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STABILIZATION OF THE CUBIC ZrO_2 PHASE IN THE SYSTEM ZrO_2–MgO

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ABSTRACT

By progressive calcination of coprecipitated gels with a molar Zr–Mg ratio of 1 : 1, at different digestion times, it is found that, at temperatures of -700 ° C, a cubic solid solution plus MgO is formed. This solid solution is transformed to a tetragonal structure at ~ 950 ° C. The amount of MgO that accompanies both solid solutions is inversely proportional to the digestion time of the precipitates.

INTRODUCTION

Zirconium dioxide has found a very important place in refractories and ceramics technology, but it requires a stabilizing agent owing to the chemical inversions that occur on heating. The oxides of Be, Mg and Ca (among the divalent metals), of Al and Y (among the trivalents metals) and of Ce and Hf (among the tetravalent metals) are the commonest stabilizers for the metastable phases of ZrO_2. A maximum increase in breakage resistance and a minimum coefficient of thermal expansion of the zirconia are obtained by stabilization of the metastable cubic ZrO_2.

Duwez et al. [1] have studied the mechanism of stabilization of the cubic zirconia phase by the addition of MgO or CaO. According to these authors, the cubic solid solution is extended from 16 to 30 mol% in the case of CaO and from 16 to 25 mol% in the case of MgO. These results are for specimens cooled from 2000 ° C. Cocco and Schromek [2] have also studied the binary equilibrium MgO–ZrO_2, and the influence of small percentages of SiO_2 in the system, as well as the type of imperfections in the solid solution with cubic structure of MgO in ZrO_2. Grain [3] also studied the system ZrO_2–MgO, with emphasis on the range 1300–1600 ° C. Viechnicki and Stubican [4] reinvestigated this phase diagram by using coprecipitated gels; the thermal stability of the defective cubic solid solutions was investigated by a study of kinetics. Finally, Sim and Stubican [5] revised the phase

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diagram over a wide range, 1370–2300 °C, and they showed that the phases $Mg_2Zr_5O_{12}$ (δ-phase) and $MgZr_6O_{13}$ (γ-phase) are metastable. The phase $Mg_2Zr_5O_{12}$ had been considered stable in 1965 by Delamarre [6]. Some evidence for the formation of $MgZr_6O_{13}$ from ZrO_2–MgO melts was presented by Rossell and Hannink [7] in 1984.

Thus, despite many investigations, disagreement over the proposed phase diagrams still exists. It is possible that the difference in results is due to the different methods of preparation of the samples employed in each instance, leading to structural factors that influence the reactivity of the solids.

In this paper, we present a study of a gel mixture of $ZrO_2 \cdot nH_2O$ and $Mg(OH)_2$; its progressive heating allowed us to obtain a solid solution of MgO in ZrO_2 with cubic structure between 680 °C and 760 °C, depending on the digestion time of the precipitates.

EXPERIMENTAL

Products

The $ZrOCl_2 \cdot 8H_2O$, $MgCl_2 \cdot 6H_2O$ and NaOH were from Merck, and of A.R. quality.

Preparation of samples

Aqueous solutions (0.05 M) of zirconium oxychloride and magnesium chloride were used, and the gel samples were prepared by precipitation from the aqueous solutions with an aqueous solution of NaOH. The precipitates were obtained by adding the NaOH solution to the solution of chlorides at the boiling point to produce a pH of 11. Digestion times of the precipitates in the mother liquors at the boiling point were 0, 0.5 and 1.5 h. The white precipitates obtained were collected by filtration on a No. 4 porosity filter and washed with cold distilled water until no chloride was present in the washings. The precipitates were dried at room temperature.

Apparatus

Thermogravimetric (TG) analysis

A Mettler TA 3000 system with TG50 attachment was used, at a heating rate of 600 °C h^{-1}.

Differential thermal analysis (DTA)

A laboratory-constructed system incorporating a vertical furnace and a temperature regulation system, both from Adamel, and a differential chromel–alumel thermocouple was used. The heating rate was 300 °C h^{-1}.

X-ray powder diffraction

A Philips PW 1130 diffractometer was used.

IR spectroscopy

A Perkin–Elmer model 683 spectrophotometer was used. The samples were prepared as a mull using Fluorolube as mulling agent for examination in the region 4000–1500 cm^{-1}.

RESULTS AND DISCUSSION

A study by X-ray powder diffraction showed that the precipitates were amorphous. The thermal analysis and IR spectroscopy showed that the gels are a mixture of $ZrO_2 \cdot nH_2O$ and $Mg(OH)_2$.

Chemical analysis of the filtrates showed that precipitation of the zirconium and magnesium present in the solution is quantitative; therefore, the Zr–Mg molar ratio in the precipitate is 1 : 1, as in the respective chloride solutions.

Thermal study

Thermal studies of the coprecipitated samples were carried out in a static atmosphere.

In Fig. 1, the TG, differential thermogravimetry (DTG) and DTA curves of coprecipitated samples obtained without digestion are shown. The TG curve shows two poorly defined steps. Between 25 °C and 750 °C, the first step corresponds to 3.4 mol of water of hydration of ZrO_2, and the second step corresponds to the hydroxyls of magnesium hydroxide. In the DTG curve these steps are well defined.

The DTA curve presents two endothermic peaks with maxima at 150 °C and 400 °C, which correspond to the two steps of the TG curve, and an exothermic peak which finishes at 680 °C; above this temperature there are no further peaks.

Figure 2 shows the TG, DTG and DTA curves of the sample obtained with a digestion time of 0.5 h. The TG curve is similar to the TG curve in Fig. 1, and shows that the first step corresponds to 2.3 mol of water of hydration and the second step corresponds to the hydroxyls of magnesium hydroxide, as in the above case. These steps are well defined in the DTG curve.

The DTA curve presents two endothermic peaks that confirm the TG data and two exothermic peaks, the first one terminating at 760 °C and the second at 980 °C.

Figure 3 shows the TG, DTG and DTA curves of the sample obtained with 1.5 h digestion time. The TG curve is similar to the TG curves

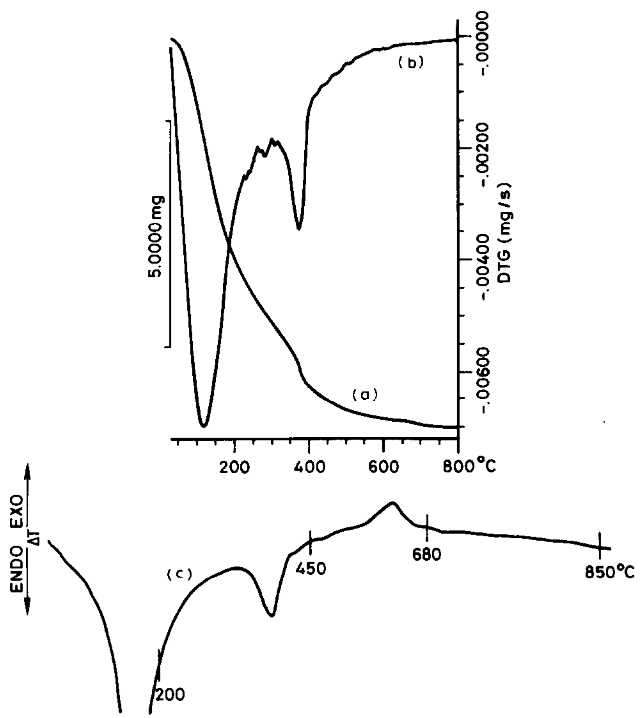

Fig. 1. TG (a), DTG (b) and DTA (c) curves of a coprecipitated sample. Zero digestion time; sample weight 25.171 mg.

mentioned above. The only difference is that the first step is smaller than in the above cases, and corresponds to 1.7 mol of water. The DTA curve is also similar to those mentioned above.

To summarize an increase in the digestion time of the precipitates in the mother liquors does not change the molar ratio of Zr to Mg; what does change is the number of moles of water of hydration of the ZrO_2, which decreases with increasing digestion time.

IR spectroscopy

The IR spectra of samples coprecipitated at different digestion times are identical. In Fig. 4, the IR spectrum of only one of them is shown.

The spectrum includes a strong, sharp band at 3680 cm^{-1} due to the hydroxyl group, another broad band at 3300 cm^{-1}, which corresponds to the stretching vibrations of water of hydration, and a band at 1640 cm^{-1} due to the H–O–H bending vibration.

X-ray diffraction

The X-ray powder diffraction analysis of the samples was carried out at predetermined points on the DTA curves. These curves showed the temperatures at which events took place in the samples during heating.

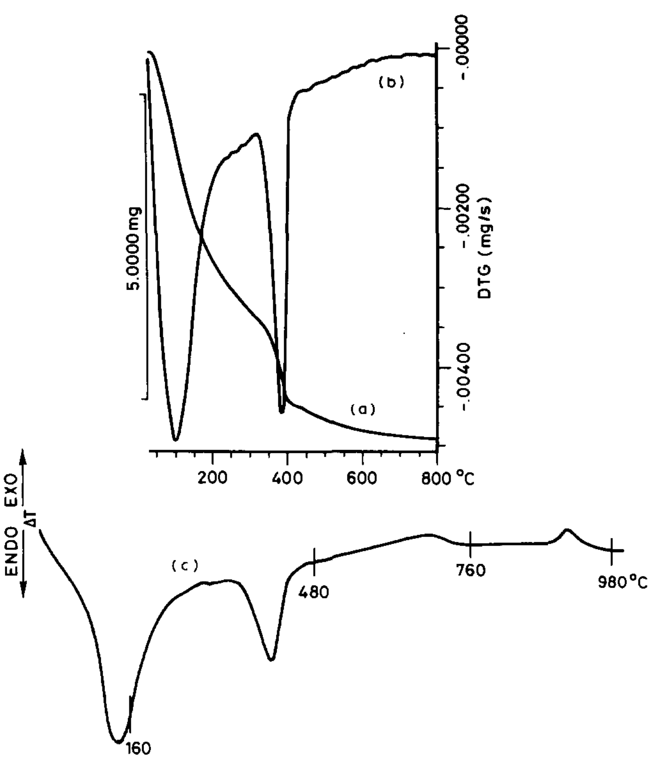

Fig. 2. TG (a), DTG (b) and DTA (c) curves of a coprecipitated sample. Digestion time 0.5 h; sample weight 23.605 mg.

Thus, during calcination of the precipitate without digestion samples were taken at the following points of the DTA curve (Fig. 1).

At 450 ° C, when the second endothermic peak had finished, the X-ray diagram showed that the sample was amorphous. At 680 ° C, when the exothermic peak had finished, the X-ray diagram corresponds to a mixture of two crystalline phases: a cubic solid solution and magnesium oxide (Fig. 5(a)).

We have calculated the lattice parameter, *a*, of the cubic solid solution as being 5.058 Å. This parameter was calculated by using the Nelson-Riley function [8].

At 950 ° C, the final temperature of the DTA curve, the X-ray diagram also shows a mixture of two crystalline phases; a solid solution, now tetragonal, and magnesium oxide (fig. 5(b)).

A comparison of the two X-ray diagrams of Fig. 5 reveals that the line at 2.9144 ($2\theta = 30.65$) is displaced to 2.9425 ($2\theta = 30.35$), the line at 2.5265 ($2\theta = 35.50$) is split into two, the line at 1.7859 ($2\theta = 51.10$) is displaced to 1.8057 ($2\theta = 50.50$), and the line at 1.5244 ($2\theta = 60.70$) is split into two. The displacement and splitting of lines correspond to the transformation of the cubic solid solution into a tetragonal solid solution; this phenomenon is not visible in the DTA curve.

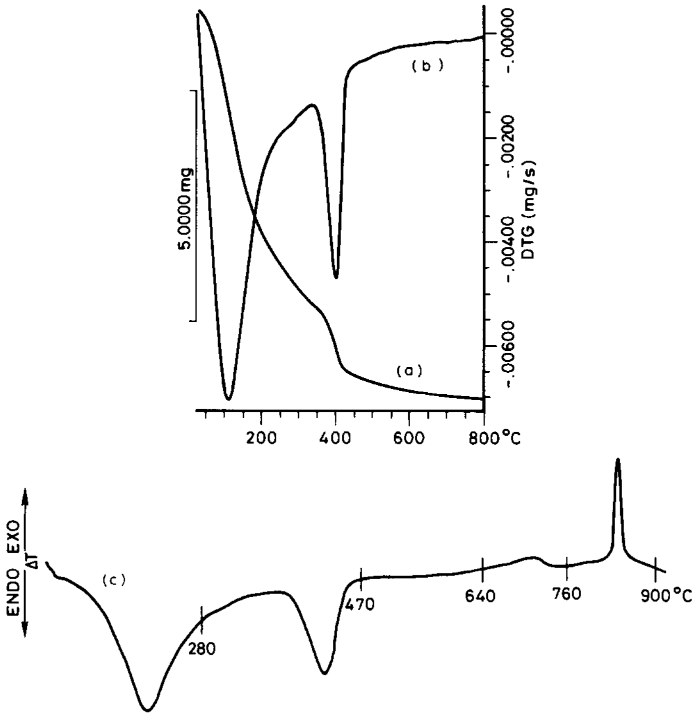

Fig. 3. TG (a), DTG (b) and DTA (c) curves of coprecipitated sample. Digestion time 1.5 h; sample weight 30.152 mg.

The magnesium oxide has not undergone any transformation as the result of the heating.

For the precipitate obtained with a digestion time of 0.5 h, the X-ray diagrams of samples taken in the DTA curve (Fig. 2) at 480 ° C after the second endothermic peak, at 760 ° C after the first exothermic peak and at 980 ° C after the second exothermic peak show the same results as in the case of the precipitate obtained with zero digestion time.

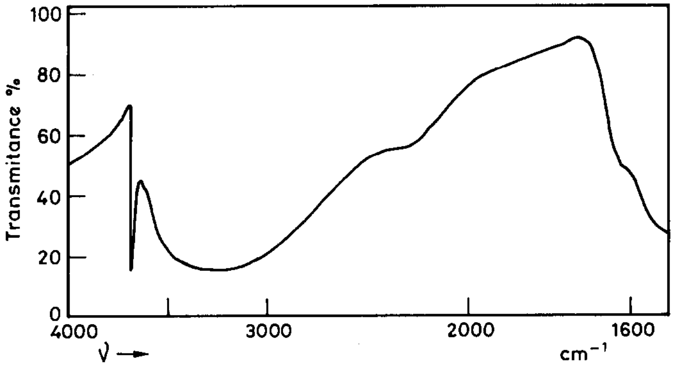

Fig. 4. IR spectra of a coprecipitated sample. Digestion time 0.5 h.

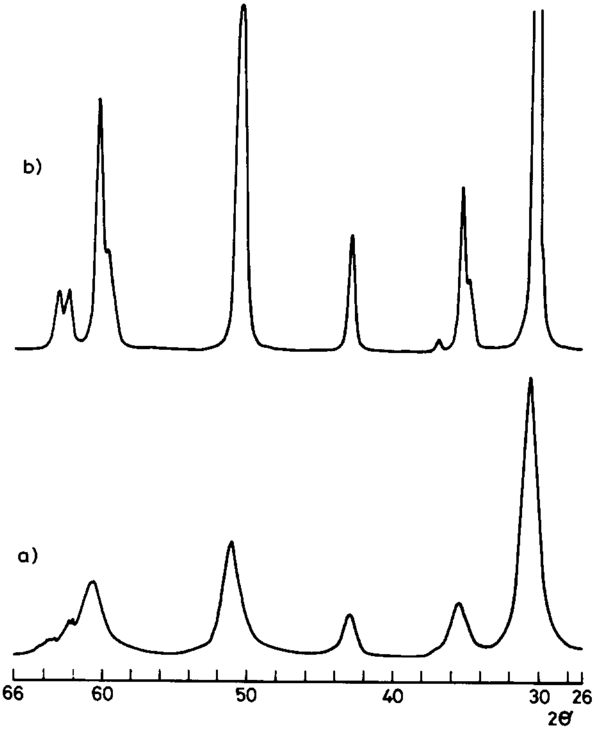

Fig. 5. X-ray diagrams. (a) Cubic solid solution plus MgO, and (b) tetragonal solid solution plus MgO.

Finally, for the precipitate obtained after a 1.5-h digestion time, the X-ray diagrams of samples taken at 470 ° C, 760 ° C and 900 ° C in the DTA curve of Fig. 3 are identical to those in the above-mentioned cases.

In conclusion, it may be stated that, for all the samples studied, the endothermic peaks correspond to the dehydration reactions of the precipitates, whereas the first exothermic peak corresponds to the formation of the cubic solution and the second exothermic peak to the transformation of the cubic solid solution into a tetragonal solid solution. All the results are summarized in Table 1.

From the diagrams of X-ray powder diffraction, and by applying the method of diffraction–absorption of Lennox [9], we have calculated the amount of magnesium oxide that accompanies the cubic solid solution and the tetragonal solid solution. The results are included in Table 1. It is evident from this table that the amount of magnesium oxide that accompanies both solid solutions is the same for the same digestion time.

Finally, the method of coprecipitation has proved useful for obtaining cubic solid solutions at low temperatures, about 700 ° C, instead of the 1400 ° C necessary when the addition of MgO to ZrO_2 is used. In this latter case the order of transformation of the solid phases as the temperature is

TABLE 1

Phases produced on heating the coprecipitated samples

Digestion time (h)	Temperature (°C)	Phases present[a]	MgO (%)	Solid solution (%)
0	470	amorphous	–	–
	680	F_{ss} + MgO	6	94
	950	T_{ss} + MgO	6	94
0.5	470	amorphous	–	–
	760	F_{ss} + MgO	5	95
	980	T_{ss} + MgO	5	95
1.5	470	amorphous	–	–
	760	F_{ss} + MgO	3	97
	900	T_{ss} + MgO	3	97

[A] F_{ss} = cubic solid solution; T_{ss} = tetragonal solid solution.

increased, as reported in refs. 3–5, is monoclinic → tetragonal → cubic. In the procedure of coprecipitation which we present in this paper the order of transformation is amorphous → cubic → tetragonal.

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