THERMAL EVOLUTION OF CERIA–ZIRCONIA METALLORGANIC PRECURSORS

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ABSTRACT

Ceria–zirconia tetragonal solid solutions were obtained by using gelled metallorganic precursors as starting materials. By drying these gels, intimately mixed powders of a quasi-amorphous nature were obtained. On firing, the tetragonal solid solution sintered directly without any separation of the single oxides.

Poorly sintered materials were obtained from the firing of dried gels but improved sinterability could be achieved by using calcined gels to prepare compressed pellets before firing.

DTA–TG evidence indicated that the organic remnants of the dried gels were responsible for their poor sintering performance. Pre-firing treatment at 550°C gave very active powders which sintered faster and better than ground crystalline mixtures.

INTRODUCTION

The engineering use of zirconia (ZrO_2) is greatly hindered by its volume increase on cooling at about 1000°C due to the tetragonal–monoclinic transformation [1]. Despite these limitations, the use of zirconia is made possible by alloying it with other oxides, which can either fully or partially stabilize the cubic structured form. The tetragonal form cannot be quenched, yet it can be stabilized through the contribution of particle size [2] and alloying oxides [3,4]. Ceria (CeO_2) was found to stabilize the tetragonal form in mixtures made to prepare samples for phase equilibria [5] or electrical conductivity studies [6].

Sintering and reaction kinetics of the two oxides have been investigated using the conventional technique of grinding and mixing the pure crystalline materials [7]. The inherent sluggishness of the reactions at subsolidus temperatures has often required very long firing periods to meet equilibrium conditions. Extended research efforts have been made for the particle production, using both physical and chemical processes.

In this paper, another method of obtaining an intimate mixture of reacting oxide particles is proposed. The co-gelling of hydrolized organometallic complexes previously dissolved in an organic medium allowed homogeneity down to the molecular level. However, during the course of the present investigation, it was found that samples prepared with "as-gelled" precursors, fired at 180°C only, delivered poorly sintered materials at 1300°C. In order to gain better insight of this negative behaviour, the thermal evolution of the "gelled" precursors has been investigated and is reported here.

EXPERIMENTAL

The metallorganic precursors of the oxide mixtures were prepared using commercially available 2-4-pentanedionate of Ce(III) and Zr tetra-*n*-butoxide. This technique proved to be very promising in the field of glasses and glass ceramics [8].

The required amounts, calculated on the basis of the actual cation concentrations, were dissolved in anhydrous ethanol. They were maintained at a simmering temperature in a round-bottom, two-necked flask, equipped with a heating mantle, stirrer and reflux condenser. The excess ethanol was distilled off after a few hours. A viscous, brown liquid remained in the flask and a small amount of water was added. Gelling could take place in a short time. A semi-solid mass was left to dry overnight on a metal pan at 180°C. The end-products, named precursors, were yellow-brown powders which under the microscope sometimes looked like vitreous chips with glassy-type fracture surfaces (Fig. 1). These materials will be referred to as "as-gelled" precursors to distinguish them from the "calcined" precursors which undergo further heat treatment.

The precursors have been examined by TG–DTA and XRD standard techniques, using Netzsch and Siemens apparatus, respectively. Samples for reaction and sintering study were prepared by pressing the calcined powders into small pellets of about $3 \, g \, cm^{-3}$ green density, to be fired at 1300°C for phase recognition and density determinations. The latter was determined by mercury picnometry. In order to compare the sintering and reactivity of these precursors, both "as-gelled" and "calcined", with samples of the same composition made by grinding and mixing together the crystalline powders, a few pellets were fired at 1300°C for various periods of time up to a constant density value. Two different zirconium oxides with different mean grain sizes of 15 and 25 μm, respectively, were used for comparison with cerium oxide powder of about 20 μm mean particle size.
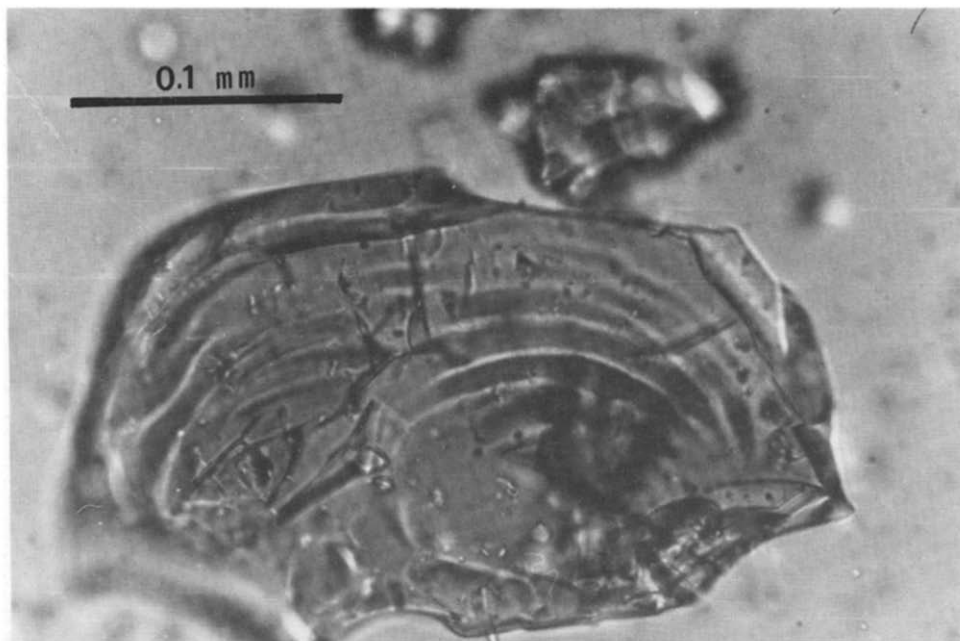
Fig. 1. 0.16 CeO$_2$–0.84 ZrO$_2$ "as-gelled" precursors. Transmitted light microscopy.

RESULTS AND DISCUSSION

Thermoanalytical curves for the precursos 0.16 CeO$_2$–0.84 ZrO$_2$ are reported in Fig. 2. Tests were carried out in air and under an atmosphere of argon. After the endothermic peak at about 100°C, which may be due to moisture desorption, two more exothermic weight losses can take place within the 250–550°C range. The weight loss rate is quite linear up to 250°C when the large exothermic effect is produced by the combustion of the organic impurities which can make up to 15% of the whole mass under investigation.

Combustion is not complete at 350°C because samples recovered at this temperature were still of a dark grey colour. Elemental analysis revealed a carbon content close to 1%. A further weight loss, accompanied by another, smaller exothermic effect, was found at 500°C and above. Runs made under an atmosphere of argon delivered black powders. They did not show any exothermic effect, yet they had about 10% weight loss. The black powders recycled in air for DTA and TG behaviour indicated only one large exothermic effect at 450°C and above, with a further weight loss of about 4%. The burn-out of a certain amount of carbon black, remaining after the previous decomposition–combustion, was considered responsible for the

second small exothermic peak in Fig. 2. Sample holders, 12 mm high and 6 mm in diameter, may have allowed only poor air exchange within the burning mass at the first exothermic event. A DTA–TG run under pure
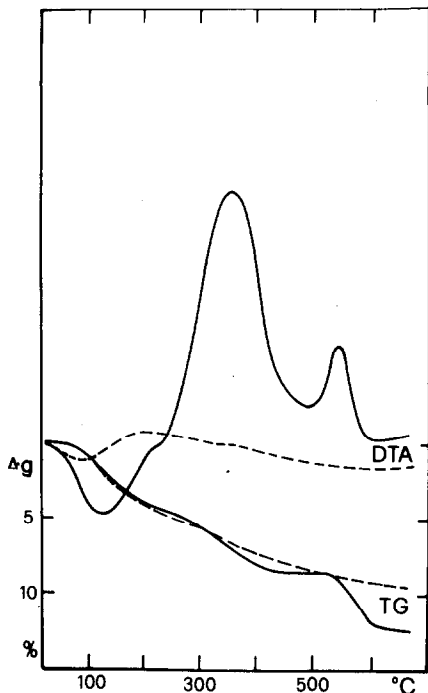

Fig. 2. Thermal analysis of 100 mg of the 0.16 CeO_2 –0.84 ZrO_2 gelled sample vs. 85 mg of the fired material. ———, Static air; — — —, flowing Ar (0.5 l min^{-1}). Pt containers 0.5 ml.

oxygen revealed only one exothermic peak at 280°C, confirming the above.

The X-ray diffraction patterns of samples collected at the various temperatures during the course of the DTA–TG investigation are presented in Fig. 3. It turned out that with a heating rate of 10°C min^{-1}, up to a peak temperature of 1300°C, the phase present at the end of the cycle could be considered to be at equilibrium. The X-ray pattern did not change even after several more hours of heating, although allowances had to be made for increased crystallinity and sintering.

Upon firing the gelled precursors, a very fine powder of a quasi-amorphous nature was obtained. It sintered directly into the tetragonal solid solution without any previous separation of the pure crystalline oxides.

Mixtures made of the ground crystalline oxides reached a steady state at 1300°C only after 200 h of firing treatment. The reacted fraction, reported in Fig. 4, was calculated by the ratio between the diffraction peak intensity of
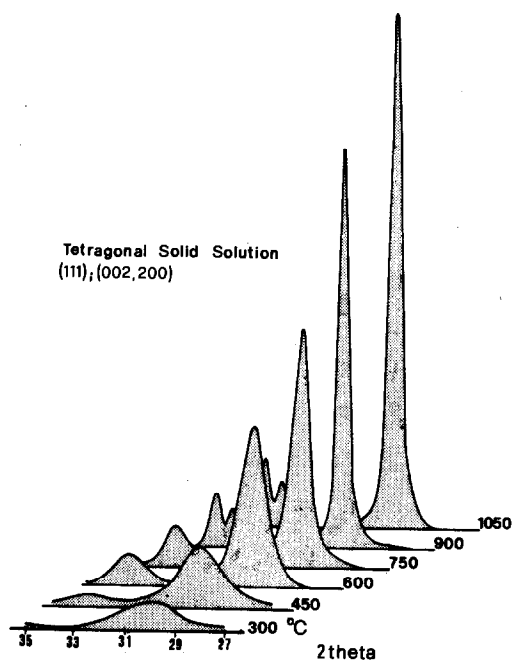
Tetragonal Solid Solution
(111)ᵢ (002,200)

Fig. 3. X-Ray diffraction patterns of a 0.16 CeO$_2$ –0.84 ZrO$_2$ gel quenched during DTA–TG analysis as a function of temperature. CuK radiation.

the newly formed tetragonal solid solution and the sum of the latter with the peak intensity of the reacting monoclinic zirconia. As expected, the finer crystalline oxides reacted faster; however, gels had already reacted during
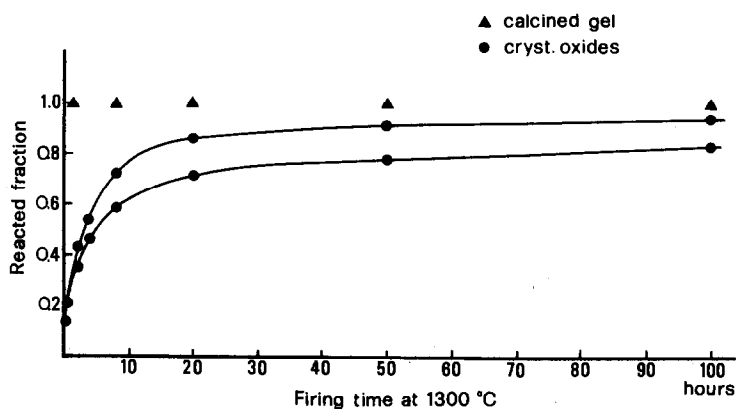
Fig. 4. Reacted fraction as a function of firing time for calcined gels (▲) and crystalline oxide mixtures (●).
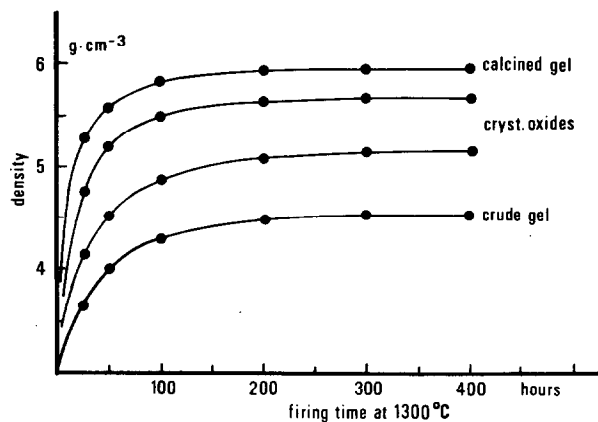
Fig. 5. Bulk densities obtained at various firing times for the indicated starting material compressed to a 3 g cm^{-3} green density. Crude gels reached 1.5–1.8 g cm^{-3} only.

the heating up period and reached the peak temperature as a single phase of tetragonal symmetry.

This outstanding performance of reactivity was not matched by the sintering ability. Pellets made with the "as-gelled" precursors heated at 1300°C for various periods of time reached density values lower than the two crystalline oxide mixtures used as reference, as shown in Fig. 5.

According to the DTA–TG analyses, the carbon burn-out could be considered responsible for having taken apart the sintering particles and prevented the necessary physical contact to allow mass transfer to occur and cause densification. However, a better sinterability was shown by the pre-fired gel precursors, as can be seen in Fig. 5. The calcining treatment of a few minutes at 550°C assured a complete carbon burn-out and delivered a bright yellow powder which could be pressed into pellets for sintering studies.

CONCLUSIONS

In this work, the combined effects of particle size and cerium oxide content were applied by using gelled metallorganic precursors as starting materials to produce ceria–zirconia tetragonal solid solutions.

By calcining the gelled precursors, intimately mixed very fine powders of a quasi-amorphous nature, were obtained. Upon firing, the tetragonal solid solution sintered directly without any previous separation of the pure oxides, whereas mixtures made of ground crystalline oxides reached a steady state only after 200 h of firing.

Although crude gels yielded poorly sintered materials, a substantially improved sinterability could be gained by using gels calcined at 550°C before being pressed into pellets for sintering studies. It was considered, on DTA–TG evidence, that organic burn-out and carbon-black contamination were responsible for the poor sintering performance shown by the crude gel precursors. A pre-firing treatment at 550°C gave very active powders which sintered faster and better than ground crystalline mixtures.

ACKNOWLEDGEMENT

REFERENCES

1 R. Ruh and T.J. Rockett, J. Am. Ceram. Soc., 53 (1970) 360.
2 R.C. Garvie, J. Phys. Chem., 69 (1965) 1238.
3 T.K. Gupta, J.H. Bechtold, R.C. Kuznicki, L.H. Cadoff and B.R. Rossing, J. Mater. Sci., 12 (1977) 2421.
4 R.C. Garvie, R.H. Hannink and R.T. Pascoe, Nature (London), 258 (1975) 703.
5 P. Duwez and F. Odell, J. Am. Ceram. Soc., 33 (1950) 271.
6 S. Roitti and V. Longo, Ceramurgia, 2 (1972) 172.
7 V. Longo and F. Ricciardiello, Ceramica, 27 (1974) 6.
8 V. Gottardi, R. Dal Maschio, G. Michelotto and G. Scarinci, Ceramica, 31 (1978) 17.