified critical avenues for research and development as well as the most exciting developments in the science and technology of sintering.

This volume contains 43 papers covering a rich diversity of the sintering science and technology topics. Another 19 papers were published in a special issue of the Journal of the American Ceramic Society (July 2009). Together, a third of the papers presented during the conference were published in these two publications. Thanks go to both the conference participants and organizers who had to meet numerous deadlines to enable the timely publication of this volume and of the special issue of the Journal.

We hope you will enjoy the papers assembled here and we are looking forward to see you in 2011 in Jeju Island, Korea at the International Conference on Sintering 2011.

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Eugene A. Olevsky
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The Co-chairs of Sintering 2008 gratefully acknowledge the advice and help given to us in organizing this meeting by colleagues on the Organizing and International Advisory Committees listed below. We also appreciate the support from the conference sponsors listed below. Support from the staff at The American Ceramic Society is gratefully acknowledged. Finally, RKB acknowledges the opportunity to work at the Whiteley Center of the University of Washington during two critical periods of editing this proceedings.

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SINTERING BEHAVIOR OF Ce₀.₉Gd₀.₁O₁.₉₅₋₆ IN REDUCING ATMOSPHERE

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ABSTRACT
At low oxygen partial pressures and high temperatures Gd-doped ceria can be reduced and the material becomes electronic conducting (e.g. 0.08 Scm⁻¹ at 800°C at a pO₂ of 10⁻¹⁶ atm for Ce₀.₉Gd₀.₁O₁.₉₅₋₆ - CGO₁₀). These properties make CGO attractive for use in oxygen membranes above 600°C. The sintering temperature of CGO ceramics might be significantly reduced, if a sintering atmosphere with very low oxygen partial pressure is applied (for example a pO₂ of 10⁻¹⁵ atm or below). In the present work, the densification behaviour of CGO₁₀ was investigated in reducing atmosphere and in air. Samples were prepared by tape casting and lamination of the single layers into multi-layers and by die pressing. A dilatometer was used to measure the sample shrinkages from room temperature to 1773 K with different constant heating rates. Based on the sintering results of pressed samples the activation energy for densification was determined. The activation energy for densification of CGO₁₀ can be reduced significantly from 770±40 to 300±40 KJ/mol by switching atmosphere from air (pO₂=0.21 atm) to highly reducing conditions (pO₂ down to 10⁻²⁰ atm), which indicated enhanced densification behaviour of CGO₁₀ in reducing atmosphere during early stage sintering.

INTRODUCTION
Ceria based solid solutions have been investigated intensively as promising electrolyte materials for intermediate temperature solid oxide fuel cells (IT-SOFC), as cathode barrier layers in SOFC¹ and as membrane material for oxygen separation membranes². The doping with gadolinium leads to one of the highest ionic conductivities in ceria among different other dopants at intermediate temperatures³ (500-600 °C). Cerium Gadolinium Oxide (CGO) has therefore been proposed as electrolyte material for stainless steel supported fuel cells⁴.

The sintering of ceria to full density requires relatively high sintering temperatures, as high as 1300°C to1600°C, depending on raw powders and processing. For many processes, such as the manufacturing of solid oxide fuel cells or membranes, it would be beneficial, if the sintering temperature to achieve dense CGO ceramics could be reduced significantly. Several studies have been under-taken on the addition of dopants to lower the sintering temperature of CGO ceramics in air⁵.⁶.⁷.⁸.⁹.¹⁰ The sintering behaviour of CGO is expected to be quite different in reducing atmosphere due to the reduction of Ce⁴⁺ to Ce³⁺ and the related change in oxygen vacancy concentration, which is expected to have a significant influence on the sintering kinetics. The influence of sintering atmosphere has so far only rarely been investigated. J.-G. Li et al.¹¹ have reported an increase in density and grain growth of nano crystalline yttria doped ceria ceramics, if the atmosphere was switched to more reducing atmosphere, e.g. from oxygen to air. Grain growth and enhanced densification in CGO compared to un-doped ceria was explained by reduction of some Ce⁴⁺ to Ce³⁺ and a correlated formation of oxygen vacancies, which should cause rapid grain boundary migration due to changed grain boundary energies¹².¹³. It is well known, that the CGO lattice shows a volume expansion upon reduction and volume reduction during re-oxidation¹³.¹⁴.

This paper investigates the densification kinetics of Ce₀.₉Gd₀.₁O₁.₉₅₋₆ at relatively low oxygen partial pressures (pO₂ = <10⁻¹⁶ atm) and compares the results to sintering in air for pressed and tape casted structures. Using a dilatometer, we sintered the CGO₁₀ with 4 different constant heating rates and we
Sintering Behavior of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ in Reducing Atmosphere

investigated the microstructure of the CGO10 samples by scanning electron microscopy (SEM) after complete re-oxidation.

EXPERIMENTAL

A commercial nano-sized Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ powder from Rhodia was used as raw material (CGO10, primary particle size less than 50 nm, d$_{50}$=0.45μm after dispersion in ethanol and BET measured specific surface area 35 m$^2$/g).

For preparing the pressed compacts, polyvinyl butyral (PVB) binder and ethanol were added and mixed with the powders in a mortar. Hard agglomerates were removed by sieving. CGO10 pellets were made using a hydraulic pressing machine at a uniaxial pressure of 200 MPa. The samples had a diameter of 5.5 mm and a length of 5.3 to 5.6 mm after pressing. The samples were pre-sintered at 1173 K to remove the binder and give the samples sufficient strength for measurement in the dilatometer.

To compare the sintering behavior of pressed samples with laminated samples, CGO multi-layered tapes were laminated from CGO10 single-layered tapes. The CGO10 powders were first ball milled in an ethanol based slurry with polyvinyl pyrrolidone (PVP) as dispersant and polyvinyl butyral as binder. Thereafter the slurry was tape cast into a 100 μm thick film. The film was finally laminated several times to a thickness of 2.5 mm and was then stamped out into rounds with a diameter of about 4 mm. Uniaxial pushrod dilatometry was conducted at heating rates of 1, 3, 5 and 10 K/min in air and in reducing atmosphere (mixture of 9 vol.% of hydrogen and 91 vol.% of dry nitrogen) up to a maximum temperature of 1773 K using a Netzsch differential dilatometer CD402. The pO$_2$ for the measurements in reducing atmosphere was recorded by a downstream pO$_2$-monitor on the dilatometer. The recorded voltages for all measurements were about 1.075 ± 0.025 V at sintering temperatures from 1173 K to 1773 K. These voltages correlate to pO$_2$ values as low as 10$^{-12}$ to 10$^{-20}$ atm. The microstructure of the sintered samples was observed using a Hitachi TM 1000 SEM.

RESULTS AND DISCUSSION

The shrinkages of laminated CGO10 samples are plotted in Figure 1 against sintering temperature. For the tape cast and laminated samples a decrease in sintering temperature and a fast densification of CGO10 under reducing atmosphere was observed compared to sintering in air. In the case of laminated CGO10 samples a significant deformation of sample shape was observed during binder removal in the temperatures range 293 K to 873 K. Even if the laminates were pre-sintered before starting the dilatometry, these samples deformed considerably and signs of delamination were observed after sintering. For this reason exact calculations of the sintering kinetics were not performed on laminated samples, but further investigation on the sintering kinetics of CGO10 in air and in H$_2$-N$_2$ atmosphere were performed on pressed samples only.
Figure 1: Shrinkages of tape cast and laminated CGO10 samples in air (blue line) and in H$_2$-N$_2$ (pink line). The heating rate was 3K/min in this experiment.

Figure 2 shows the variations of shrinkage with temperature of the pressed CGO10 compacts sintered in air and in reducing atmosphere with the constant heating rates of 1 and 10 K/min, respectively. The onset temperature for densification of CGO10 in reducing atmosphere is 150 K lower than the onset temperature for sintering in air. This indicates that densification of CGO10 in reducing atmosphere was significantly enhanced at low temperature. It is also noted that, for a fixed sintering atmosphere, either air or H$_2$-N$_2$, the compact with slower heating rate (1 K/min) achieved the same shrinkage at lower sintering temperature compared to that with higher heating rate (10 K/min). Similar effect of heating rate on densification was reported by Ewsuk et al$^{15}$ when they investigated the sintering behaviour of ZnO. This fact was explained as the increased diffusion time for densification at a certain temperature resulted from the lower heating rate$^{16}$.

The variations of shrinkage rate with temperature of the pressed CGO10 compacts sintered in air and in reducing atmosphere with the constant heating rates of 1 and 10 K/min, respectively, are presented in Figure 3. Compared to that of sintered in air, the shrinkage rate maximum (absolute value considered in this work) of the compact sintered in reducing atmosphere is larger and also occurred at lower sintering temperature, which corresponds to a high densification rate in early stage sintering for reducing sintered CGO10. On the other hand, the shrinkage rate maximum with the heating rate of 10 K/min is larger than that of with 1 K/min for the compacts sintered both in air and in H$_2$-N$_2$. This is mainly attributed to the temperature effect$^{17}$, as it could be seen that the temperature for reaching maximal shrinkage rate of the compact with higher heating rate is higher than that of with lower heating rate.
Sintering Behavior of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-\delta}$ in Reducing Atmosphere

With respect to Figures 2 and 3, it is noted that the early-staged densification of CGO10 in H$_2$-N$_2$ was significantly enhanced compared to that sintered in air. To understand the densification difference caused by different sintering atmospheres more clearly, the activation energies for densification of the compacts sintered in both air and H$_2$-N$_2$ are evaluated from the densification law and the experimental results.

From the densification law\textsuperscript{17}, the shrinkage rate $\frac{d\left(\frac{\Delta l}{l_0}\right)}{dt}$ is correlated to the activation energy $Q$ for densification as

$$\frac{d\left(\frac{\Delta l}{l_0}\right)}{dt} = A \exp\left(-\frac{Q}{RT}\right) f\left(\frac{\Delta l}{l_0}, L\right)$$

where $A$ is a material constant independent of temperature $T$, $R$ is the gas constant, and $f\left(\frac{\Delta l}{l_0}, L\right)$ is a function of shrinkage $\frac{\Delta l}{l_0}$ and grain size $L$. Rearranging and taking the logarithm of both sides of Equation 1, gives

$$\ln\left(-\frac{d\left(\frac{\Delta l}{l_0}\right)}{dt}\right) = -\frac{Q}{RT} + \ln\left(\frac{A}{R}\right) + \ln[f\left(\frac{\Delta l}{l_0}, L\right)]$$

For pressure less sintering, the grain size is only the function of shrinkage, that is, independent of the sintering conditions, for example, the heating rate\textsuperscript{18}. Therefore, the activation energy could be evaluated from the slope of the plot of $\ln\left(-\frac{d\left(\frac{\Delta l}{l_0}\right)}{dt}\right)$ versus $1/T$ at a given shrinkage. In the present work, the data of shrinkage rate and temperature at three different shrinkages (-0.025, -0.050, -0.075) obtained from four different constant heat rates (1, 3, 5, 10 K/min) were used, and the corresponding plot is shown in Figure 4. The activation energy for densification of CGO10 in early stage air sintering is $770\pm 40$ KJ/mol, which is close to that of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ reported by Jud et al\textsuperscript{16}. The activation energy for densification of CGO10 in early stage reducing sintering is $300\pm 40$ KJ/mol, which is much lower.
Figure 2: Variation of shrinkage with temperature of pressed CGO10 compacts sintered in air and in a mixture of 9%H₂-91%N₂ at different heating rates of 1 and 10 K/min.
Figure 3: Variation of shrinkage rate with temperature of pressed CGO10 compacts sintered in air and in a mixture of 9%H₂-91%N₂ at different heating rates of 1 and 10 K/min.
Sintering Behavior of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-\delta}$ in Reducing Atmosphere

Figure 4: Variation of $\ln[-T(dI/dt)]$ with reciprocal temperature of pressed CGO10 compacts sintered in air and in a mixture of 9%H$_2$-91%N$_2$ at different heating rates of 1, 3, 5 and 10 K/min (best fitting straight lines are shown).

The present dilatometry experiment shows quite different densification behaviour of CGO10 sintered in air and in reducing atmosphere, especially, the fast densification of CGO10 in H$_2$-N$_2$ in early stage sintering. In addition, the appearance and the microstructure of the investigated reducing sintered compacts also showed some difference. Figure 5 shows a pressed CGO10 compact before and after sintering in the dilatometer in reducing atmosphere. The CGO10 is black after sintering at reducing atmosphere due to the occurrence of the reduction of ceria from Ce$^{4+}$ to Ce$^{3+}$. After the CGO10 ceramic was removed from the dilatometer and had contact with air, the sample changed back to white/yellow colour after a couple of minutes. During colour change the sample heated up and gained weight due to re-oxidation (take up of oxygen).
The effect of sintering atmosphere on the microstructure of the CGOIO ceramics after sintering at 1773 K is shown in Figure 6. The sample sintered in air resulted in relative small grains, with grain size of about 2 μm (figure 6, left side), whereas the one sintered under strongly reducing atmosphere led to excessive grain growth with grain sizes of 10 μm and above. Furthermore the CGOIO ceramic fabricated under reducing atmosphere shows cracks along the CGOIO grain boundaries (figure 6, right side). This phenomenon needs further investigations, but is most likely caused by stresses in the ceramic that occur during re-oxidation and the accompanied volume reduction of the CGOIO lattice.

Figure 6: Excessive grain growth of CGOIO during sintering under reducing atmosphere. SEM pictures of CGOIO ceramic after sintering to 1773 K in air (on the left side) and in 9%hydrogen-91%nitrogen atmosphere (on the right side).

CONCLUSIONS

- Fast densification for CGOIO during early stage sintering in reducing atmosphere is shown. The activation energy for densification can be reduced significantly from 770±40 to 300±40 KJ/mol by switching atmosphere from air (pO₂=0.21 atm) to highly reducing conditions (pO₂ down to 10⁻²⁰ atm).
Sintering Behavior of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-\delta}$ in Reducing Atmosphere

It is of further interest to find out more details about the mechanism of sintering of CGO10 under reducing atmosphere. Principally it sounds reasonable, that the reduction of ceria and creation of oxygen vacancies accelerates the sintering. In a future paper, further investigations on the grain growth and vacancy formation of CGO10 during sintering under different atmospheres will be reported. For practical application in multilayer structures the influence of the volume change of CGO10 on the microstructure during sintering in reducing atmosphere and during subsequent exposure to air needs further attention.

LITERATURE

HYDROGEN SORPTION PROPERTIES OF Ti-OXIDE/CHLORIDE CATALYZED Na,LiAlH₆

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ABSTRACT
Mechano-synthesis through mechanical alloying (MA) has been employed to obtain a nanocrystalline complex sodium lithium alanate, namely, Na₂LiAlH₆ from starting materials NaH and LiAlH₄. Different Ti-based additives were milled together with starting materials in order to achieve improved hydrogen absorption kinetics. Hydrogen titration experiments showed that the material processed with 5 mol% TiCl, has the fastest ab- and desorption kinetics, but at the sacrifice of hydrogen capacity. This could be correlated to the formation of NaCl during milling and after absorption. Differential scanning calorimetry (DSC) results demonstrate that the endothermic peak of TiCl, doped material shifted 53 °C to lower temperatures.

INTRODUCTION
Light metal-hydrides exhibit a great potential in safe and reliable hydrogen storage and have the highest storage capacity by volume. Alkali alanates have a high hydrogen capacity e.g. NaAlH₄ and LiAlH₄ have a hydrogen capacity of 7.4 and 10.5 wt.%, respectively. Decomposition of these materials is obtained in several steps and are not reversible at moderate conditions of hydrogen pressure, for NaAlH₄:

\[3\text{NaAlH}_4 \rightarrow \text{Na}_2\text{AlH}_6 + 2\text{Al} + 3\text{H}_2\uparrow\]  \hspace{1cm} (1)

\[\text{Na}_2\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + 3/2\text{H}_2\uparrow\] \hspace{1cm} (2)

\[\text{NaH} \rightarrow \text{Na} + 1/2\text{H}_2\uparrow\] \hspace{1cm} (3)

Nevertheless, irreversibility of these materials is the drawbacks to use them as hydrogen storage materials. Although there are more than one dissociation step of alkali alanates and irreversibility, these new class of materials are considered because of their low absorption temperature as well as high hydrogen content. One of the pioneers of the synthesis of different alanates using chemical methods
Hydrogen Sorption Properties of Ti-Oxide/Chloride Catalyzed Na\textsubscript{2}LiAlH\textsubscript{6}

was Bogdanovic and co-workers\textsuperscript{1,2}. However, chemical methods require high hydrogen pressures and relative high temperatures, for example Na\textsubscript{2}LiAlH\textsubscript{6} has been prepared from NaH+LiAlH\textsubscript{4} in toluene under 300 bar H\textsubscript{2} at 433 K or by the reaction of NaAlH\textsubscript{4}+LiH+NaH in heptane under hydrogen pressure\textsuperscript{3}. Furthermore, producing sodium lithium alanate (Na\textsubscript{2}LiAlH\textsubscript{6}) results in a change of equilibrium pressure to lower value\textsuperscript{4}. An alternative technique such as mechanical alloying (MA) has been employed to produce nanocrystalline alanates by Zaluska and Huot\textsuperscript{5}. On the other hand, TiO\textsubscript{2} has been successfully used\textsuperscript{6} as catalyst in Mg-based hydrogen storage materials. For sodium alanate (NaAlH\textsubscript{4}), TiCl\textsubscript{4} was found to be one of the most effective catalysts up to now\textsuperscript{7,8}. Due to the high reactivity of Na with Cl, the general solid state reaction proposed by Sandrock\textsuperscript{8} after milling is:

\begin{equation}
(1-x)\text{NaAlH}_4 + x\text{TiCl}_4 \rightarrow (1-4x)\text{NaAlH}_4 + 3x\text{NaCl} + x\text{Ti} + 3x\text{Al} + 6x\text{H}_2
\end{equation}

where \(x\) is the mole fraction of TiCl\textsubscript{4}, added to the initial material. Sandrock suggested that TiCl\textsubscript{4} act just as precursor and the real catalyst could be, according to the reaction, the zero-valent Ti. In addition, the real catalyst could also be Ti\textsubscript{H}_x, Ti-alloy or some intermetallic compounds formed during milling. Sun et al.\textsuperscript{9} used titanium n-butoxide (Ti(Oct\textsubscript{x})) and zircon n-propoxide (Zr(Opr\textsubscript{x})) as catalysts on NaAlH\textsubscript{4} and supposed that Ti and Zr doping results in lattice substitution of Na-cations.

In this paper, we describe the preparation of nanocrystalline Na\textsubscript{2}LiAlH\textsubscript{6} by simple method of ball milling with TiO\textsubscript{2} and TiCl\textsubscript{4} addition in order to find out the catalytic effect of the additions on the hydrogen sorption kinetics in Na\textsubscript{2}LiAlH\textsubscript{6}.

EXPERIMENTAL

The powders used were NaH (95% purity, Aldrich Germany), LiAlH\textsubscript{4} (98% purity, Alfa Aesar Germany), TiO\textsubscript{2} (99.5% purity, Alfa Aesar Germany) and TiCl\textsubscript{4} (99.999% purity, Aldrich Germany). The milling was carried out in a Fritsch P5 planetary ball mill using an initial ball-to-powder mass ratio of 10:1. All handling of the powders, including milling and weighting, was performed inside a glove box under continuously purified argon atmosphere (oxygen and moisture content <20ppm). A small amount of powders were removed at regular time intervals to monitor the structural changes during the milling. X-ray diffraction (XRD) experiments were conducted in a Bruker Axs-D8 Advance using Cu K\alpha radiation. Alkali metals are very sensitive to exposure to air (and much more after milling) and any contact results in their hydration. To avoid exposure to air during XRD measurements, the powders were covered with a thin plastic foil, which had a negligible or easily deductible contribution to the diffraction pattern. For the sorption measurements, sample holders were sealed inside the glove box and attached to a hydrogen titration apparatus\textsuperscript{10}. Kinetic measurements were performed in a temperature range 180 to 230 °C. DSC experiments were carried out in a Netzsch 404 apparatus with a heating rate of 5 K/min. this apparatus is located into a glove box under continuously argon flow.

RESULTS AND DISCUSSION

Milling process

Figure 1 shows the X-ray diffraction patterns of powders milled at 100 h without and with catalysts. Formation of Na\textsubscript{2}LiAlH\textsubscript{6} after milling without catalyst was successfully obtained\textsuperscript{11}. By adding TiO\textsubscript{2}, traces of LiAlH\textsubscript{4} and NaH still remain. However, by adding TiCl\textsubscript{4}, the reaction is more complex because some Na\textsubscript{2}LiAlH\textsubscript{6} was decomposed to LiH and Al and additionally NaCl phase is formed. Similar reaction was observed in using TiCl\textsubscript{4} in NaAlH\textsubscript{4} during mechanical alloying\textsuperscript{6}. Although the results are not included in this paper, NaCl is already formed after 2 hours milling, which confirms the