JOURNAL OF MATERIALS SCIENCE **35** (2000) 667–672

Influence of some precipitation variables on thermal behavior of ZrO_2-Y_2O_3 and ZrO_2-CeO_2 precipitated gels

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The scope of this work consisted of producing pure zirconia powders, yttria stabilized zirconia powders and ceria stabilized zirconia powders from zirconium oxychloride and yttrium and cerium chlorides using urea as precipitating agent and polyacrylic acid as dispersing agent. A factorial analysis was designed to study the effects of some precipitation variables (precipitation temperature, precipitation time, urea concentration, yttria concentration, ceria concentration and polyacrylic acid concentration) on the thermal behavior of zirconia gels using differential scanning calorimeter (DSC). It was observed that the addition of yttrium and cerium in the solution raised the crystallization temperature of the gels, due to changes on the characteristics of the Zr—OH bonds caused by the substitution of zirconium by yttrium or cerium. For the ZrO_2-Y_2O_3 system, the presence of polyacrylic acid increased the crystallization temperature. It was suggested that polyacrylic acid promoted the formation of a random polymeric structure of zirconia gels that required higher temperatures to crystallize. *© 2000 Kluwer Academic Publishers*

1. Introduction

Among advanced ceramic materials, zirconia (ZrO_2) plays an important role due to its excellent chemical resistance, refractory character, ionic conductivity and polymorphic nature [1]. The dehydration and crystallization kinetics of zirconia gels has been widely investigated particularly because the selection of an adequate thermal treatment is a fundamental step to avoid the formation of defects originated by loss of volatiles and by the subsequent crystallization.

Some researches [1–3] have been carried out to investigate associations between zirconium hydroxide structure and final zirconia powder. There are two basic zirconium hydroxide structures, which are the zirconium tetramer and a *zig-zag* zirconium chain joined by a double hydroxide bond, being one of them stable depending on the preparation route.

Most researches [2–4] concerning thermal behavior of zirconia gels investigate the effect of stabilizing oxides on endothermic and exothermic peaks. They concluded that the presence of stabilizing oxides does not affect the endothermic peak which is commonly associated to the dehydration of zirconia gels. On the other hand, exothermic peaks that are related to zirconia crystallization are considerably influenced by the presence of stabilizing oxides. Studies using several oxides, such as yttria [2], alumina [3] and calcia [4], showed that crystallization temperature increased with yttria content. According to Srinivasan et al. [2], the relaxation of polymeric structure of zirconium to the formation of crystalline phase was reduced by the presence of yttria, suggesting that the substitution of zirconium by yttrium in this polymeric structure modified the characteristics of Zr—OH bonds.

Avilla and Muccillo [5] studied the thermal behavior of zirconia gels precipitated at pH = 6, 10.4 and 13.5 from zirconium oxychloride and washed with acetone and toluene. No effect was observed of precipitation variables on the temperature of thermal effects.

2. Experimental

2.1. Precipitation experiments

Zirconia gels were prepared using zirconium oxychloride (5×10^{-2} mol dm^{-3}) as precursor and urea (2 mol dm^{-3} and 4 mol dm^{-3}) as precipitating agent. Yttria-stabilized zirconia gels (6 mol% Y_2O_3-ZrO_2) and ceria-stabilized zirconia (22 mol% CeO_2-ZrO_2) were produced using yttrium and ceria chlorides, respectively. Some experiments used polyacrylic acid (MW = 750,000, dosage = 0.5 mg/g zirconia) as dispersing agent.

Precipitation temperatures employed were 85 °C and 95 °C with an accuracy of ±1 °C. Precipitation times established were 30 min and 120 min. The pH value of all experiments were maintained between 7.5 and 8.0.

The precipitated material was exhaustively washed with distilled and deionized water followed by one stage of ethanol washing and filtration.

A detailed explanation of precipitation experiments can be found elsewhere [6].

2.2. Differential scanning calorimeter

Experimental procedure adopted for DSC tests consisted in previously heating zirconia gels at 50 °C for 12 h. For DSC tests, a Perkin-Elmer apparatus was employed and the experimental conditions consisted of an initial temperature of 30 °C and a final temperature of 650 °C with a heating rate of 10 °C min^{-1}.

2.3. Statistical design of precipitation experiments

Considering the diversity of precipitation variables (precipitation temperature, precipitation time, urea concentration, yttria concentration, ceria concentration, polyacrylic acid concentration) to be investigated, a statistical design of precipitation experiments was chosen. Basically, these experiments were blocked in two systems, ZrO_2-Y_2O_3 and ZrO_2-CeO_2, where each variable assumed a minimum and a maximum value. A matrix relating all possible combinations among these precipitation variables for the two levels examined was developed. This procedure aimed to evaluate the variables that markedly affected the crystallization temperature of zirconia gels by obtaining 5 main effects of the variables, 10 two-variable interactions, 10 three-variable interactions, 5 four-variable interactions, a five-variable interaction and the result average. These effects, interactions and average were calculated using Yate's algorithm [6], extensively adopted at factorial analysis of experiments.

The estimate of experimental standard error was determined from three replicated experiments where all variables assumed their central conditions (precipitation temperature = 90 °C, precipitation time = 75 min, urea concentration = 4 mol dm^{-3}, polyacrylic acid concentration = 0.25 mg/g zirconia, for ZrO_2-Y_2O_3 system, yttria concentration = 3 mol %; for ZrO_2-CeO_2 system, ceria concentration = 11 mol %). Therefore, it could be distinguished whether these effects and interactions were related to an experimental error or effectively influenced the crystallization temperature of zirconia gels.

The standard deviation calculated for these replicates allowed to estimate the t-Student value for the effects and interactions obtained by Yate's algorithm. At this study, the confidence level was set to 95% and the degree of freedom was 31, resulting in a critical value of

TABLE I Statistical design of experiments related to ZrO_2-Y_2O_3 system

Sample	Temperature[a] (t)	Time[b] (h)	Urea concentration[c] (u)	Yttria concentration[d] (y)	Polyacrylic acid concentration[e] (p)	Identification of the effects
1	−	−	−	−	−	average
2	+	−	−	−	−	*t*
3	−	+	−	−	−	*h*
4	+	+	−	−	−	*th*
5	−	−	+	−	−	*u*
6	+	−	+	−	−	*tu*
7	−	+	+	−	−	*hu*
8	+	+	+	−	−	*thu*
9	−	−	−	+	−	*y*
10	+	−	−	+	−	*ty*
11	−	+	−	+	−	*hy*
12	+	+	−	+	−	*thy*
13	−	−	+	+	−	*uy*
14	+	−	+	+	−	*tuy*
15	−	+	+	+	−	*huy*
16	+	+	+	+	−	*thuy*
17	−	−	−	−	+	*p*
18	+	−	−	−	+	*tp*
19	−	+	−	−	+	*hp*
20	+	+	−	−	+	*thp*
21	−	−	+	−	+	*up*
22	+	−	+	−	+	*tup*
23	−	+	+	−	+	*hup*
24	+	+	+	−	+	*thup*
25	−	−	−	+	+	*yp*
26	+	−	−	+	+	*typ*
27	−	+	−	+	+	*hyp*
28	+	+	−	+	+	*thyp*
29	−	−	+	+	+	*uyp*
30	+	−	+	+	+	*tuyp*
31	−	+	+	+	+	*huyp*
32	+	+	+	+	+	*thuyp*

[a] − = 85 °C; + = 95 °C.
[b] − = 30 min; + = 120 min.
[c] − = 2 mol dm^{-3}; + = 6 mol dm^{-3}.
[d] − = 0 mol %; + = 6 mol %.
[e] − = 0 mg/g; + = 0.5 mg/g.

TABLE II Statistical design of experiments related to ZrO_2-CEO_2 system

Sample	Temperature[a] (t)	Time[b] (h)	Urea concentration[c] (u)	Ceria concentration[d] (c)	Polyacrylic acid concentration[e] (p)	Identification of the effects
33	−	−	−	−	−	average
34	+	−	−	−	−	*t*
35	−	+	−	−	−	*h*
36	+	+	−	−	−	*th*
37	−	−	+	−	−	*u*
38	+	−	+	−	−	*tu*
39	−	+	+	−	−	*hu*
40	+	+	+	−	−	*thu*
41	−	−	−	+	−	*c*
42	+	−	−	+	−	*tc*
43	−	+	−	+	−	*hc*
44	+	+	−	+	−	*thc*
45	−	−	+	+	−	*uc*
46	+	−	+	+	−	*tuc*
47	−	+	+	+	−	*huc*
48	+	+	+	+	−	*thuc*
49	−	−	−	−	+	*p*
50	+	−	−	−	+	*tp*
51	−	+	−	−	+	*hp*
52	+	+	−	−	+	*thp*
53	−	−	+	−	+	*up*
54	+	−	+	−	+	*tup*
55	−	+	+	−	+	*hup*
56	+	+	+	−	+	*thup*
57	−	−	−	+	+	*cp*
58	+	−	−	+	+	*tcp*
59	−	+	−	+	+	*hcp*
60	+	+	−	+	+	*thcp*
61	−	−	+	+	+	*ucp*
62	+	−	+	+	+	*tucp*
63	−	+	+	+	+	*hucp*
64	+	+	+	+	+	*thucp*

[a] − = 85 °C; + = 95 °C.
[b] − = 30 min; + = 120 min.
[c] − = 2 mol dm^{-3}; + = 6 mol dm^{-3}.
[d] − = 0 mol %; + = 6 mol %.
[e] − = 0 mg/g; + = 0.5 mg/g.

t-Student distribution (t_{crit}) of 1,696 [6]. Comparing t_{crit} with t-Student values obtained for each effect and interaction investigated, their significance was evaluated.

The representation of the matrixes of both systems and their associated effects and interactions are shown in Tables I and II.

A similar procedure was adopted by Monteiro [7] for the precipitation of alumina precursor powders in the presence of polyacrylic acid.

3. Results and discussion

The results obtained for ZrO_2-Y_2O_3 system and for ZrO_2-CeO_2 system are summarized in Table III.

3.1. Zirconia-yttria system

Tests performed in a differential scanning calorimeter showed that thermograms profiles were very similar except by a shift at temperatures related to exothermic reactions. Some thermograms are presented at Fig. 1.

All samples presented a large endothermic peak between 30 and 250 °C with highest heat flow values at 90 and 150 °C associated with water loss as suggested by several authors [2–5]. On the other hand, the exothermic peak observed for all samples may be attributed to the oxide crystallization. Variations on crystallization temperatures were investigated by statistical analysis to evaluate which variables affected the crystallization behavior of zirconia gels.

Table IV presents crystallization temperatures obtained for the three replicates with precipitation variables at central conditions, whilst Table V shows the results obtained at the significance test of t-Student.

Since no variable interaction was relevant, the interpretation of individual effects of yttria concentration (factor y) and polyacrylic acid concentration (factor p) was done. For the range of concentrations studied, both an increase in the yttria concentration and in the polyacrylic acid concentration, separately, promoted a shift towards higher crystallization temperatures.

The effect of the addition of stabilizing oxides on the increase of crystallization temperature observed in this work was also verified by other researchers [2–4]. According to Srinivasan *et al.* [2], the relaxation of zirconium polymeric structure is essential for the formation of the crystalline phase. The presence of yttria reduced the kinetics of this relaxation, suggesting that the substitution of zirconium by yttrium at this polymeric structure influenced the characteristics of Zr—OH bonds.

TABLE III Crystallization temperatures obtained from statistical design of precipitation experiments for ZrO_2-Y_2O_3 system and for ZrO_2-CeO_2 system

ZrO_2-Y_2O_3 system		ZrO_2-CeO_2 system	
Sample	Crystallization temperature, (°C)	Sample	Crystallization temperature, (°C)
1	480	33	480
2	480	34	480
3	480	35	480
4	480	36	480
5	480	37	480
6	480	38	480
7	490	39	490
8	490	40	490
9	480	41	510
10	510	42	540
11	510	43	580
12	520	44	580
13	480	45	640
14	480	46	610
15	480	47	530
16	510	48	580
17	480	49	480
18	480	50	480
19	480	51	480
20	480	52	480
21	480	53	480
22	480	54	480
23	490	55	490
24	490	56	490
25	560	57	530
26	520	58	560
27	610	59	570
28	570	60	620
29	500	61	620
30	520	62	600
31	510	63	580
32	510	64	600

TABLE IV Crystallization temperature and calculated standard deviation for replicates at central conditions of the variables studied for ZrO_2-Y_2O_3 system

Replicate	Crystallization temperature
1	510
2	515
3	520
Standard deviation	5.00

TABLE V Significance test of t-Student for crystallization temperature for ZrO_2-Y_2O_3 system (confidence level = 95%)

	Crystallization temperature effects (°C)	t-Student value	Significance of the effects (confidence level = 95%)
Average	499.38		$t_{\text{crit}} = 1{,}696$
Main effects			
y	32.50	2.25	Significant
p	25.00	1.73	Significant

At the moment, concerning the synthesis of zirconia powders, the role of polyacrylic acid has been considered in terms of its feasibility as a dispersing agent. Therefore, no investigation appraised the effect of polymers used at precipitation process on the thermal behavior of these powders. It is suggested that polyacrylic acid interfered on the organization of zirconium polymer in a tridimensional fluorite-type structure for ZrO_2-Y_2O_3 system, resulting in a higher temperature for the crystallization process. Reactions between polyacrylate ions ($RCOO^-$), produced by polyacrylic acid dissociation, and available sites for polymerization reactions of zirconium tetramers may be the mechanism responsible for the greater randomness of the polymeric structures produced.

TABLE VI Crystallization temperature and calculated standard deviation for replicates at central conditions of the variables studied for ZrO_2-CeO_2 system

Replicate	Crystallization temperature
1	570
2	570
3	560
Standard deviation	5.77

TABLE VII Significance test of t-Student for crystallization temperature for ZrO_2-CeO_2 system (confidence level = 95%)

	Crystallization temperature effects (°C)	t-Student value	Significance of the effects (confidence level = 95%)
Average	529.69		$t_{\text{crit}} = 1{,}696$
Main effects			
y	96.88	5.03	Significant

A similar statistical analysis was performed to investigate the influence of the studied variables and their interactions on the enthalpy of crystallization. The results indicated that the enthalpy of crystallization was not affected by the variables within the selected range.

All zirconia powders produced had essentially tetragonal-monoclinic structures and the volumetric fraction of tetragonal phase essentially depended on the interaction of time-urea concentration-polyacrylic acid concentration (*hup* factor) and on the yttria concentration (factor y) [6].

3.2. Zirconia-ceria system

Analogous to the ZrO_2-Y_2O_3 system, the ZrO_2-CeO_2 system presented similar thermograms for all samples, apart from the observed shift of temperatures associated to exothermic reactions. Typical thermograms of the ZrO_2-CeO_2 system are shown at Fig. 2.

Concerning the endothermic reactions, they were detected between 30 and 250 °C with maximum peaks at 90 and 150 °C related to the evaporation of residual water.

The exothermic peaks were attributed to zirconia crystallization. However, the identification of the precipitation variables that affected the crystallization temperature was only possible by the statistical analysis. Table VI shows the crystallization temperatures obtained at the three replicates of precipitation experiments using the variables investigated at their central conditions.

Table VII presents the statistical results of t-Student significance test for crystallization temperature.

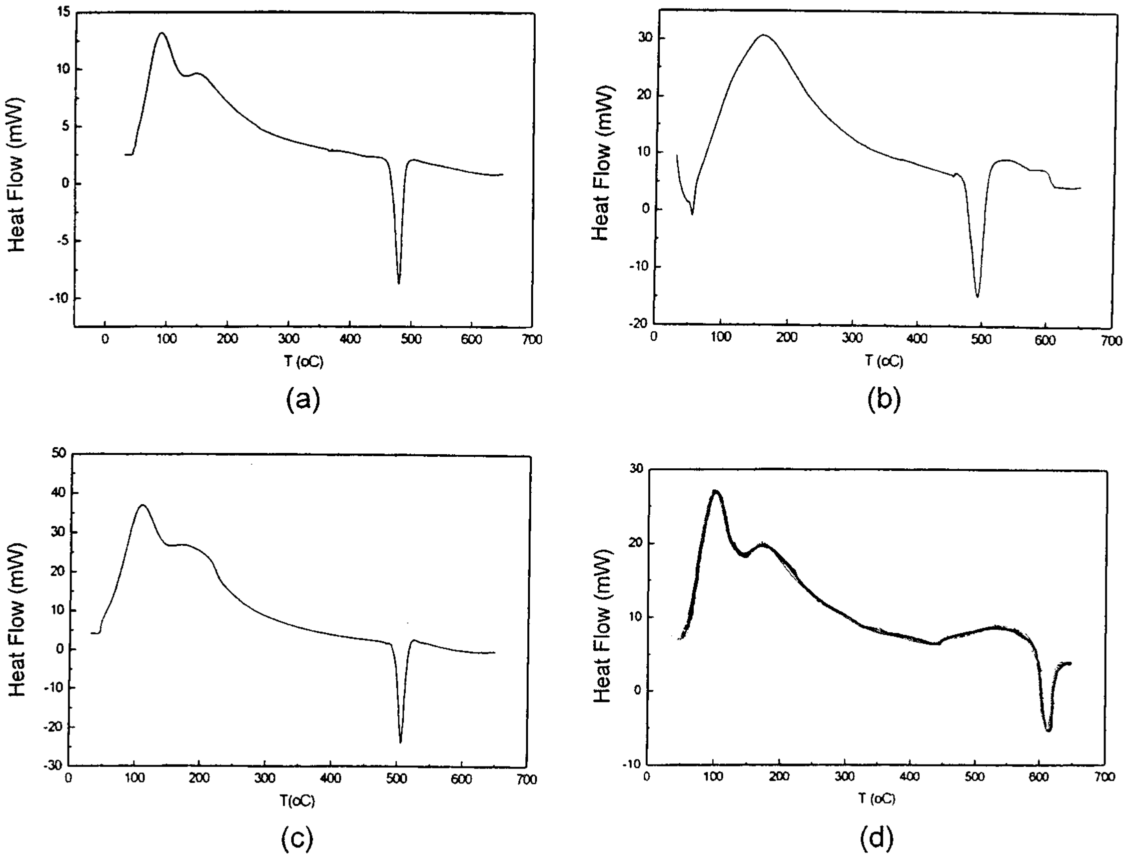

Figure 1 DSC curves for ZrO_2-Y_2O_3 system (precipitation temperature = 85 °C, precipitation time = 120 min, urea concentration = 2 mol dm^{-3}): (a) yttria concentration = 0 mol %; polyacrylic acid concentration = 0 mg/g ZrO_2; (b) yttria concentration = 0 mol %; polyacrylic acid concentration = 0.5 mg/g ZrO_2; (c) yttria concentration = 6 mol %; polyacrylic acid concentration = 0 mg/g ZrO_2; (d) yttria concentration = 6 mol %; polyacrylic acid concentration = 0.5 mg/g ZrO_2.

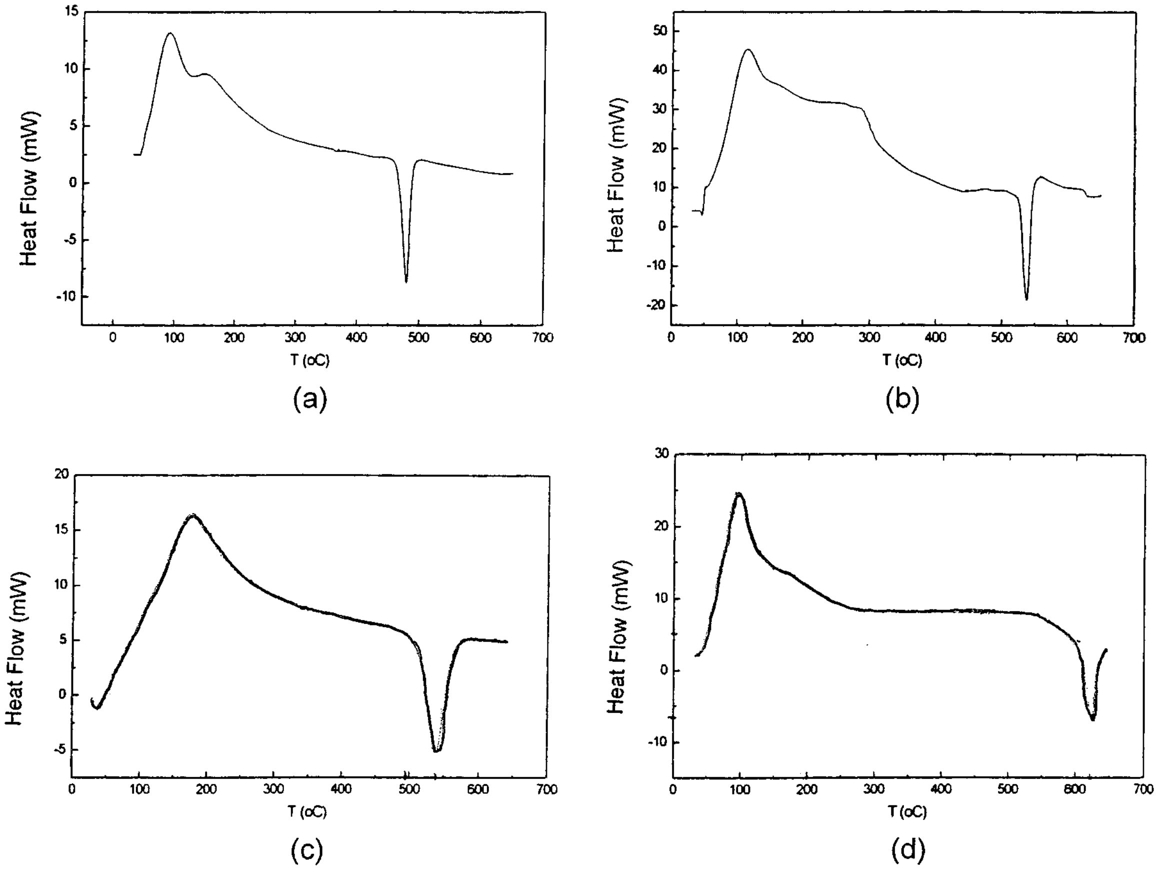

Figure 2 DSC curves for ZrO_2-CeO_2 system (precipitation temperature = 95 °C, precipitation time = 30 min, urea concentration = 2 mol dm^{-3}): (a) ceria concentration = 0 mol %; polyacrylic acid concentration = 0 mg/g ZrO_2; (b) ceria concentration = 0 mol %; polyacrylic acid concentration = 0.5 mg/g ZrO_2; (c) ceria concentration = 22 mol %; polyacrylic acid concentration = 0 mg/g ZrO_2; (d) ceria concentration = 22 mol %; polyacrylic acid concentration = 0.5 mg/g ZrO_2.

Ceria concentration was the unique significant variable, reinforcing that, as observed with other stabilizing oxides, the presence of ceria at the crystalline structure promoted an increase in crystallization temperature. This behavior indicated that the characteristics of Zr─OH bonds were markedly affected by the substitution of zirconium by cerium at polymer structure, provoking a reduction on the kinetics of crystalline transformation.

It is important to remark that for the ZrO_2-CeO_2 system, the presence of polyacrylic acid at the concentration studied did not affect the crystallization temperature.

For zirconia-ceria system, no significant effect on the enthalpy of crystallization was noted for the investigated variables.

The powder structure obtained was tetragonal-monoclinic for all samples and the fraction of tetragonal phase was dependent on time (factor h) and polyacrylic acid concentration (factor p) detailed discussion on zirconia powder structures can be found elsewhere [6].

4. Conclusions

- Additions of yttrium or cerium to the solution elevated the crystallization temperature of zirconia gels due to alterations on the nature of Zr─OH bonds produced by the substitution of zirconium by yttrium or cerium at the polymeric structure.
- For zirconia-yttria systems, the presence of polyacrylic acid raised the crystallization temperature of zirconia gels, indicating that reactions between polyacrylate ions ($RCOO^-$) and some available sites at zirconium tetramers for polymerization reactions might be the mechanism responsible for a higher randomness of the polymeric structures produced. A random polymeric structure would correspond to higher temperatures for the crystallization reaction.
- No effect of polyacrylic acid additions was observed for zirconia-ceria system at the experimental conditions studied.

Acknowledgements

The authors gratefully acknowledge CAPES for financial assistance, Prof. Roberto Avillez and Prof. Helio Kohler for helpful discussions during the course of this study.

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Received 30 July 1998
and accepted 22 July 1999