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On Phase Reactions in the System Curium Oxide + Oxygen

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The behaviour of the system $CmO_x + O_2$ during isobaric thermogravimetric analysis is found to be different from that previously reported. The differences are discussed, and explained as resulting from a higher sample purity. The earlier sample was contaminated by ~2.5% AmO_x which, we believe, suppressed the monotropic conversion of cubic $CmO_{1.5+\delta}$ to monoclinic Cm_2O_3. The hypothesis is consistent with other reports of the behaviour of pure CmO_x, and explains some hitherto puzzling features of the earlier isobaric study.

Introduction

As expected, isobaric thermogravimetric analyses of the curium oxide system in the composition range $1.5 \leqslant 0/Cm \leqslant 2.0$ (*1*, *2*) have revealed behaviour rather similar to that observed for the systems $PrO_x + O_2$ and $TbO_x + O_2$. Several intermediate phases appeared to be stable over a range of ambient conditions. The latest and most thorough study of this sort is by Chikalla and Eyring (*3*), who identified stable intermediate phases with the compositions $x \simeq 1.72$ and 1.82, and a nonstoichiometric σ phase with $x \lesssim 1.64$.

By comparison with the behaviour of the two lanthanide systems two features of their results seem to us to be significant. First, the composition ranges of the ordered intermediate phases were much wider: second, the CmO_x phase reactions were more sluggish, i.e., they extended over a wider temperature range.

As Chikalla and Eyring pointed out, these are both characteristic of impure solids and, indeed, their CmO_x sample contained 2.5 wt% of AmO_x. AmO_2 is relatively difficult to reduce (*4*),[1] and one might expect that the presence of its fluorite-type structure would interfere with CmO_x phase reactions, which clearly involve fluorite-related structure types when $x > \sim 1.5$ (*2*, *5*).

In a concurrent attempt to examine this system we used a purified sample of CmO_x. Its behaviour is rather different from that described in most previous reports, and we wish to comment on some features of the two sets of isobars—our own and those of Chikalla and Eyring.

Experimental

Curium oxide. The oxide as supplied (from the Oak Ridge National Laboratory, via the USAEC and the AAEC) was taken up in 6 *M* nitric acid; the solution evaporated to dryness, and the residue taken up in 50 μl of 5 *M* lithium nitrate in 20% methyl alcohol with the pH adjusted to 2.0. This solution was then transferred to an

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[1] Even under the most strongly reducing conditions employed by Chikalla and Eyring, *viz.* $p_{O_2} = 2$ Torr at 950°C, pure americium oxide would only be reduced to $AmO_{1.97}$ (*4*).

ion-exchange column (Amberlite 400, converted to the nitrate) together with a 50 μl wash.

The column was eluted with the lithium nitrate–methyl alcohol solution. The first 20 ml of eluant contained Al, Fe, rare earths, etc., and was discarded. The next 25 ml contained the Cm (Am < 0.04%) and was collected. The Cm was then largely separated from the Li by precipitating it as $Cm(OH)_3$ with aqueous ammonia. After centrifuging and removing the supernatant liquid, the precipitate was taken up in 0.02 *M* nitric acid and the solution extracted several times with a solution of di-2-ethyl-hexyl phosphate. This removed the Cm from the aqueous phase, in which the Li remained, reducing the lithium contaminant to $\ngtr 0.05$ ppm. The organic phase was then extracted with 2 *M* nitric acid, which removed the Cm, while the Pu remained in the organic layer. This aqueous phase was then extracted with benzene (to remove any organic phosphate), and the Cm in the aqueous solution precipitated with aqueous oxalic acid, after first being transferred to the small Pt bucket used in the thermogravimetric analysis. The precipitate was washed, then dried under a heat lamp.

Thermogravimetry. The small Pt bucket (6 × 5 mm) containing the partly dried curium oxalate hydrate crystals (weighing approx 9.4 mg) was suspended from a Cahn *RG* vacuum microbalance arranged for thermomicrogravimetry. The usual technique of a programmed temperature rise and fall (R.T. to 1200°K at 1°K/min) while the sample was exposed to a selected pressure of oxygen had been refined to yield a weighing accuracy of about ±1 to 2 μg (*6*). For the CmO_x sample, weighing approx 6 mg, this corresponds to a precision in composition of $\delta x \simeq 0.01$. The balance reading and sample temperature were simultaneously recorded for both blank and actual runs. The differences between the corresponding sample and blank weights were then plotted against temperature to give a series of isobars for the range $10 < p_{O_2} < 750$ Torr. (The blank corrections ranged up to 50 μg, but were usually 10–30 μg.)

Subsequently a separate series of runs was carried out on a second, freshly purified, CmO_x sample of slightly larger size. These were simply to provide a qualitative confirmation of the behaviour observed in the first series. Blank runs are not available for this second set, and they are shown uncorrected for buoyancy, etc. This does not obscure the general pattern of behaviour.

Observations

The temperatures at which phase reactions start are similar in both studies (±10°K). The main differences observed by us are as follows. First, the phase reactions are more rapid, which is consistent with the higher purity. Second, on cooling from approx 1175°K in an oxygen pressure of less than about 150 Torr oxidation never proceeds beyond $CmO_{\sim 1.62}$.

These differences are illustrated by Fig. 1, which shows our isobar at 52 Torr and that of Chikalla and Eyring at 50 Torr. The behaviour observed by Chikalla and Eyring on cooling, i.e., in oxidation, resembles that of the analogous lanthanide systems much more than do our own results.

Discussion

Chikalla and Eyring (*3*) made the following comments which are relevant to these differences.

(i) Reduction with H_2 occurred rapidly to $CmO_{1.545}$ at temperatures up to 673°K. Further heating caused a *slow* weight loss with increasing temperature, producing $CmO_{1.525}$ at 1073 to 1173°K. They could offer no explanation for the very slow drift in weight when *x* was less than 1.545.

(ii) A "bulge of stability [occurs] in the ($\sigma\iota$) region, in oxidation near a composition of Cm_6O_{10} ($= CmO_{1.67}$); and"

(iii) [there is a] "lack of consistent closure of the loop at ι ($CmO_{1.72}$) which may be significant."

It is also clear from their results that

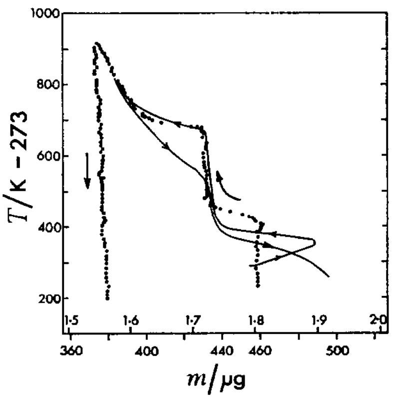

FIG. 1. $CmO_x + O_2$ isobars: ···, this work at $p_{O_2} = 52$ Torr; ——, Chikalla and Eyring at $p_{O_2} = 50$ Torr.

(iv) The behaviour was not reversible in the σ region, $1.5_3 \lesssim x \lesssim 1.6_4$.

In contrast, in our experiments we saw no $(\sigma\iota)$ phase of comparable composition width (cf. (ii) above); but there were very large composition differences between reduction and oxidation (heating and cooling) in the temperature range where ι ($CmO_{1.72}$) existed on heating (cf. (iii) above). In addition, as already mentioned, σ appeared to oxidise little or not at all when cooled at low oxygen pressures. *Thus* (ii)–(iv) *are very much more marked in our experiments.*

Our isobars (e.g., Figs. 2 and 3) suggest to us that ι is often present during the oxidation part of a run, but that the *average* sample composition is highly oxygen-deficient with respect to the ι composition ($Cm_7O_{12} = CmO_{1.714}$). A simple explanation, which appears to fit all the facts known to us, is that this is because ι is "mixed" with a reduced oxide. To anticipate our subsequent reasoning we suggest that a considerable monotropic conversion of σ ($CmO_{1.6+}$) to B-type Cm_2O_3 occurs during the highest temperature portion of the run. A much smaller conversion in the sample of Chikalla and Eyring accounts for (i), (ii) and (iii), and for the greater prominence of $(\sigma\iota)$ in their results. Their observation (i) is a consequence of the considerable structural rearrangement involved in passing from the cubic to the monoclinic system (*7*, *8*)—a reconstructive transformation severely hampered in their case by the *cubic* fluorite-type AmO_2 impurity.

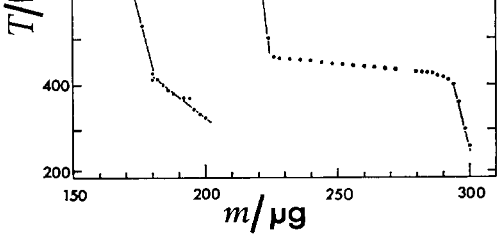

FIG. 2. $CmO_x + O_2$ isobar uncorrected by "blank" run, $p_{O_2} = 164$ Torr.

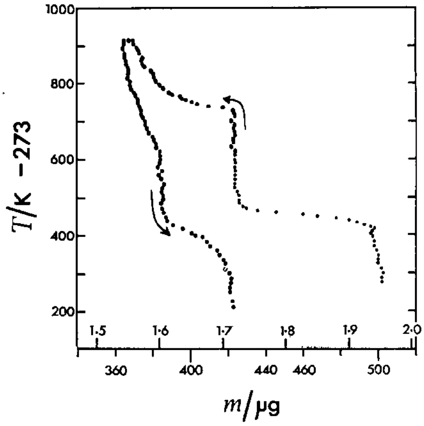

FIG. 3. $CmO_x + O_2$ isobar, $p_{O_2} = 234$ Torr.

In our experiments the degree of conversion is usually one-half to two-thirds. This being so, one would expect the composition in the ι stability region to be $1.57 \lesssim x \lesssim 1.61$ (1/2 to 2/3 of $CmO_{1.5}$ plus 1/2 to 1/3 of $CmO_{1.72}$). This is the case. Furthermore, one might also expect to see the $\sigma \rightarrow \iota$ reaction, but at a lower composition and with a change in composition about one-half to one-third of that for $\iota \rightarrow \sigma$. This is also observed (Fig. 3, 1080–900°K). The $B + \iota$ mixture eventually oxidises on cooling, either completely to ι (e.g. Fig. 3) or to the dioxide, depending on the ambient oxygen pressure. Sometimes the oxidation of ι is obvious, but temperatures are low (< 793°K), and the almost simultaneous but slower oxidation of the B-type sesquioxide usually obscures it (e.g. Fig. 2).

This interpretation, involving $B\sigma$ and $B\iota$ "pseudophases," is substantiated and clarified by some observations of Mosley (*5*). Using a relatively pure sample of CmO_x he observed that:

(a) In 1 atm pressure of oxygen, and in the temperature range in which ι is stable, the oxygen/curium ratio was much lower on cooling than on heating *if the sample had been heated to 1273°K, but not after heating to only about 1023°K.*

(b) A rather stable reduced CmO_x—prepared by heating in helium ($Cm_{\sim 1.54}$) or a helium plus hydrogen mixture ($CmO_{\sim 1.52}$)—reduces further, to $CmO_{1.50}$, at approx 1173 or 1033°K, respectively.

(c) The monoclinic B-type Cm_2O_3 oxidises fairly rapidly *only in the temperature range 523–793°K.*

It seems likely that as with the conversion of cubic σ-PrO_x to hexagonal A-type Pr_2O_3 (*8*), the transformation of the cubic σ-CmO_x to the monoclinic *B*-type Cm_2O_3 occurs at a temperature which increases with increasing p_{O_2}, and, therefore (more fundamentally), with increasing oxygen content of the σ-phase $CmO_{1.5+\delta}$. This explains why the profiles of the Chikalla and Eyring isobars are different from ours: their fluorite-type $AmO_{\sim 2}$ contaminant stabilises the cubic structure, and raises the $\sigma \rightarrow B$ transformation temperature. In their sample there is therefore a much smaller degree of conversion to the *B*-type. It is significant that at the highest oxygen pressures, we also observed the oxidation of $CmO_{\sim 1.6}$ to CmO_2 *at 793°K* (cf. (c) above). The temperature at which this oxidation commences decreases with decreasing oxygen pressure: in our experiments the lowest were 703 to 713°K, at oxygen pressures of 235–280 Torr—the product then being Cm_7O_{12}.

Conclusion

The above discussion suggests that σ-CmO_x is even more unstable with respect to *B*-Cm_2O_3 than is σ-PrO_x to *A*-Pr_2O_3. In the range of oxygen pressures employed by us (10–730 Torr) *B*-Cm_2O_3 is stable at least down to 793°K; while in the same pressure range *A*-Pr_2O_3 oxidizes at temperatures not lower than 1173°K. Qualitatively, however, the metastability of the cubic lower oxides of curium is quite analogous to that of the lower praseodymium oxides, which are isostructural for $x > 1.5$.

The difference between the behaviour of our sample of CmO_x and that of Chikalla and Eyring we believe to be another example of the sometimes dramatic effect of an appropriate impurity on the thermodynamic and structural behaviour of a solid. In this context "appropriate" means able to exist coherently (or semicoherently) within the matrix of the major component. Extreme differences in reaction kinetics in the $PrO_x + O_2$ system have recently been observed, and interpreted as resulting from impurity levels two orders of magnitude lower than the 2.5% AmO_x involved here (*9*).

Such effects are presumably to be explained in terms of Ubbelohde's ideas on the stress resulting from the coherence of phases of similar structure (*10*). He suggested that impurities may "lubricate" a transformation: our experiences with the praseodymium and curium oxides show that the reverse may sometimes be the case.

A simple test of the hypothesis used to explain our observations would be to cool a pure CmO_x sample from approx 1223°K to room temperature in an oxygen pressure of less than 150 Torr. Oxidation of the *B*-Cm_2O_3 would not then occur, and the product could be checked for its presence by X-ray diffraction. Unfortunately, it has not yet been possible for us to carry out this experiment.

Sample Purity

A 1 mg portion from the CmO_x at the end of our first series of runs was analyzed spectrographically. The only large impurity was platinum, which was said to be present at a level in the order of a few per cent. This corresponds to a few tens of micrograms of Pt in the 1 mg CmO_x sample, or several monolayers on its surface. If it were *in* the sample then all our arguments collapse: we believe it is present *on* the sample surface. (The "evaporation" of Pt when it is heated to a high temperature in O_2 is a well-known phenomenon.)

Our main reason for discounting the significance of the analysis is simply the sharpness of the observed CmO_x phase reactions, and the narrow composition range of the ordered Cm_7O_{12} phase. These are strongly indicative of high purity. Furthermore, even the earliest runs of the second series (with a freshly purified CmO_x sample) showed the same sort of behaviour as that under discussion. We attribute the unusually high Pt analysis to the very large proportion of exposed surface with such a very small sample.[2]

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[2] Subsequent experiments (F. J. Lincoln and B. G. Hyde, unpublished) confirm this argument. The results using an alumina bucket and hangdown wire are identical with those obtained with platinum.

Finally we would like to thank Dr. W. C. Mosley, Savannah River Laboratory of E. I. du Pont de Nemours & Co., Aiken, S. Carolina, for a copy of his lecture (*5*).

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