Journal of Thermal Analysis, Vol. 37 (1991) 907–913

THERMAL DECOMPOSITION OF CERIUM OXALATE AND MIXED CERIUM-GADOLINIUM OXALATES

S. El-Houte and M. El-Sayed Ali

METALLURGY DEPT., N. R. C., A. E. A., CAIRO, EGYPT

(Received September 14, 1987; in revised form July 20, 1990)

Cerium oxalate and mixed cerium-gadolinium oxalates containing 20 and 50 mol% gadolinium were subjected to thermal decomposition. Thermal analysis showed that cerous oxalate is transformed to cerium oxide in two steps. The first step involves the endothermic removal of 10 mol of water, with a calculated activation energy of 78.2 kJ/mol. The second step involves the exothermic decomposition of the anhydrous oxalate, with an activation energy of 112.6 kJ/mol. The water content in the mixed cerium-gadolinium oxalates decreases with increasing gadolinium content, while the temperature of exothermic decomposition of the anhydrous oxalate increases with it.

Cerium oxide doped with different rate earths, such as yttria [1, 2] and gadolinia [3, 4], exhibits high ionic conductivity. The oxide doped with gadolinia has an even higher ionic conductivity than calcia-doped zirconia [3]. This has drawn attention to the use of these materials as solid electrolytes in oxygen sensors and for energy production in fuel cells, especially at relatively low temperatures.

These mixed oxides could be obtained directly by mechanically mixing the required amounts of oxides, pressing and sintering. However, this simple technique involves the risk of the production of a heterogeneous material [2]. This makes the use of chemical mixing (by a coprecipitation technique) necessary for producing homogeneous materials with uniform composition.

The coprecipitation is performed by adding the mixed salt solution to a solution of ammonia [5], urea [6] or ammonium carbonate [7]. In this work, the coprecipitation was carried out by adding the mixed salt solution (nitrates) to ammonium oxalate solution. The thermal decomposition of the precipitated oxalates was studied.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Preparation of oxalates

1 Cerium oxalate

Cerous nitrate hexahydrate (Rhône-Poulenc Chimie Fine, Paris) was dissolved in distilled water. The cerium oxalate was precipitated by dropping the nitrate solution into a 20% excess ammonium oxalate solution, while stirring vigorously. The pH was controlled between 6 and 7 during the precipitation by the addition of ammonium hydroxide. The precipitate was then filtered off, washed sevcral times with distilled water and dried at room temperature for several days.

2 Mixed cerium–gadolinium oxalates

The calculated ammounts of gadolinium oxide (Rhône–Poulenc Chimie Fine, Paris) needed to prepare the different mixed oxalate compositions were weighed and dissolved in dilute nitric acid. The gadolinium nitrate solutions were then mixed with cerium nitrate solution, and the coprecipitation was carried out under the same conditions as above.

Thermal analysis

Thermal analysis was carried out with a micro TG–DTA thermo analyser unit DTG–30 (Shimadzu, Japan), with which simultaneous TG–DTA curves were recorded (R–123T Recorder). Open aluminium crucibles were used. The TG scale ranged from ± 0.5 mg to ± 100 mg and the DTA scale from ± 5 μV to ± 500μV.

The powders were calcined at 1000° and X–ray diffraction patterns were then obtained using copper K α radiation. Values of the lattice parameter at $\theta = 90°$ were determined by extrapolation of the measured data according to the method of Nelson and Riley [8].

Results and discussion

Thermal decomposition of cerium oxalate

Figure 1 shows the simultaneous TG and DTA results obtained on the precipitated cerium oxalate at different heating rates. The TG curve displays two well-defined weight losses, corresponding to the DTA peaks. At a heating rate of 5 deg/min the first endotherm, at 130°, corresponds to the

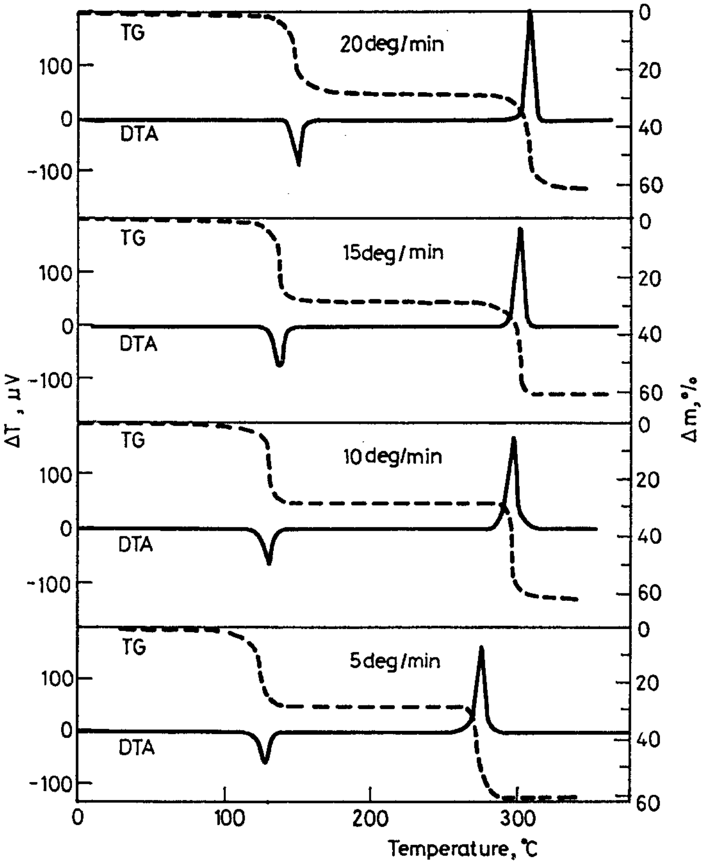

Fig. 1 Simultaneous TG and DTA for cerous oxalate at different heating rates

weight loss resulting from the removal of 10 mol of H_2O. The second weight loss corresponds to the decomposition of the oxalate, with an exothermic peak at 275°. From the TG analysis, it could be deduced that the precipitate is hydrated cerous oxalate of the form $Ce_2(C_2O_4)_3 \cdot 10H_2O$.

The thermal analysis at different heating rates showed that the activation energy for the dehydration of the hydrated cerous oxalate is 78.2 kJ/mol, and that for the decomposition of the anhydrous cerous oxalate to cerium oxide is 112.6 kJ/mol.

The activation energies were estimated by using different methods based on both TG and DTA data. As for the TG methods, we applied those described by Criado and Ortega [9] and by Freeman and Carroll [10]. For

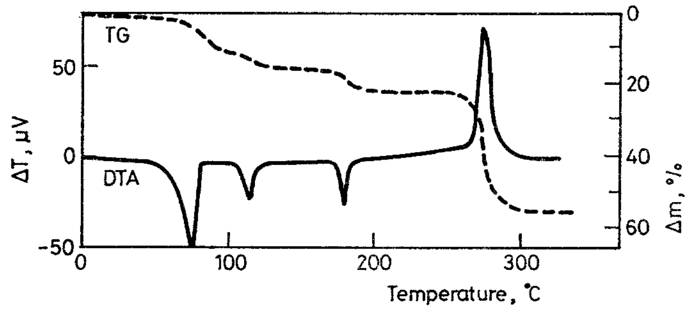

Fig. 2 Simultaneous TG and DTA for mixed cerium–20 mol% gadolinium oxalates at a heating rate of 5 deg/min

the estimation based on DTA, the peak temperature displacement as a function of the heating rate was used as given by Kissinger [11].

In addition, the relation between the temperature difference ΔT and $1/T$ (described by Piloyan [12]) was used.

The calculated activation energy values obtained from the above four methods were found to agree with each other within ± 10% and had the average values stated above.

Thermal analysis of decomposition of mixed cerium–20 mol% gadolinium oxalates

The precipitated mixed oxalates of cerium and gadolinium exhibited three well-defined weight losses for water removal, at temperatures of 75, 115 and 180°. As shown in the TG and DTA curves in Fig. 2, these dehydration reactions are all endothermic ones. This is followed by the exothermic decomposition of the anhydrous mixed oxalate at 275°, at a heating rate of 5 deg/min. This temperature is identical with that of the decomposition of cerium oxalate.

From the TG analysis, it was found that the mixed cerium-gadolinium oxalates have the general formula $Ce_{1-x}Gd_x(C_2O_4)_{2-x/2}\cdot nH_2O$, where x is the mole fraction of Gd. The cerium in the mixed salts was present as Ce(IV), in contrast with Ce(III) in the pure cerium oxalate. This is attributed to the presence of nitric acid, which acts as an oxidizing agent. This nitric acid was used to dissolve the Gd_2O_3 to obtain it in the nitrate form, as mentioned above.

The amount of water removed showed that the value of n in the above expression was 5, i. e. 5 mol of water. Three of them were removed at 75°, one at 115° and one at 180°.

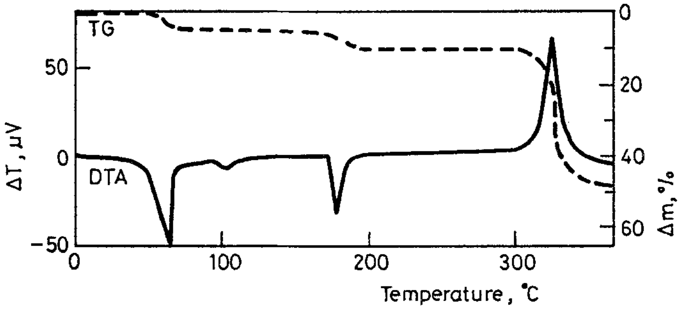

Fig. 3 Simultaneous TG and DTA for mixed cerium–50 mol% gadolinium oxalate at a heating rate of 5 deg/min

Thermal decomposition of mixed cerium–50 mol% gadolinium oxalates

The precipitated mixed cerium–50 mol% gadolinium oxalates exhibited very similar behaviour to that of the mixed oxalates containing 20 mol% gadolinium, as shown in Fig. 3, i. e. three steps for water removal, at 65, 100 and 180°. The weight loss in the second step, at 100°, is smaller than that for the mixed oxalate containing 20 mol% gadolinium Fig. 2. Further, the overall weight loss for water removal is relatively small.

The dehydrated mixed oxalates containing 50 mol% Gd decomposed exo thermally to give mixed oxides at a temperature of 325°. This temperature is higher than those for pure cerous oxalate and the mixed oxalate containing 20 mol% Gd. Similar behaviour was observed earlier in the decomposition of mixed cerium and gadolinium carbonates [7].

TG analysis showed that the composition followed the same general formula as for the compound containing 20 mol% Gd, but with $x = 0.5$ and $n = 2$, as calculated from the total weight losses corresponding to water removal, i. e. the chemical formula of the precipitated mixed cerium–50 mol% gadolinium oxalates is

$$Ce_{0.5}Gd_{0.5}(C_2O_4)_{1.75}\cdot 2H_2O.$$

X-ray diffraction of final products

The X-ray diffrection patterns of the final decomposition products in the form $Ce_{1-x}Gd_xO_{2-x/2}$ (after calcination at 1000°) for pure cerous oxalate and for the mixture containing 20 mol% Gd reveal a singel-phase fluorite structure with a lattice parameter of 5.142 and 5.424, respectively. For the oxide containing 50 mol% gadolinium, two phases coexist; a fluorite phase and a cubic phase, as shown in Table 1. This is in agreement with published results on the ceria-gadolinia system [9]. From the above, we find that carefully coprecipitated salts produce homogeneous mixed oxides after calcination, and a complete solid solution could be obtained.

Conclusion

The thermal decomposition of precipitated cerous oxalate takes place in two steps; the first step involves endothermic water removal, and the second step involves exothermic decomposition to cerium oxide. On the other hand, the thermal decomposition of the coprecipitated cerium and gadolinium oxalates takes place in four steps; the first three are endothermic steps of water removal, and the fourth is the exothermic decomposition to the mixed oxides.

Table 1 Diffraction pattern of coprecipitated mixed oxides calcined at 1000°C

Composition	*d*	*I/I.*	Comments
	3.1178	100	
20% Gd_2O_3	2.696	23.5	
	1.631	33.4	F
	1.5621	6.9	
	1.3542	5.1	
	1.2431	11.6	
	1.2118	7.4	
	4.3745	2.2	C
	3.1104	100	F, C
	2.6945	29.4	F, C
	2.5411	1.7	C
	2.3015	3.3	C
	2.1189	1.9	C
	1.9096	41.4	F, C
50% Gd_2O_3	1.7542	1.2	C
	1.626	1.9	C
	1.6324	30.6	F, C
	1.5941	2.0	C
	1.5617	6.0	F, C
	1.2431	8.8	F, C
	1.1072	7.1	C

F = Fluorite, C = Cubic

References

1 A. S. Nowick, *et. al.* In Fast ion transport in solids, (P. Vashiahta, J. N. Mundy and G. K. Shenoy, eds), Elsevier/North Holland, Amsterdam 1979, pp. 673-679.
2 K. El-Adham, Thesis, Univ. Grenoble, Grenoble, 1978.
3 T. Kudo and H. Obayashi, J. Electrochem. Soc., 122 (1975) 142.
4 K. Heggstad, J. Holm and O. T. Sorensen, Ris-M-2478, 1985.
5 J. L. Woodhead, Science Ceramics, 9 (1977) 29.
6 J. J. Bentzen, P. L. Husum and O. T. Sorensen, 6th CIMTEC Meeting, Milan, 1986.
7 N. Afify, A. S. Abdel Halim and S. W. El-Houte, to be published.
8 J. B. Nelson and D. P. Riley, Proc. Phys. Soc., London, 57 (1945) 168.
9 J. M. Criado and A. Ortega, J. Thermal Anal., 29 (1984) 1075.
10 E. S. Freeman and Carroll Thermal methods of analysis, by W. W. Wendland, Wiley & Sons 1974, p. 47.
11 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
12 Piloyan *et. al*, Thermal methods of analysis, W. W. Wendlandt, Wiley & Sons, 1974, p. 189.
13 D. V. Bevan, W. W. Barker and R. L. Martin, Proc. 4th Conference on Rare Earth Research, Phoenix, Ariz, 1964 (L. Eyring Ed), 1965, p .441.

Zusammenfassung — Zeroxalat und Zer-Gadolinium-Mischoxalat mit 20 bzw. 50 mol% Gadolinium wurden einer thermischen Zersetzung unterzogen. Die Thermoanalyse zeigte, daß Zeroxalat in zwei Schritten in Zeroxid überführt wird. Der erste Schritt mit der Aktivierungsenergie von 78.2 kJ/mol besteht in der endothermen Abgabe von 10 mol Wasser. Der zweite Schritt mit der Aktivierungsenergie 112.6 kJ/mol umfaßt die exotherme Zersetzung des wasserfreien Oxalates. Der Wassergehalt der Zer-Gadolinium-Mischoxalate nimmt mit steigendem Gadoliniumgehalt ab und die Temperatur für den exothermen Zersetzungsvorgang der wasserfreien Oxalate nimmt mit steigendem Gadoliniumgehalt zu.