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Synthesis and sintering properties of cerium oxide powders prepared from oxalate precursors

J. M. HEINTZ, J. C. BERNIER
Département Science des Materiaux, ENSCS, UA 440 du CNRS, 1 Rue Blaise Pascal, 67008 Strasbourg Cedex, France

Fine cerium oxide powders obtained by low-temperature decomposition from oxalate and hydrazinate oxalate are compared. Studies of thermal behaviour and disagglomerating capability are given. The preparation of oxide powders by chemical and physical methods is able to give a dispersed suspension, and leads with appropriate recovery to increased green density and final density after sintering.

1. Introduction

It is now well established that an easily sinterable ceramic powder may be composed of regular, fine grains with a narrow size distribution. The state of agglomeration is another parameter which must be controlled in order to obtain good green densities. Barringer and Bowen [1], in the case of TiO_2, have described some methods for preparing monodisperse powders (use of pure reagents and proper concentration of products). The role of pH has been emphasized by Yan and Rhodes [2] in order to obtain dispersed suspensions.

A good way to improve densities could be the synthesis of new precursors that give fine powders and possess disagglomeration properties. The field of fine powder ceramics of rare earth oxides is not still very extensive; we can mention the results reported by Mehrotra and co-workers [3, 4] from rare earth alkoxides, and the application to ceramics by Mazdiyasni [5]. However, the conditions are not easy to realize and very expensive.

Recent work has suggested the importance of hydrazine complexes in the formation of spinel ferrites, by considerably reducing the calcination temperature [6–8]. During the decomposition, hydrazine acts as a fuel. The same principal could be used to obtain ceramic rare-earth oxides at very low temperatures.

The present work reports the synthesis and the properties of a new precursor of CeO_2, and a method of dispersion and packing that increases the sintered density.

2. Experimental procedure

The precursor hydrazinate oxalate of cerium was prepared from hydrazine hydrate, $N_2H_4 \cdot H_2O$, and cerium oxalate, $Ce(C_2O_4)_3 \cdot H_2O$. Two different methods were investigated.

At first, according to Krylov *et al.* [9], the preparation was carried out in a closed dessicator; N_2H_4 was placed on the bottom of the desiccator and the cerium oxalate was put in a petri dish. The desiccator was evacuated every 2 to 3 days to remove the products of dissociation or oxidation. The hydrazinate oxalate of cerium is theoretically formed within 40 days with 4 molecules of hydrazine. We observed, during this time, an increase from the starting mass but we did not notice any change in the X-ray pattern, which was always that of cerium oxalate. Consequently we have no longer worked in this way.

As an alternative, the synthesis of hydrazinate oxalate of cerium was carried out in air (in fact our product underwent partial carbonation during the reaction) by mixing cerium oxalate and hydrazine hydrate. We added an excess of hydrazine with regard to oxalate, based on a final composition with four N_2H_4 molecules and two cerium atoms. The solution was carefully mixed for 6 h, filtered and then dried during one day in a desiccator. This stage is the most delicate: a violent drying starts up the decomposition of the product by "burning" the NH_2NH_2 molecules. We observed finally a whiteish powder.

Physical and thermodynamical properties of the precursors were measured. Assessments of particle size was obtained from X-ray line broadening and transmission electron microscopy (TEM). The chemical formula of the compound was given by chemical microanalysis for carbon, hydrogen and nitrogen. Thermogravimetric analysis (TGA) studies were made on Ugine–Eyraud (Setaram, Lyon, France) balance in air; differential thermal analysis (DTA) measurements were also carried out in air with a Thermanalyse instrument, using a heating rate of $2^\circ C\,min^{-1}$. Infrared spectra were recorded with a Beckman IR10, using a KBr matrix. Sintering studies were performed with a dilatometer (Adamel Lhomargy DI24, Paris). Oxide powders were mixed with methyl cellulose as binder, compacted at $7\,tonne\,cm^{-2}$ and then dried overnight at 100° C. The samples were sintered in air at a heating rate of $7^\circ C\,min^{-1}$ and a step at 550 to 600° C in order to eliminate the binder; the final temperature was kept at 1440° C for 10 min. After cooling

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TABLE I X-ray powder diffraction data for the two precursors

Cerium oxalate		Cerium hydrazinate oxalate	
d_{hkl} (nm)	I*	d_{hkl} (nm)	I
		0.9111	vl
		0.8485	s
		0.70860	vl
0.6731	l	0.6845	l
0.6602	l	0.6513	m
0.6349	m2	0.6347	vl
0.5526	s2	0.5812	l
0.5377	s1	0.5337	m
0.4909	m3	0.4346	vl
0.4836	m1	0.4297	vl
0.4729	vl		
0.4288	s3		
0.3454	vl		

*s = strong, m = medium, l = low, vl = very low.

TABLE II Infrared spectra data of cerium hydrazinate oxalate in the range of N–N and NH_2 vibrations

Wave number (cm^{-1})	Assignment
1280	NH_2 wagging
1170	NH_2 twisting
1100 1080	NH_2 twisting
960 930	ν(N–N)

to room temperature, the pellets were weighed and measured for density. A second value of density was given by the water displacement method.

3. Results and discussion

3.1. Synthesis and thermodynamic behaviour

Process control of the hydrazinate precursor of cerium was followed by X-ray and IR measurements.

The X-ray pattern gives one particularly strong line for d = 0.8485 nm (Table I). The IR spectrum shows distinctly the band due to N–N and NH_2 vibrations (Table II and Fig. 1) between 900 and 1200 cm^{-1}.

The results of chemical analysis for carbon, nitrogen and hydrogen are given in Table III, and we can deduce from it the formula type of a precursor by taking account of carbonation during the reaction time; we obtained

$$Ce_2(C_2O_4)_3(N_2H_4)_3(H_2O)_{11/2}(CO_2)_{3/4}$$

This product was then submitted to TGA and DTA analysis. In Fig. 2 we notice an initial loss of weight, more rapid for the hydrazinate oxalate of cerium, but between 40 and 200° C it was not possible to attribute the steps to the loss of hydrazine or water. Oxalate decomposition is observed towards 260° C, and CeO_2 could be obtained from 300° C. In fact the thermal behaviours of oxalate and hydrazinate oxalate seem to be very similar; this is expected since the addition of hydrazine does not strongly modify the molecular structure.

Thermal effects are more interesting: the presence of hydrazine (Fig. 3) is revealed by a large exothermic peak near 100° C, in contrast with oxalate decomposition that gives only endothermic effects before oxalate decomposition (Fig. 4). Measurements of energy dissipation were made (Table IV). In order to use the exothermic property of our precursor we tried isothermal decomposition at 200° C from 5 h. The product we obtained had CeO_2 characteristics (Xr halo) but the loss of weight indicated that calcination was incomplete. The exothermic effect resulting from the decomposition of hydrazine is not sufficient to obtain crystallized CeO_2 at very low temperatures.

TABLE III Chemical data for cerium hydrazinate oxalate

Composition (%)		
Carbon	Nitrogen	Hydrogen
10.54	3.05	11.39

TABLE IV Comparative data for heat of decomposition of the two precursors

Sample	T (° C)		
	115	190	290
Cerium oxalate		Endothermic, $-85\,J\,g^{-1}$	Exothermic, $+967\,J\,g^{-1}$
Cerium hydrazinate oxalate	Exothermic, $+318\,J\,g^{-1}$		Exothermic, $+1065\,J\,g^{-1}$

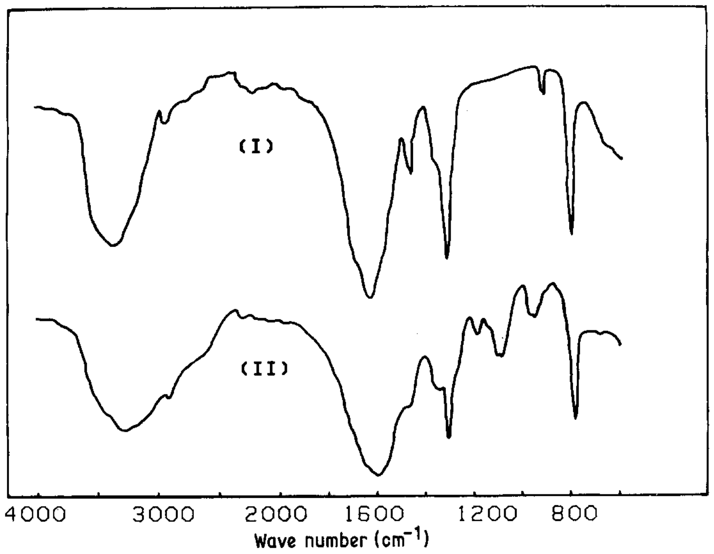

Figure 1 Infrared spectra of the two precursors: (I) cerium oxalate, (II) cerium hydrazinate oxalate.

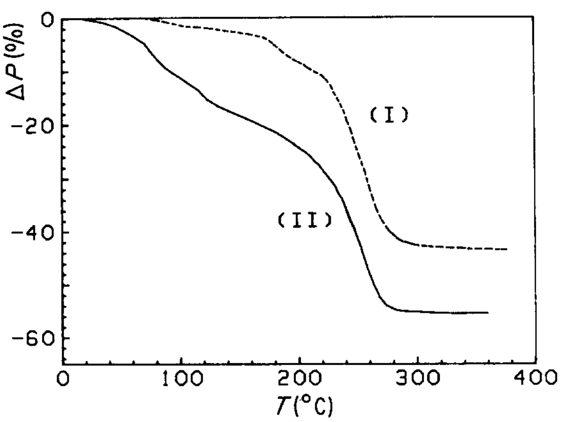

Figure 2 Thermogravimetric analysis of the two precursors: (I) cerium oxalate, (II) cerium hydrazinate oxalate.

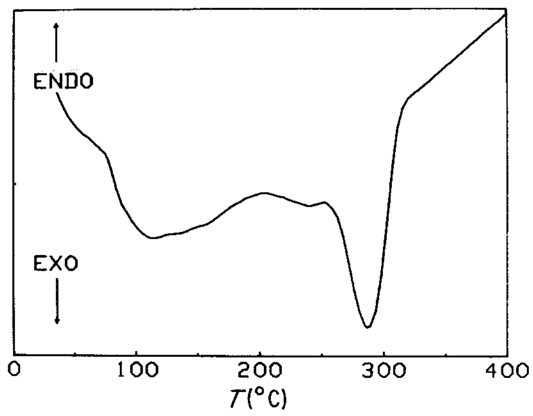

Figure 3 Differential scanning calorimetry of cerium hydrazinate oxalate.

3.2. Analysis of CeO$_2$

This point of our study was concerned with cerium oxide obtained after calcination of oxalate(I) or hydrazinate oxalate(II). The final temperature was 375° C with a heating rate of 80° C h^{-1}. We obtained CeO$_2$, although a long-range ordered structure was not truly proved. Grain-size determination by X-ray techniques gave respectively 6.4 and 6.0 nm for (I) and (II). TEM observations led to the same result; this was expected, as the TGA experiment proved that the decomposition scheme was similar for the two precursors. However, the powder seemed more disagglomerated for (II) and we can see there the influence of hydrazine.

Disagglomeration experiments were then carried out on these powders to focus on this point. Sedimentation measurements were performed in aqueous solutions at different pH values after ultrasonic treatment for half an hour. The results are given in Table V. As deduced from TEM, we notice that (II) gives a more disagglomerated powder in all cases. The interest in our precursor is revealed here, and its disagglomeration facility could be used for ceramic applications.

3.3. Sintering studies

This work was carried out with CeO$_2$ powders obtained from (I) and (II). Some samples were dispersed in aqueous solutions (pH 5 and 2) under ultrasonic stirring for 30 min. The powders were recovered by centrifugal settling (3000 r.p.m. for 30 min) and dried for 15 h at 95 to 100° C. The results are presented in Table VI and the linear shrinkage curves in Figs. 5 to 8.

The influence of hydrazinate precursor could be seen both on the green density (+ 2%) and the sintered density (+ 1.5%). For ultrasonicated powders two important points must be underlined:

(i) As emphasized before (Table V), and according to Yan and Rhodes [2], the pH of the solution is very important: for pH 5 the compact sinters poorly and

TABLE V Sedimentation data for samples (I) and (II) against pH

Sedimentation time (min)	*h* (cm)*					
	CeO$_2$ ex-oxalate			CeO$_2$ ex-hydrazinate oxalate		
	pH 1.95	pH 2.82	pH 8.5	pH 1.87	pH 2.8	pH 6.7
10		0.1	0.5			0.4
30	0.5	0.5	Translucent	0.2	0.2	1.0
60	0.7	0.7	Clear solution	0.4	0.4	Translucent
180	1.0	1.0	Clear solution	0.5	0.5	Clear solution

**h* = height of clear solution in the test tube (12 cm) after sedimentation.

TABLE VI Results of density measurements in different dispersion media

Sample*	Temperature (° C)	Green density†	Sintered density (% theoretical)		Remarks
			Measured	Water displacement	
ex-CeOx	550	53.25	87.2	89.8	Powder dispersed in acid medium (pH 2) but CH$_3$COOH $\xrightarrow{\Delta}$ CO$_2$; pores present
ex-CeHyOx	550	56.6	76.1	80.3	
ex-CeOx	400	48.9	87.4	89.6	Powder dispersed in aqueous medium (pH 5); agglomeration occurred
ex-CeHyOx	400	50.9	88.4	91.9	
		49.5	86.9	89.4	
		51.8	94.5	97.8	Powder dispersed in chloride solution (pH 2)

*Theoretical density of CeO$_2$ = d_{th} = 7.13 g cm^{-3}.
†ex-CeOx = cerium oxalate; ex-CeHyOx = cerium hydrazinate oxalate.

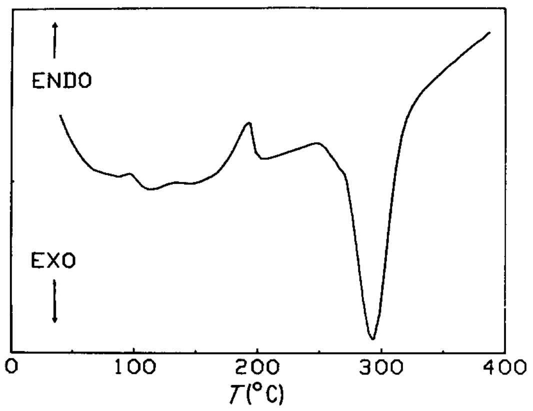

Figure 4 Differential scanning calorimetry of cerium oxalate.

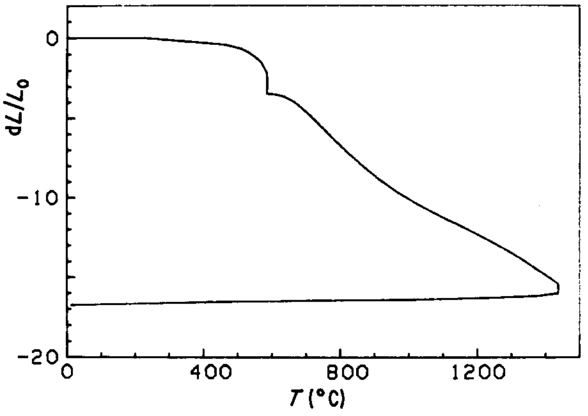

Figure 6 Linear shrinkage against temperature of CeO_2 ex-hydrazinate oxalate.

the powder re-agglomerates despite the ultrasonic action.

(ii) The choice of the acid is important. The decomposition of CH_3COOH gives CO_2, which produces pores in the early stage of sintering and reduces the final density.

Conversely for pH 2, in chloride solution, the powder stays in suspension and the recovery by centrifugation gives a good packing of the grains; there is an increase of green density of 1%, i.e. 3% more than the ex-oxalate sample.

The most interesting result is observed for the final density of the powder (II) dispersed in acid solution (HCl): + 8% compared to (I). This improvement does not result from a grain size selection but only from disagglomeration in the appropriate medium, and centrifugation recovery that certainly pre-packed the powder before pressing. In this way, cerium oxide compacts of density exceeding 95% of theoretical density are obtained by dynamic sintering at 1430° C.

The shrinkage behaviour of (I) (Fig. 5) is classical with an inflection after 500° C. In Fig. 6, the beginning of shrinkage takes place early but the kinetics are less rapid than for (I) and the sintering is not ended at 1440° C.

In Figs. 7 and 8 we show curves for ultrasonicated powders, and their behaviour is quite different from that of previous samples. Sintering occurred in two steps, the first at about 450° C and the second after 1100° C with fast kinetics. In both cases sintering is ended at 1400° C. Cerium oxide dispersed in an aqueous medium (pH 5, Fig. 7) follows the same shrinkage law (hydrazinate oxalate precursor characteristic) as the one in Fig. 6 up to 1100° C. The influence of disagglomeration can be observed after this temperature, but the pH of the medium prevents a real disagglomeration and inter-aggregate pores can not be eliminated, which explains why the sintering ends with a poor final density. In the case of powder dispersed in chloride solution (Fig. 8) sintering occurs completely in a few degrees between 1100 and 1400° C, proving that disagglomeration is effective.

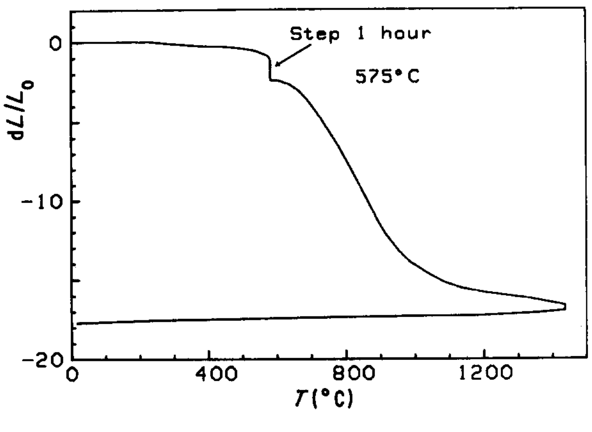

Figure 5 Linear shrinkage against temperature of CeO_2 ex-oxalate.

4. Conclusion

Physical and chemical characteristics of the precursor play a large role in the sintering capability of ceramic oxide powders. Two precursors of cerium oxide which appear very close from the structural point of view – same base product and same law of thermal decomposition – present different DTA curves, and this behaviour implies a better disagglomeration of the oxide obtained after calcination of hydrazinate. Improvement of the final density of a ceramic can be achieved by looking at sintering parameters such as pressure, temperature and time, but also at the preparation of the powder before compaction. Consideration of the disagglomeration capability of the powder, the choice of the dispersion medium, and the centrifugation recovery, lead to a real improvement in

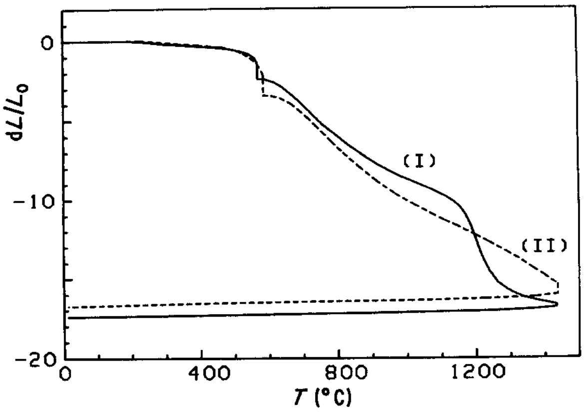

Figure 7 Linear shrinkage against temperature: (I) CeO_2 ex-oxalate dispersed in aqueous medium (pH 5), (II) CeO_2 ex-hydrazinate oxalate.

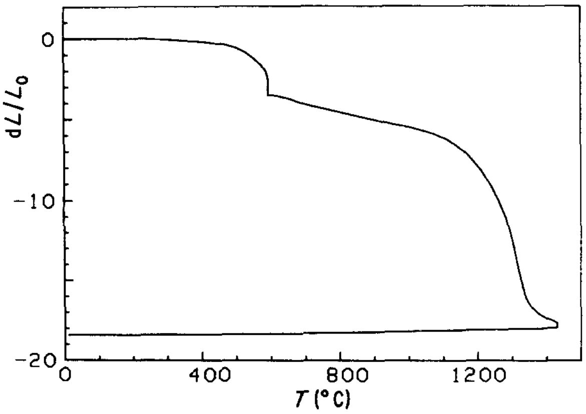

Figure 8 Linear shrinkage against temperature of CeO_2 ex-hydrazinate oxalate dispersed in chloride solution (pH 2).

sintering: + 8% for CeO_2 prepared from hydrazinate oxalate compared to oxalate alone.

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