THERMAL DECOMPOSITION OF PRASEODYMIUM-LANTHANUM MIXED OXALATE
IN VARIOUS ATMOSPHERES

Yoshihiko WATANABE[1], Sunao MIYAZAKI[2], Toshio MARUYAMA[2] and Yasutoshi SAITO[2]

[1]Chemistry Deparptment, The National Defense Academy of Japan, 1-10-20
Hashirimizu, Yokosuka 239 (Japan)

[2]Research Laboratory of Engineering Materials, Tokyo Institute of Technology,
4259 Nagatsuta-cho, Midori-ku, Yokohama 227 (Japan)

ABSTRACT

Thermal decomposition of praseodymium-lanthanum mixed oxalate has been stud-
ied by TG, DTA and EGA in $He+O_2(4:1)$, He and CO_2 atmospheres up to 1280 K at a
heating rate of 0.25 Ks^{-1}. The dehydration process of decahydrate oxalate is
almost same in every atmosphere. Both DTA and EGA curves indicate that four
reaction steps account for the decomposition of anhydrous oxalate. Thermal
stability of the carbonate and intermediate oxide carbonates increases with
raising the mole fraction of La and is most in CO_2.

INTRODUCTION

Lanthanide oxides play important roles in refractories, heat- and corrosion-
resistant additions, electronic materials and many other industrial ramifica-
tions. These oxides are usually obtained by the decomposition of their salts.
Properties of oxides thus obtained depend strongly on the kind of the starting
salt and also on the decomposition process. Thus, the thermal decomposition of
the lanthanide oxalates has been widely investigated (ref.1), but that of the
mixed lanthanide oxalates has not been thoroughly studied. As is well known,
praseodymium offers extensively nonstoichiometric oxides depending on the oxy-
gen pressure and the temperature. The nonstoichiometric feature is expected to
vary with the addition of other lanthnide elements such as lanthanum. In order
to obtain the praseodymium-lanthanum mixed oxide of definite property, authors
have made a reseach on the thermal decomposition of praseodymium-lanthanum mixed
oxalates in various atmospheres using multiple thermal analysis of TG, DTA and
EGA.

METHODS
Materials

Commercial praseodymium black oxide and lanthanum oxide both 99.9% in purity
were used, and all other chemicals were of A.R. Quality. A mixed oxalate was
obtained by precipitation from the solution of desired composition in dilute

nitric acid by addition of oxalic acid. The precipitate was washed by distilled water and ethyl alcohol, and then was air-dried at room temperature. Pure Pr and La oxalates and five kinds of mixed oxalates in which the mole fraction of Pr, X = 0.9, 0.7, 0.5, 0.3 and 0.1, were prepared and used for the experiment. All of the oxalates were analysed by ignition to the oxides around 1200 K. The oxide contents approximately agreed to those calculated for the respective oxalates decahydrates. The X-ray diffraction patterns of the mixed oxalates showed homogeneous monoclinic phases and were quite different from those of physical mixture of praseodymium and lanthanum oxalates.

Apparatus and Procedures

The thermal decomposition was performed by a thermobalance SSC/560GH (Seiko Denshi Kogyo Ltd.) attaching an EGA equipment involving thermal conductivity detectors (TCD) (ref.2). The schematic arrangement of the apparatus is shown in Fig.1. Using about 20 mg of oxalate and α-Al$_2$O$_3$ as a reference material for DTA, TG-DTA-EGA curves were simultaneously obtained in the atmospheres of He+O$_2$ (4:1) and He, and TG-DTA curves in CO$_2$ atmosphere. Gases were supplied from cylinders through flow rate controller (FRC) with a flow rate of 2×10^{-6}~2.5×10^{-6} m^{3}s^{-1}. The oxygen content of the He+O$_2$ mixed gas was checked by employing a calcia stabilized zirconia (CSZ) oxygen sensor. In EGA, He+O$_2$ or He as a carrier gas was introduced into the thermobalance passing through the reference cells of TCD-1 and TCD-2. Gases evolved from the

Fig. 1. Schematic arrangement of TG-DTA-EGA apparatus.

sample was transported with the carrier gas to a tube containing Mg(ClO$_4$)$_2$ which absorbs H$_2$O, and subsequently introduced into the sample cells of TCD's. A trap packed with Ascarite was properly placed between TCD-1 and TCD-2 in order to absorb CO$_2$ liberated. For eliminating CO in evolved gas, CO was oxidized to CO$_2$ by passing through a trap filled with I$_2$O$_5$ kept at 425 K and then absorbed by Ascarite. X-ray diffraction patterns were obtained with a diffractometer using Ni-filtered CuK$_\alpha$ radiation.
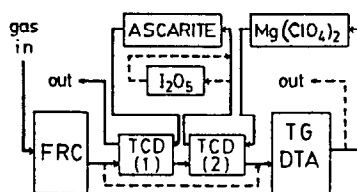
RESULTS AND DISCUSSION

Thermal Analysis in He+O$_2$ (4:1) Atmosphere

TG, DTA and EGA curves were simultaneously obtained at a heating rate of 0.25 Ks^{-1}. The results are shown in Figs. 2, 3 and 4 respectively.

The dehydration begins near 315 K and proceeds rapidly around 390 K accompanying a large endothermic peak of DTA. Nearly 90% of H_2O has liberated up to about 450 K and then the sample gradually approaches the anhydrous oxalate up to near 620 K. The dehydration reveales the same behavior in the whole range of the composition of the samples and in all the atmospheres employed in this study. There is little evidence for the stable intermediately hydrated oxalate.

The decomposition of the anhydrous oxalate begins immediately after the completion of dehydration accompanying a small exothermic peak of DTA and a small CO_2 evolution peak of EGA. These small peaks become vague with increasing the mole fraction of La. As are shown in Fig.4, the EGA curves with H_2O, CO_2 and CO absorbers are identical to those with H_2O and CO_2 absorbers indicating that CO evolved during the decomposition is instantly oxidized to CO_2. Thus, the area under the EGA curve with H_2O absorber should be proportional to the amount of CO_2 detected and hence to the extent of the decomposition reaction.

Although there are not any plateaus or plateau-like parts in TG curves except those which correspond to the dioxide
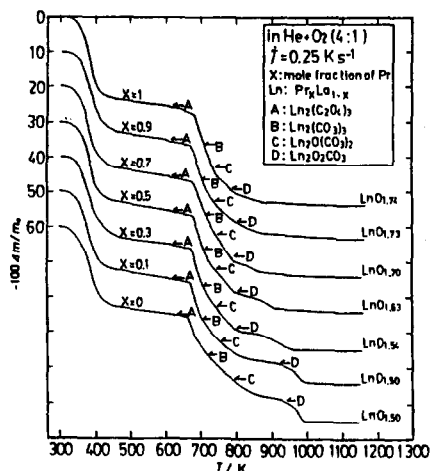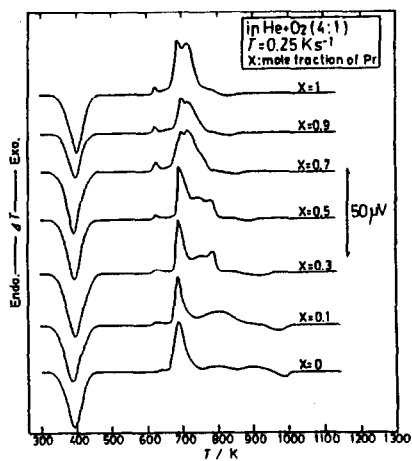

Fig. 2. TG curves in He+O_2.
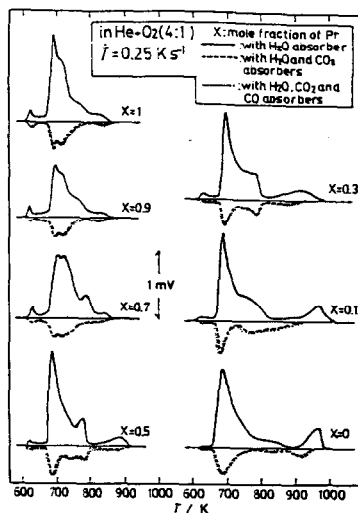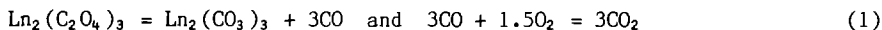

Fig. 3. DTA curves in He+O_2.

Fig. 4. EGA curves in He+O_2.

carbonate in La rich composition, it is likely that the EGA curve detecting CO_2 can be fractionated into four peaks and that decomposition reaction should account for each peak. The first peak is the biggest and hence this peak is attributed to the reactions:

$$Ln_2(C_2O_4)_3 = Ln_2(CO_3)_3 + 3CO \quad \text{and} \quad 3CO + 1.5O_2 = 3CO_2 \qquad (1)$$

where Ln denotes Pr_xLa_{1-x}. Subsequent three peaks correspond to the following reactions:

$$Ln_2(CO_3)_3 = Ln_2O(CO_3)_2 + CO_2, \qquad (2)$$

$$Ln_2O(CO_3)_2 = Ln_2O_2CO_3 + CO_2 \qquad (3)$$

and

$$Ln_2O_2CO_3 = Ln_2O_3 + CO_2. \qquad (4)$$

Since Pr^{3+} is easily oxidized to Pr^{4+} in $He+O_2$ (4:1) atmosphere; the average basicity of metals constituting the compound is lowered, and resultant oxides and/or probably intermediate oxide carbonates show wide-spread nonstoichiometry (ref.3). The lowered basicity and the nonstoichiometry possibly make carbonate and oxide carbonates unstable. Thus, the peaks in EGA curve overlapped more tightly in Pr rich composition and the decompsotion process became complicated.

X-ray diffraction patterns of the final oxides showed that the interplanar spacing of f.c.c. related lattice continuously increased as the mole fraction of La increased and also showed that the diffraction peaks became broad due to the distortion of the lattice by the addition of La. The f.c.c. related structure was maintained up to $X = 0.3$, and at the composition of $X = 0.1$ diffraction patterns showed the peaks of hexagonal sesquioxide phase coexisting with the f.c.c. related pahse.

Thermal Analysis in He Atmoshpere

Pr^{3+} is hardly oxidized in He atmosphere. The decomposition of anhydrous oxalate became more sluggish in Pr rich composition compared with in $He+O_2$ (4:1) atmosphere. Hence, difference in the decomposition process is presumably due to the small discrepancy in the chemical properties between Pr^{3+} and La^{3+}.

TG, DTA and EGA curves obtained are shown in Figs. 5, 6 and 7. In every composition, anhydrous oxalate begins to decompose about 630 K higher than in $He+O_2$ atmosphere by 10 K. The small peak which appeared in $He+O_2$ atmosphere especially much evident in Pr rich composition diminished in He atmosphere.

At the initial stage of the decomposition, there exists an endothermic peak in DTA curves and evolutions of CO_2 and CO are recongnized in EGA curves. The evolution of CO temporarily ceases at about 750 K and DTA curves showed that the evident endothermic process completes once at the same temperature which corresponds to the composition of $Ln_2O(CO_3)_2$ in TG curves. This stage is apparently expressed by the miscelaneous reactions of (1) and (2) except oxidation of CO and subsequently goes through decomposition to give $Ln_2O_2CO_3$.

During the decomposition of $Ln_2O(CO_3)_2$ to $Ln_2O_2CO_3$, EGA curves shows that

the evolved gas contains very small quantity of CO, in which a mass loss corresponds to the change in the EGA curves. On the other hand, no DTA is detected for this stage. This is supposed to be due to the slow rate and low heat of reaction (3).

Difference of the chemical properties between Pr and La is evidently shown in the stability of $Ln_2O_2CO_3$. As the mole fraction of La increases, the plateau designating the dioxide carbonate becomes more evident, the second endothermic peak in DTA curve and the corresponding EGA peak are observed more obviously.

In this stage, the evolution of CO markedly takes place again. The decomposition of praseodymium dioxide carbonate with CO evolution has not been accepted (ref.4). As discussed in the previous papers (ref.2 and 5), however, carbon deposited in the preceding stage could be converted into CO according to the endothermic reaction as

$$C + CO_2 = 2CO \qquad (5)$$

under the sufficient partial pressure of CO_2 at high temperatures.

X-ray diffraction patterns of the end oxides showed that of a hexagonal sesquioxide. The color of the oxide became darker in Pr-rich composition due to the finely divided carbon residue.
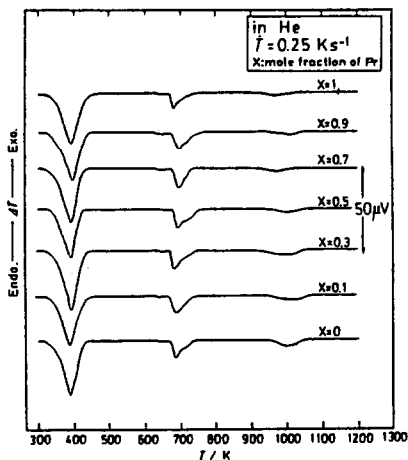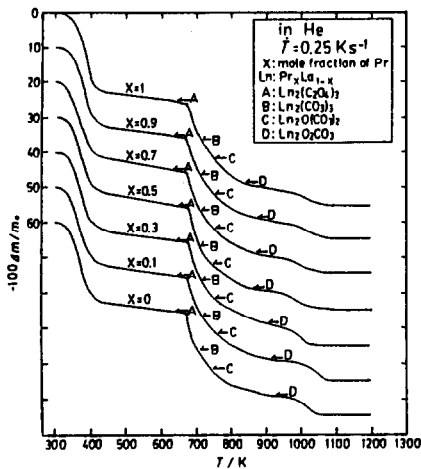

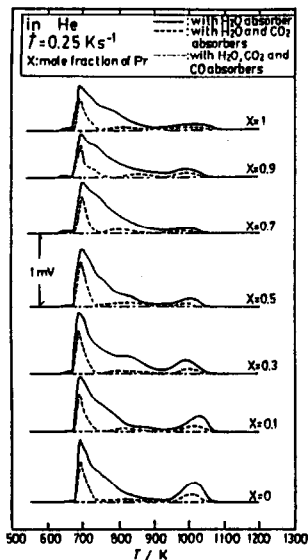Fig. 5. TG curves in He.

Fig. 6. DTA curves in He.

Fig. 7. EGA curves in He.

Thermal Analysis in CO_2 Atmosphere

In order to confirm the formation of the intermediate carbonate or oxide carbonates, thermal analysis was carried out in CO_2 atmosphere. Figures 8 and 9 show TG and DTA curves respectively obtained in a stream of CO_2 at a heating rate of 0.25 Ks^{-1}. The decomposition of anhydrous oxalate starts around 660 K higher than in any other atmospheres of the present study. The TG curves display more distinct breaks and plateaus in the formation of intermediates, particularly at the composition of $Ln_2O_2CO_3$ of which decomposition temperature rise from 1090 to 1190 K with increasing content of La.

The final product of the decompoaition is estimated to be Ln_2O_3. When this oxide is cooled in CO_2 at a rate of 0.25 Ks^{-1}, the oxide absorbs CO_2 and gives $Ln_2O_2CO_3$ which is stable at room temperature in the composition range of $X \leqq$ 0.3. The X-ray pattern of $La_2O_2CO_3$ agreed with that reported by ASTM. At the composition of $X = 0.5$, the oxide absorbs nearly 40% of CO_2 expecting to give the dioxide carbonate. Its X-ray pattern showed the coexistence of the the sesquioxide and dioxide carbonate.
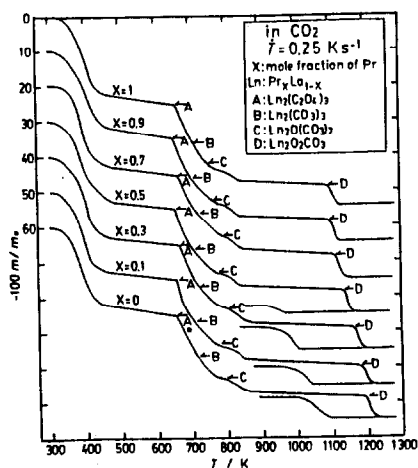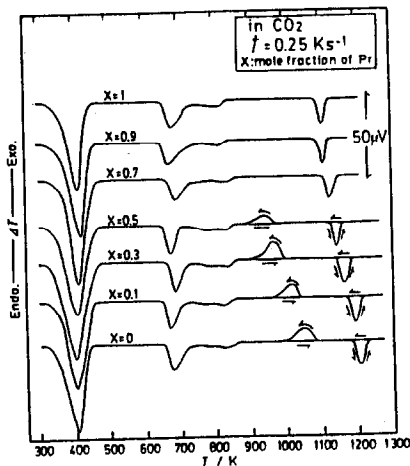
Fig. 8. TG curves in CO_2.   Fig. 9. DTA curves in CO_2.

REFERENCES

1 Y. Saito and S. Sasaki, NETSUSOKUTEI, 7 (1980) 67-72.
2 Y. Saito, Y. Shinata, K. Yokota and K.Miura, Nippon Kinzoku Gakkaishi, 38 (1974) 792.
3 L. Eyring, in C.N.R. Rao (Eds.), Solid State Chemistry, Marcel Dekker, Inc., New York, 1974, pp. 565-634.
4 R.C. Ropp and E.E. Gritz, in L. Eyring (Eds.), Rare Earth Research III, Gordon and Breach, New York, 1965, pp. 719-744.
5 H. Kaneko, Y. Saito, M. Umeda and K. Nagai, Nippon Kagaku Kaishi (1977) 792.