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SYNTHESIS AND SINTERING PROPERTIES OF CERIUM OXIDE POWDERS PREPARED FROM OXALATE PRECURSORS

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RESUME - Des poudres fines d'oxyde de cérium obtenues par décomposition à basse température d'oxalate et d'hydrazinate oxalate sont comparées. On examine la dégradation thermique de ces composés ainsi que leurs aptitudes à la désagglomération. L'utilisation de ces propriétés, associée à un précompactage de la poudre par centrifugation conduit à une amélioration importante des densités en cru et des échantillons frittés.

ABSTRACT - Fine cerium oxide powders obtained by low temperature decomposition from oxalate and hydrazinate-oxalate are compared. Studies of thermal behaviour, desagglomeration ability are given. The preparation of oxide powders by chemical and physical methods is able to give disperse solution and leads with appropriate recovering to increased green density and final density after sintering.

1/ INTRODUCTION

It is now well established that an easily sinterable ceramic powder must be composed of regular, fine grains with a narrow size distribution. The degree of agglomeration is another parameter which must be controlled in order to obtain good green densities. For example the role of pH has been emphasized by YAN and RHODES (1) in order to obtain good dispersion.

So, a good way to improve densities could be the synthesis of new precursors that give fine powders and present desagglomeration properties. The field of fine powder ceramics of rare earth oxides is not still very extended; we can mention the results reported by MEHROTRA and coworkers (2-3) about rare earth alkoxides and their use in ceramics by MAZDIYASNI (4). However, the experiments are not easy to realize and actually expensive.

Recent work has suggested the importance of hydrazine complexes for the formation of spinel ferrites, with considerably reduced calcination temperature (5-7). During the decomposition, hydrazine acts as a fuel. The same principle could be used for the obtention of rare-earth oxides ceramics at low temperature.

The present work reports the synthesis and the properties of a new CeO₂ precursor and the dispersion and packing way that increases the density of sintered samples.

2/ EXPERIMENTAL PROCEDURE

The cerium hydrazinate oxalate precursor was prepared from hydrazine hydrate (N₂H₄·H₂O) and cerium oxalate (Ce₂(C₂O₄)₃·H₂O).

The synthesis of cerium hydrazinate oxalate was carried out in air (in fact our product undergoes partial carbonatation during the reaction) by mixing cerium oxalate and hydrazine hydrate. An excess of hydrazine was added in order to

get a molar ratio $N_2H_4:Ce$ of 4:2. The suspension was carefully mixed for 6 hours, filtered and then dried during one day in a dessicator. This stage is the most delicate : a too violent drying starts up the decomposition of the product by "burning" the NH_2NH_2 molecules. A whitish powder was finally obtained.

Physical and thermodynamical properties of the precursors have been investigated. Assessments of particle size were obtained from X-rays lines broadening and Transmission Electron Microscopy. T.G.A. studies were made in an Uguine-Eyraud balance in air; D.T.A. measurements were also carried out in air with a Thermanalyse instrument using an heating rate of $2^\circ/mn$. Infrared spectra were recorded with a Beckman IR 10, using a KBr matrix. Sintering studies were performed with an Adamel Lhomargy DI24 dilatometer. Oxide powders were mixed with methyl cellulose as a binder, compacted at $7 T/cm^2$ and then dried for the night at $100^\circ C$. The samples were sintered in air, with an heating rate of $7^\circ/mn$ and a step was observed at $550-600^\circ C$ in order to eliminate the binder; the final temperature was kept during 10mn at $1440^\circ C$. After cooling to room temperature, the pellets were weighted and measured for density. Density has been independently determined by the water displacement method.

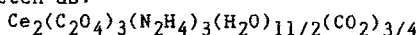
3/ RESULTS AND DISCUSSION

3.1/Synthesis and thermodynamic behaviour

The achievement of a cerium hydrazinate precursor was controlled both by X-rays and IR measurements.

The X-rays pattern gives one more strong line for $d=0.8485 nm$. The IR spectrum shows distinctly the N-N and NH_2 vibration absorption bands (Fig 1) between 900 and $1200 cm^{-1}$.

The chemical formula of our precursor was deduced from microanalysis on C, N and H; it can be written as:



T.G.A. and D.T.A. have then been performed on this product. On figure 2, one observes an initial loss of weight more rapid for the cerium hydrazinate oxalate compared to oxalate, but between 40 and $200^\circ C$ it was not possible to relate the successive steps to the nature of the volatil species (hydrazine or/and water). Oxalate decomposition is observed near $260^\circ C$ and CeO_2 could be obtained beyond $300^\circ C$. In fact the thermal behaviour of oxalate and hydrazinate oxalate seems to be very close; this is expected since the addition of hydrazine does not strongly modify the molecule structure

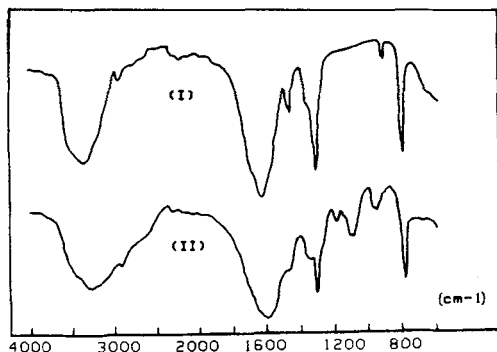


Fig 1 : Infrared spectra

(I) Ce Oxalate ; (II) Ce Hydrazinate Oxalate

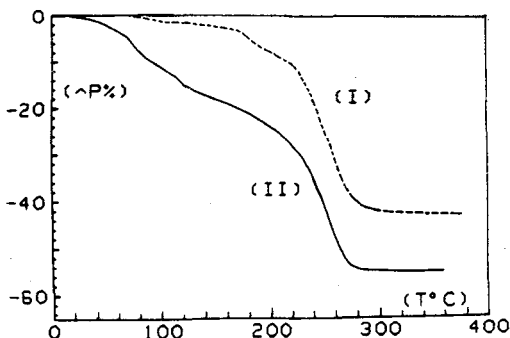


Fig 2 : Thermogravimetric analysis

D.T.A. effects are more interesting: the presence of hydrazine (Fig 4) is accompanied by a large exothermic peak near $100^\circ C$ whereas oxalate decomposition presents only endothermic effects before oxalate decomposition (Fig 3). In order to use exothermic properties of our precursor we tried isothermic decomposition at

200°C during 5 hours. The obtained product had CeO₂ characteristics (X-rays halo) but the weight loss indicated that the calcination was incomplete. The exothermic effect resulting from the decomposition of hydrazine is not sufficient to obtain crystallized CeO₂ at low temperature.

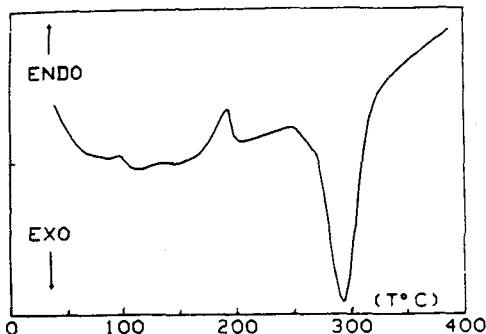


Fig 3 : DTA of Ce Oxalate

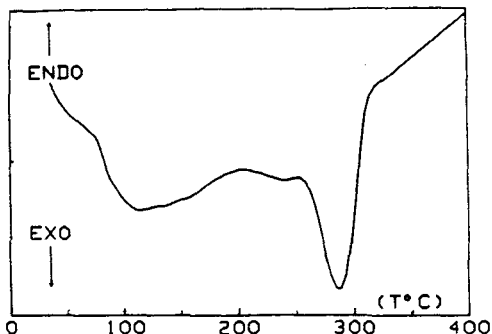


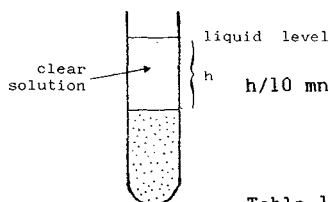
Fig 4 : DTA of Ce Hydrazinate Oxalate

3.2/CeO₂ Analysis

This point of our study was turning on cerium oxide obtained after calcination of oxalate(I) or hydrazinate oxalate(II). The final temperature was 375°C with an heating rate of 80°C/hour . CeO₂ was obtained although the long distance structure was not truly proved. Grain size determination by X-rays techniques gives us 6,4 and 6,0 nm for (I) and (II) respectively. The microscopy (TEM) observation leads to the same result ; it is expected as TGA experiments prove that the decomposition scheme is similar for the two precursors. However, the powder seems more desagglomerated for (II) and this can be related to the influence of hydrazine.

Desagglomeration attempts were then realized on these powders . Sedimentation measurements were realized in aqueous solutions at different pH, after ultrasoning treatment during half an hour. The results are given in table 1. As deduced by TEM, sample (II) gives a better desagglomerated powder in all cases. The interest of our precursor is revealed here and its desagglomeration ability could be used for ceramic application.

sample	CeO ₂	ex Oxalate		CeO ₂	ex hydrazinate-Oxalate	
pH (of the suspension)	1,95	2,82	8,5	1,87	2,8	6,7
h/10mn		0,1 cm	0,5 cm			0,4 cm
h/30mn	0,5 cm	0,5 cm	Translucent	0,2 cm	0,2 cm	1 cm
h/1 h	0,7 cm	0,7 cm	clear solution	0,4 cm	0,4 cm	Translucent
h/3 h	1 cm	1 cm	clear solution	0,5 cm	0,5 cm	clear solution



h/10 mn = height of clear solution in the test tube (12 cm) after 10 mn

Table 1 : Sedimentation data of sample (I) and (II) vs pH

3.3/Sintering study

This work has been carried out with CeO_2 powders, issued from (I) and (II). Some samples were dispersed in aqueous solutions (pH 5 and 2) under ultrasonic stirring during 30 mn. The powders were recovered by centrifugal settling (3000 tr/mn during 30 mn) and dried for 15 hours at 95-100°C.

Sample	green (% d_{th}) density	sintered density (% d_{th}):		Remarks	
		geometric measurement	water displacement		
ex CeOx	550°C	53.25	87.2	89.8	{ Powder dispersed in acetic acid medium (pH=2)
ex CeHyOx	550°C	56.6	76.1	80.3	
ex CeOx	400°C	48.9	87.4	89.6	Powder dispersed in aqueous medium (pH=5) agglomeration:
ex CeHyOx	400°C	50.9	88.4	91.9	
"		49.5	86.9	89.4	
"		51.8	94.5	97.8	Powder dispersed in hydrochloric acid medium (pH=2)

Table 2 : Density measurements vs dispersion medium ; all results are given in percentage of theoretical density of CeO_2 ($d_{th}=7.13 \text{ g/cm}^3$)
 ex CeOx = Ce Oxalate ex CeHyOx = Ce Hydrazinate Oxalate

The influence of hydrazinate precursor can be noticed both on green density (+2%) and sintered density (+1.5%) (Table 2). For "ultrasonned powders" two important points must be underlined:

i) As before emphasized (table 1), and according to YAN (1), the pH of the solution is very important: for pH=5 the compact sinters poorly; the powder re-agglomerate despite the ultrason action.

ii) The choice of the acid is not indifferent. as illustrated by the poor densification for powders dispersed in acetic acid. The linear shrinkage curve for this sample shows the inhibition of the final stage of densification.

Conversely for pH=2, in hydrochloric solution, the powder stays in suspension and the centrifugation recovering gives a good stacking of the grains accompanied by an increase of green density of one per cent, i.e 3% more than ex-oxalate.

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

The shrinkage behaviour of ex-Oxalate sample (Fig 5) is classical with an inflexion after 500 °C. In Fig 6, we observe ex-hydrazinate oxalate oxides. We notice for (I) that the kinetics of shrinkage is slower than in Fig 5 and the sintering is not complete at 1440°C.

Samples (II) and (III) which are "ultrasonned powder" exhibit quite a different behavior. Sintering occurred in two steps, first about 450°C and second one after 1100°C with fast kinetics. In both cases sintering is ended at 1400°C. Cerium oxide dispersed in aqueous medium (II-pH=5) follows the same shrinkage law (hydrazinate oxalate precursor characteristic) as (I) up to 1100°C. Desagglomeration influence can be observed after this temperature but the pH medium prevents a real desagglomeration and inter-aggregate pores cannot be eliminated explaining the poor final density of the sintering process. In the case

of powder dispersed in hydrochloric solution (III) sintering completely occurs in a few degrees between 1100 and 1400°C suggesting desagglomeration is effective.

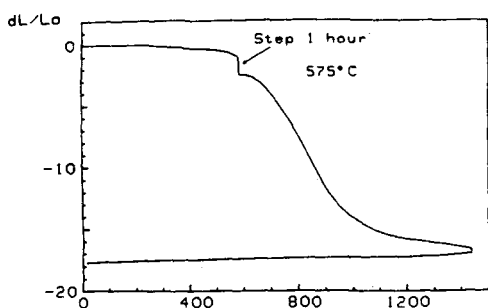


Fig 5 : Linear shrinkage vs temperature of CeO_2 ex Oxalate

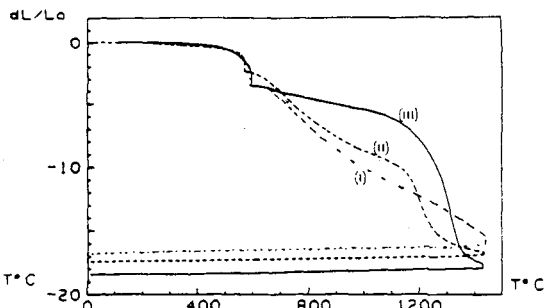


Fig 6 : Linear shrinkage vs temperature of ex Hydrazinate Oxalate

(I) : Non dispersed Oxide ; (II) : Oxide dispersed at pH=5 and (III) at pH=2

4/ CONCLUSION

Physical and chemical characteristics of precursors play a large main role in sintering ability of ceramic oxide powders. Two precursors of cerium oxide which appear very close from a structural point of view - same base product and same thermal behavior law - present different D.T.A. curves involving a better desagglomeration of the oxide obtained after calcination of hydrazinate. Improvement of the final density of ceramics can be done by varying sintering parameters such as pressure, temperature and time, but also preparation of the powder before pressing ; consideration of powder desagglomeration ability, choice of the dispersion medium, and centrifugation recovering, lead to a real improvement of sintering : +8 % for CeO_2 issued from hydrazinate-oxalate compared to ex-oxalate.

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