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REDUCTION REACTIONS IN DOPED CERIA CERAMICS STUDIED BY DILATOMETRY

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Abstract

Reduction of pure and doped CeO_2 to CeO_{2-x} is associated with an expansion. The behaviour of pure CeO_2, $Ce_{0.9}Ca_{0.1}O_{1.9}$, $Ce_{0.8}Ca_{0.2}O_{1.8}$ and $Ce_{0.6}Gd_{0.4}O_{1.8}$ at 1000°C in the oxygen partial pressure range from 0.21 atm to 10^{-18} atm is described. The results show that even though the nominal concentration of oxide vacancies are equal in the two mostly doped cerias, the CaO-doped one expands much more than the Gd_2O_3-doped one. The max. expansion of CeO_2 was about 2.2%, of $Ce_{0.8}Ca_{0.2}O_{1.8}$ 1.5%, and $Ce_{0.6}Gd_{0.4}O_{1.8}$ 0.8%. The results are compared with high temperature XRD data from literature.

1. INTRODUCTION

Ceria-based materials have been proposed as anode materials for solid oxide fuel cells [1]. When pure CeO_2 is reduced it becomes non-stoichiometric, CeO_{2-x}, and at the same time both electronic and oxide ionic conductivity are induced. The reduction is also associated with a gradually increasing expansion which limits its practical application in the fuel cell. The expansion as well as the conductivities may be to some degree controlled by doping with di- or trivalent metal oxides such as CaO or Gd_2O_3. Here "doped" means "solid solution" which may be up to 40 atom %.

The degree of reduction is usually described by the oxygen partial pressure or x in CeO_{2-x}. The reduction reaction can be expressed:

$$CeO_2 \rightleftharpoons CeO_{2-x} + \frac{x}{2} O_2(\text{gas})$$

leading to oxide vacancy formation and expansion of the CeO_2 fluorite lattice. As the lower valent oxides also introduce oxide vacancies doping with such oxides might limit the degree of reduction, and thus the expansion.

The purpose of this work is to determine the expansion of ceria-based materials as a function of oxygen partial pressure, type of dopant and degree of doping.

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2. EXPERIMENTAL

The ceramic samples examined were 10-15 mm long with a cross section of approximately 4 x 4 mm^2. All samples were made by uniaxial pressing. The pure CeO_2 was a commercial powder (Reacton 99 9% CeO_2). Powders of the composition $Ce_{0\,9}Ca_{0\,1}O_{1\,9}$, $Ce_{0\,8}Ca_{0\,2}O_{1\,8}$ and $Ce_{0\,6}Gd_{0\,4}O_{1\,8}$ were prepared from $Ce(NO_3)_3 \cdot 6H_2O$ (Merck, >98.5%), $Ca(NO_3)_2$ and $Gd(CH_3COO)_3$ (both 99.9%) by a process similar to that of Pechini [2].

All samples were sintered at 1600°C in air for 2h. The porosity of the pure CeO_2 sample was 32% and less than 10% for the others.

The isothermal dilatometry was performed in a Netzsch 402 E dilatometer with a dynamic atmosphere furnace. The samples were heated by 2°C/min. to 1000 °C in air and kept at 1000°C ± 1°C while the gas composition was varied. A flow of 150 ml/min. was maintained throughout the experiment. The oxygen partial pressure in the exhaust gas was monitored by a zirconia electrochemical cell at 1000°C.

The following gas compositions were used in the reduction experiments: Dry air, dry N_2, 1% and 9% H_2 in N_2 containing 3% H_2O, and "dry" 9% H_2 in N_2 (0.15% H_2O). After a change of gas composition at the furnace inlet the exhaust gas composition was completely changed after 1 hour in most cases. The dimensional changes of the sample caused by reactions with the gas were followed by the dilatometer, and the gas was changed after a constant length was reached Finally, the samples were cooled by 2°C/min. to room temperature in dry 9% H_2 in N_2

3. RESULTS AND DISCUSSION

Figure 1 shows the change in sample length relative to the sample length in air at 1000°C as a function of time for the CeO_2 sample. The composition of the gas is also indicated. As can be seen the response to a change in gas is fast, usually 2-3 hours to obtain a new equilibrium. The changes in dimension are reversible as was demonstrated by partial reoxidation followed by strong reduction.

Figure 2 presents the relative expansion as a function of oxygen partial pressure Pure CeO_2 exhibits a much higher relative expansion than the doped compositions at the same oxygen partial pressure, and the Gd-doped sample shows a lower expansion than the Ca-doped ones

Figure 3 compares the expansion measured by dilatometry with literature data obtained by combining high temperature XRD data [3] with thermodynamic data [4]. The XRD data [3] were not reported exactly for 1000°C, but it was stated that the thermal expansion coefficient was found to be $11.8 \cdot 10^{-6} K^{-1}$ independent of x in CeO_{2-x}. This is, however, in disagreement with preliminary dilatometric measurements from this study where the reduced ceria had a thermal expansion coefficient of $14.2 \cdot 10^{-6} K^{-1}$ and the oxidized had $12.6 \cdot 10^{-6} K^{-1}$. The deviation between the curves of Figure 3 is believed to be related to this discrepancy.

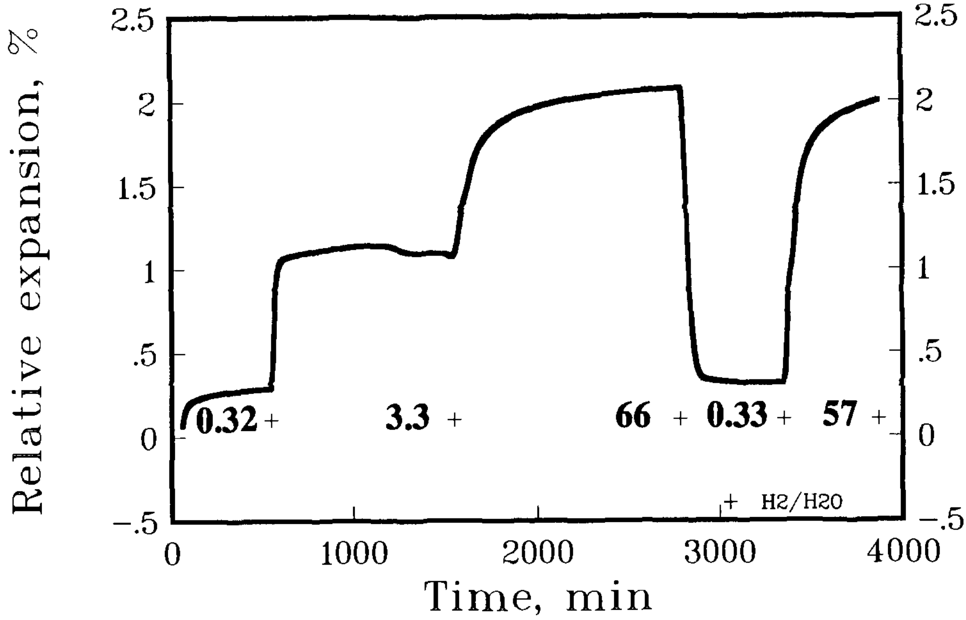

Figure 1 Isothermal dilatometry for CeO_2 at 1000°C Reference sample length is in .21 atm. O_2. Variations in gas composition are indicated by H_2/H_2O ratios.

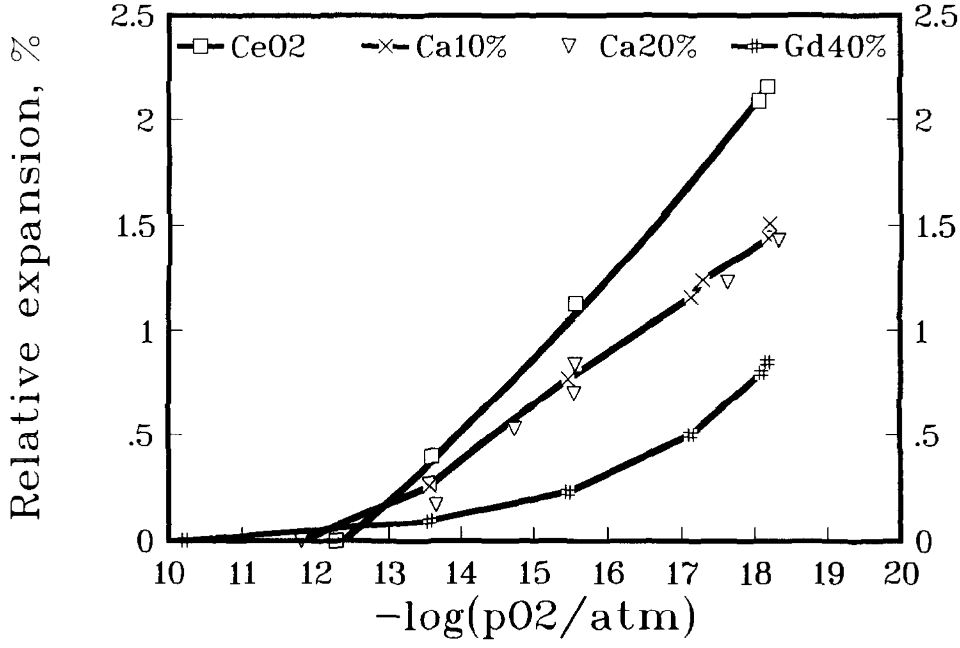

Figure 2. Relative expansion at 1000°C as a function of oxygen partial pressure. CeO_2, Ca 10%, Ca 20%, and Gd 40% mean pure ceria, $Ce_{0.9}Ca_{0.1}O_{1.9}$, $Ce_{0.8}Ca_{0.2}O_{1.8}$ and $Ce_{0.6}Gd_{0.4}O_{1.8}$, respectively.

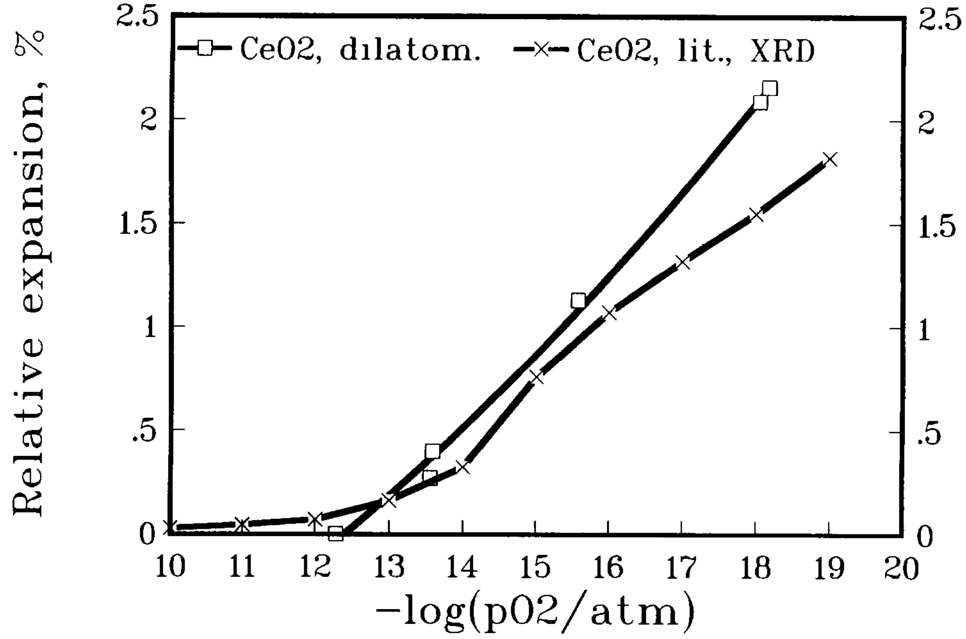

Figure 3. Relative expansion at 1000°C for pure ceria as a function of oxygen partial pressure. Comparison between literature data from XRD-measurements [3] and isothermal dilatometry (this work).

4. CONCLUSION

The reduction and the associated expansion of CeO_2 is suppressed to some extent by doping with CaO and Gd_2O_3, the latter being the most efficient.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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