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THERMALLY INDUCED CHANGES IN THE CERIA ZIRCONIA SYSTEM

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ABSTRACT

The redox behaviour of ceria zirconia alloy (50 mol %) has been investigated by thermoanalytical methods under controlled atmospheres (air, oxygen and argon with 5% hydrogen). The supposed non-stoichiometry (CeO_x-ZrO_2, x being a function of oxygen pressure and temperature) is proved by weight changes which are accompanied by volume variations investigated via thermodilatometry. These phenomena are attributed to the redox equilibrium of Ce(+3)-Ce(+4) associated with oxygen vacancies. The reduced material is characterized by a cubic unit cell, larger than that previously reported for the tetragonal structure of the same oxidized sample.

INTRODUCTION

Ceria zirconia sintered materials have been extensively investigated to disclose phase relations and properties. Most of the diagrams indicated that samples containing 60 and 50 mol % ceria were a single phase of cubic symmetry and the investigation of Tani et al. (1) extended the cubic field to the 40 mol % ceria content at 1600°C. On the contrary, we found that samples in the range between 60 and 40 mol % ceria, heated at 1600 °C, did deliver a single phase of tetragonal symmetry when a "non quenching" cooling rate was applied. Furthermore, for lower ceria concentrations, two phases were found to co-exist, both of them with a tetragonal symmetry, one with "low" and the other with "high" ceria content: CeTZP° and CeTZP' respectively (2,3).

The discrepancies mentioned above were supposed to be kinetically driven redox processes. In fact, it has been widely recognized that CeO_2 becomes increasingly reduced toward a Ce_2O_3 composition, both at high temperature and at low oxygen partial pressures (4).

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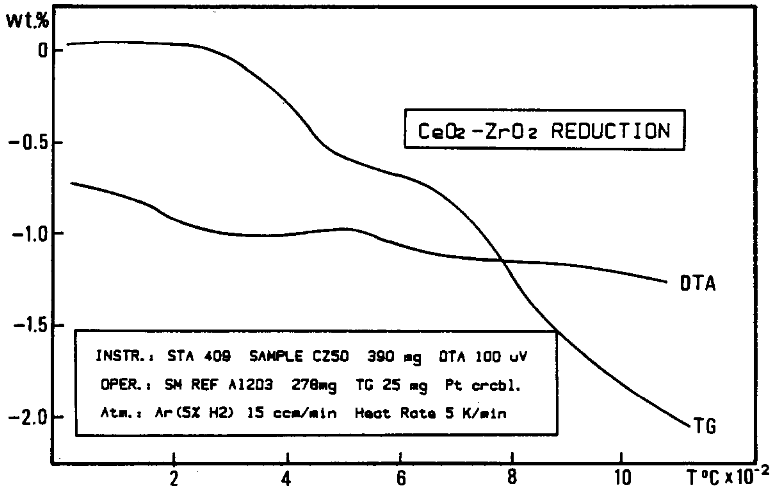

Fig. 1 - STA analysis of the reduction step.

The presence of 5 % volume of hydrogen in argon provides the reducing environment, in fact, in a simply neutral atmosphere, no weight loss could be recorded up to 1200°C.

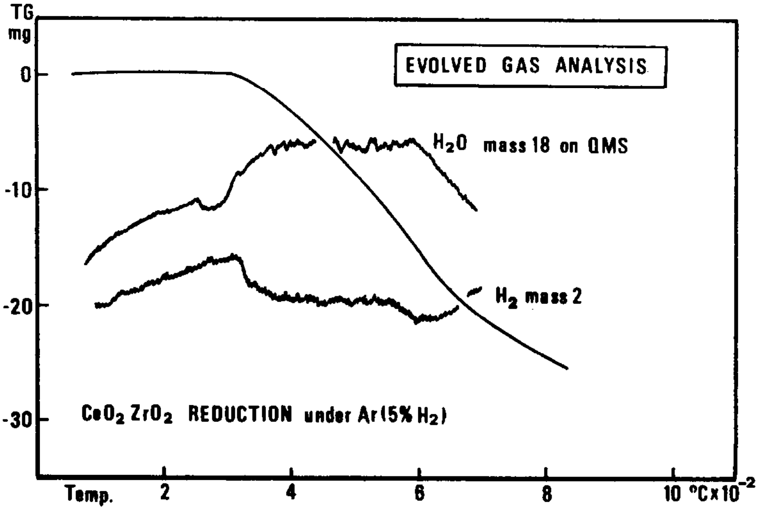

Fig. 2 - STA + EGA analysis od the reduction step.

The Evolved Gas Analysis (EGA) performed with the on-line Quadrupole Mass Spectrometer (QMS) shows that, as soon as the material exhibits a weight loss, there is a sensible increase in the concentration of mass number 18 (H2O) and a parallel decrease of the Hydrogen (H2) concentration, being oxygen taken from the ceria zirconia alloy.

The reduction of Ce(+4) to Ce(+3) is accompanied by the formation of one oxygen vacancy for each pair of ceric ions being reduced. In fact, it has been pointed out that the electrical conductivity is greatly influenced by the redox condition of the material (5). Therefore, the ceria zirconia system should be better represented by $ZrO2$, $CeO2$ and $Ce2O3$ ternay diagram. This paper is aimed at the thermoanalytical investigation of the above mentioned redox reaction.

EXPERIMENTAL

To prepare the samples, ceria and zirconia powders of commercial origin and 99.0 % nominal purity were used. Mixtures were obtained using agate balls and mortar. The samples were of the "high silica" type with contamination as high as 2 mol %. The mix and mill period, of not less than 24 hours, delivered a slurry which was dried, pressed as flat disks and heated according to the following cycle: heating up to 1600°C at a 10°C/min rate, soaking for 4 hours, cooling at about 30°C/min to 1000°C, and then to room temperature in additional 3 hours. The cooling rate allowed the sample to rearrange into the tetragonal CeTZP' structure. The samples "as fired" exhibited a slightly grey colour, darker within the pellet's body, lighter at the surface. "Oxidized" samples were obtained after annealing, in air, i.e. keeping them at 900°C for at least 4 hours and let them cool down in further 8 hours. The colour became pale yellow.

The samples were investigated via STA thermoanalysis (TG+DTA) equipped "in line" with a QMS (Quadrupole Mass Spectrometer) and thermodilatometry (TDM) under controlled atmospheres: oxygen or air to assure an oxidizing environment and Ar, Ar+H2 (5% vol) to provide both a neutral and a reducing atmosphere. The equipment used were Netzsch STA 409 and TDM 402 steered with an appropriate software by an HP 86 personal computer.

RESULTS AND DISCUSSION

The annealed samples were considered "fully oxidized" materials because they did not show any further weight gain under oxygen through a whole firing cycle up to 1200°C. Their X-ray diffraction confirmed the tetragonal symmetry previously reported (3). The annealed samples were analysed under a 5% H2-Ar atmosphere. The results are reported in Fig. 1. There is an increasing weight loss, beginning at temperatures of about 300°C, which is accomplished only after the isothermal step, 1 hour at 900°C. It compares fairly well with the theoretical value (2.71%) calculated according to the following reaction:

$$2\ (CeO_2\text{-}ZrO_2)\ \text{---}\ Ce_2O_3\text{-}ZrO_2 + 1/2\ O_2$$

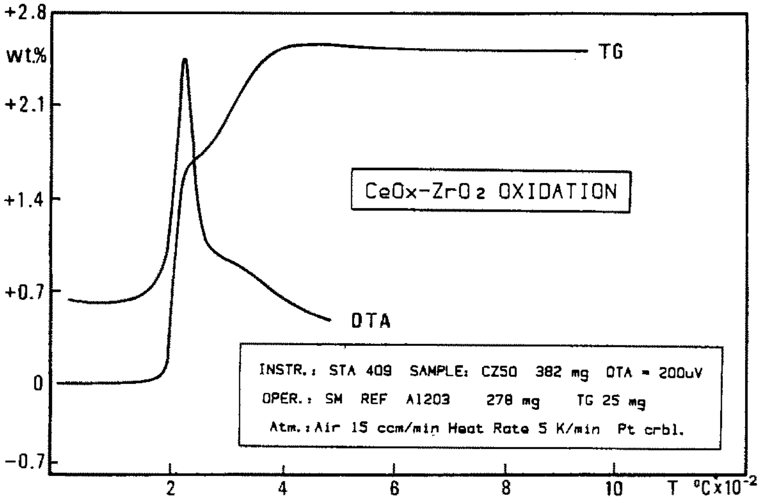

Fig. 3 - STA analysis of the oxidation step.

The recovered "reduced" sample was recycled in the STA apparatus under an oxidizing atmosphere, either oxygen or air, Fig. 3. In both cases, with different rates of the weight-gain, a rapid oxidation could be recorded, beginning at temperatures as low as 250°C. The measured DTA exotherm was very large, as it pertains to an oxidation reaction, on the contrary, the reduction process in Fig. 1 did not show any evident DTA peak. The trend of the DTA during the whole weightloss was slightly endothermic.

We have explained this lack of evident DTA effects by taking into account two different and contemporary phenomena: the oxygen loss of the crystal lattice (endothermic) and the formation of a water molecu (exothermic) on the crystal surface. Most probably, we assume, the two events are of quite similar energy content and their overall effect is close to nil. Furthermore, the experiments indicated that there is a quite different kinetic between oxidation (very rapid in air, flashing in oxygen) and reduction. The latter is rather slow and it is accomplished only in a couple of hours, during the isothermal step which was fixed at 900°C. The water molecules' release rate may dictate the overall reduction velocity.

Further investigation will be necessary to pin down the rate determining parameters as, for instance, the bulk porosity. In fact, it is quite obvious that materials with continuous or closed porosity will behave differently. In our case the porosity of the original material was about 15%.

The evidence of a continuous, labyrinth type of porosity is given by the Scanning Electron Microscope (SEM) image of the sample which sustained 12 redox TDM cycles Fig. 4.

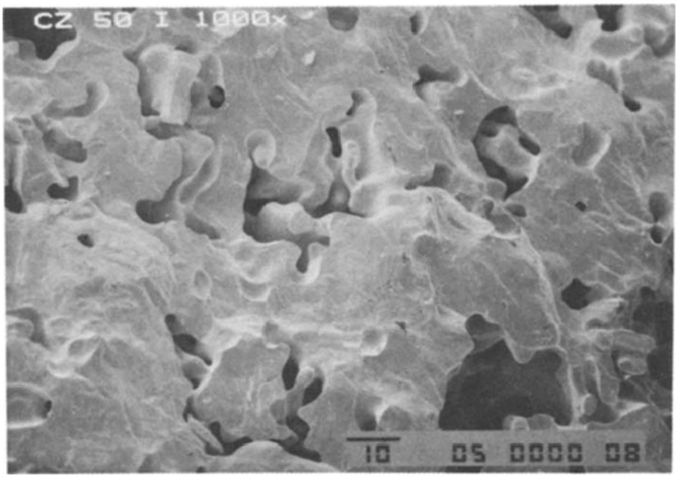

Fig. 4 - SEM image of the fracture surface after 12 redox TDM cycles.

We think that this porosity is due to the silica contamination, responsible liquid phase formation at grain boundaries, during the sintering stage at 1600°C. (6). The nature of the grain boundary is still under investigation; however, its morphology claims for a Chemically Induced Grain-boundary Migration mechanism (CIGM) which may take place in ceramic systems depending on the surrounding atmosphere (7).

The water molecules, evolved during the Ar(5% H_2) treatment, might help to dig into the glassy grain boundaries, building a void labyrinth, as the reducing cycles proceed. At the moment we do not have a quantitative measurement to support this assumption, which is based only on the trend of the onset temperatures of the reduction steps. We have observed that these latter move to lower values as the cycles increase. This might be interpreted as an indication that water moves more and more freely through the increasing porosity.

It is worth pointing out that samples (3x3x10 mm) maintained their integrity after several TDM cycles, in spite of the large dimensional variation exhibited by the "reduced" and the "oxidized" states.

The mechanical strains could be accommodated in the material, thanks to its labyrinth type of porosity which provided "branching" mechanism to the propagating crack.

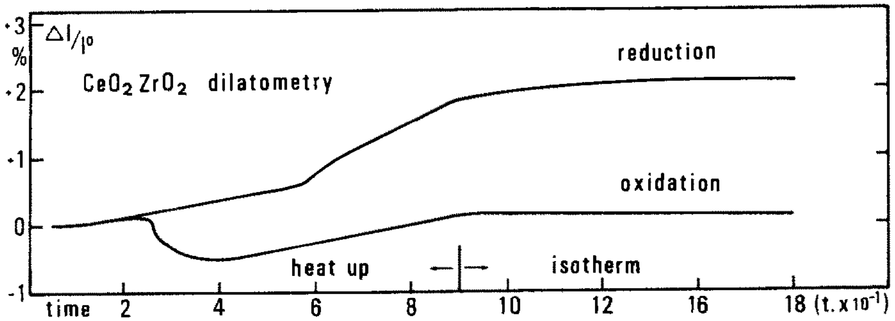

Fig. 5 - TDM, sample 10 mm in silica holder. Ar+5%H2 (reduction), air (oxidation), 15 ccm/min. Heat.rate 10°K/min. Isotherm at 900°C. Time is minutes.

The TDM measurements compare fairly well with the XRD data which indicated a smaller unit cell for the "oxidized" tetragonal materials. As the reduced form is necessarily accompanied by oxygen vacancies, we suggest that there is a lack of chemical bonds which allow the structure to expand. On the other hand, when the vacancies are filled up with oxygen, the restored chemical bonds pull the structure back again.

CONCLUSION

We look forward to investigating this contraction - expansion behavior with respect to the mechanical properties of surface compressed layered composite ceramic materials.

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