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THERMAL STABILITY OF OSMIUM MIXED OXIDES. II. $CaOsO_3$ DECOMPOSITION PRODUCTS: CONDITION FORMATION OF DEFECT PYROCHLORES $Ca_2Os_2O_{7-x}$

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ABSTRACT

The thermal decomposition of $Ca_2Os_2O_7$ by DTA, thermogravimetry and X-ray powder diffraction has been studied. Orthorhombic $Ca_2Os_2O_7$ evolves oxygen slowly above 855 ± 5 °C transforming into the intermediate orthorhombic $Ca_2Os_2O_{7-x}$ up to $x \sim 0.16$. At $x = 0.16$–0.20 a new cubic phase begins to form. The cubic phase $Ca_2Os_2O_{7-y}$ has a pyrochlore structure type and its homogeneity region is spread to $y \sim 0.60$. The cubic $Ca_2Os_2O_{7-y}$ stability is discussed. Above 1018 ± 7 °C pyrochlores $Ca_2Os_2O_{7-y}$ decompose completely into CaO, osmium metal, osmium tetroxide and oxygen.

INTRODUCTION

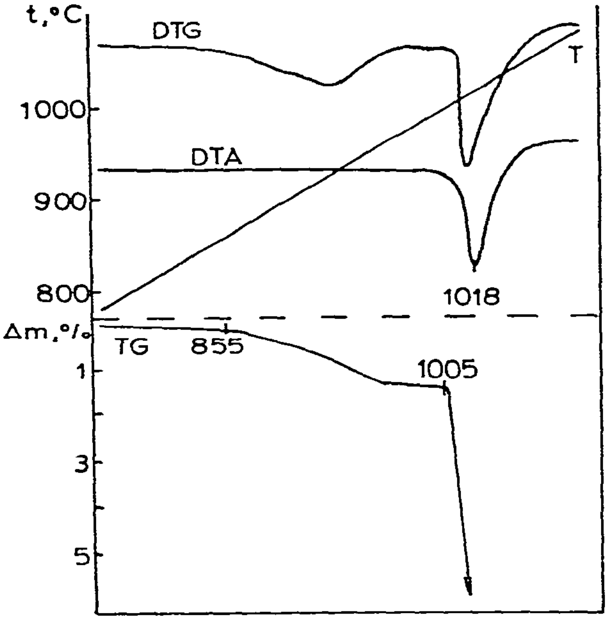
In Part I[1] we have found an intermediate $Ca_2Os_2O_7$ with an orthorhombic structure ($Ca_2Nb_2O_7$ type) in the thermal decomposition of $CaOsO_3$. During an investigation of its thermal stability we have determined that the orthorhombic phase loses oxygen gradually and forms a series of phases $Ca_2Os_2O_{7-x}$ with a pyrochlore structure. In this paper we describe the formation conditions and the region of homogeneity for cubic $Ca_2Os_2O_{7-x}$.

EXPERIMENTAL

The starting material, powdered orthorhombic $Ca_2Os_2O_7$, was prepared by the thermal decomposition of $CaOsO_3$ under conditions described in Part I[1], together with the instrumental procedures.

RESULTS

On the basis of X-ray, DTA and thermogravimetry data it was stated that the orthorhombic $Ca_2Os_2O_7$ loses oxygen very slowly above 855 ± 5°C. This process



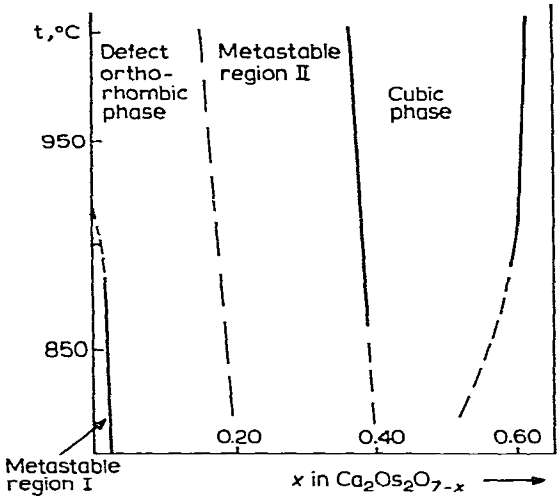


Fig. 1. The thermal decomposition of $Ca_2Os_2O_7$ in air. Heating rate 5 °C min^{-1}.

Fig. 2. Phase diagram of system $Ca_2Os_2O_{7-x}$ in region $0 \leq x \leq 0.65$.

TABLE 1

$Ca_2Os_2O_{7-x}$ PHASE COMPOSITION IN A TEMPERATURE INTERVAL 850–1015 °C

Temp. (°C)	*Heating time (min)*	*Cooling process*	*Product formula*	*Phase symmetry*[a]
835 ± 5	120	Quenching (Q)	$Ca_2Os_2O_7$	O
	2	Slow cooling(SC)[b]	$Ca_2Os_2O_7$	O
850 ± 5	120	Q	$Ca_2Os_2O_{6.82\pm0.06}$	O
	120	SC	$Ca_2Os_2O_{6.89\pm0.04}$	O
	2	SC[b]	$Ca_2Os_2O_{6.95\pm0.02}$	O
	660	SC	$Ca_2Os_2O_{6.83\pm0.03}$	O
930 ± 5	120	Q	$Ca_2Os_2O_{6.64\pm0.08}$	O + C
	120	SC	$Ca_2Os_2O_{6.66\pm0.05}$	O + C
	1020	SC	$Ca_2Os_2O_{6.56\pm0.03}$	C
945 ± 5	2	SC[b]	$Ca_2Os_2O_{6.77\pm0.03}$	O
970 ± 8	180	Q	$Ca_2Os_2O_{6.45\pm0.06}$	C
970 ± 6	2	SC[b]	$Ca_2Os_2O_{6.52\pm0.05}$	C
1000 ± 8	120	Q	CaO + osmium metal	
1000 ± 5	2	SC[b]	CaO + osmium metal + $Ca_2Os_2O_{6.45\pm0.05}$	

[a] O = orthorhombic, C = cubic.
[b] In Derivatograph's kiln.

is shown on the TG curve (see Fig. 1). It was shown that the starting phase retains the same orthorhombic symmetry over a temperature range with a definite (but not large) oxygen deficiency. $Ca_2Os_2O_{7-x}$ phase compositions in the temperature interval 850–1015 °C are given in Table 1. A new cubic phase $Ca_2Os_2O_{7-x}$ is beginning to

TABLE 2

X-RAY POWDER PATTERN FOR $Ca_2Os_2O_{6.45\pm0.06}$

I	d_{obs} (Å)	d_{calc} (Å)	h k l
14	5.96	5.88	1 1 1
7	5.13	4.133	2 0 0
11	3.630	3.626	2 2 0
16	3.088	3.093	3 1 1
100	2.964	2.963	2 2 2
38	2.566	2.565	4 0 0
3	2.292	2.296	4 2 0
3	2.092	2.098	4 2 2
11	1.976	1.969	5 1 1
44	1.813	1.815	4 4 0
4	1.733	1.736	5 3 1
8	1.566	1.558	5 3 3
10	1.546	1.548	6 2 2
12	1.481	1.481	4 4 4
		1.436	7 1 1
4	1.422	1.428	6 4 0
9	1.370	1.376	6 4 2
		1.331	7 3 1
5	1.283	1.280	8 0 0

form at x = 0.16–0.20. Phase transition from the orthorhombic defect phase $Ca_2Os_2O_{7-x}$ into a cubic phase occurs gradually at a small rate, hence the transition is a diffuse process only. The phase diagram of the $Ca_2Os_2O_{7-x}$ system is given in Fig. 2.

The cubic phase $Ca_2Os_2O_{7-x}$ has a pyrochlore structure. It is difficult to determine precise boundaries for the stability area of the phase. Judging from the results it can be located between the composition $Ca_2Os_2O_{6.58}$ and $Ca_2Os_2O_{6.38}$. In this interval (i.e. $0.42 \leq x \leq 0.62$) the unit cell parameter changes slightly and it has the value 10.240 ± 0.005 Å for average compositions $Ca_2Os_2O_{6.45\pm0.06}$ and $Ca_2Os_2O_{6.5\pm0.05}$ respectively. X-ray powder diffraction data are given in Table 2.

The phases $Ca_2Os_2O_{6.50\pm0.10}$ exhibit metallic conductivity with a room temperature resistivity $(2.0\text{–}5.6) \times 10^{-2}$ ohm-cm. During heating the weight of this phase is gradually diminished with the formation of the stable phase $Ca_2Os_2O_{6.45\pm0.06}$ below 980 °C. Above 1005 ± 5 °C on the TG curve we again observe mass loss while a large endothermic peak on the DTA curve has the maximum at 1018 ± 7 °C (Fig. 1). These effects do not experimentally depend on the heating rate. The observed process is the thermal decomposition of the defect pyrochlore $Ca_2Os_2O_{6.45\pm0.06}$ with the formation of a gaseous phase containing osmium tetroxide and oxygen. The solid residue is a mixture of CaO and osmium metal with approximate mole composition 2 : 1 (the average value is 2.11 : 1.00 on the data of three analyses). On the basis of these results, the $Ca_2Os_2O_{6.45}$ thermal decomposition reaction may be represented by the equation

$$Ca_2Os_2O_{6.45} \rightarrow 2\,CaO + Os + OsO_4 + 0.225\,O_2 \qquad (1)$$

DISCUSSION

The formation of a cubic phase with the formula $Ca_2Os_2O_{7-x}$ occurs gradually above 855 ± 5 °C on heating of the orthorhombic $Ca_2Os_2O_7$ and first of all depends on the heating rate and the total heating time. However, it ought to be emphasized that the existence of a continuous set of $Ca_2Os_2O_{7-x}$ species with any numerical x value in each of the phase fields is doubtful. Our numerous experiments have shown that in the stability area of orthorhombic phases there are no phases in the fields $0.00 < x \leq 0.02$ and $0.26 \leq x < 0.33$ while for cubic phases there are unstable compositions near phase area boundaries (i.e. for values $x \sim 0.42$ and $x \sim 0.62$). It may be concluded that the formation process of the cubic phase $Ca_2Os_2O_{6.48 \pm 0.10}$ is a second order structural phase transition.

It is difficult to comprehend clearly the processes of oxidation or reduction in the valence-mixed compound $Ca_2Os^{IV}_{2-x}Os^{VI}_xO_7$ since oxygen evolution must initiate a reduction of Os(VI) to the Os(IV) oxidation state, although at elevated temperature and under active oxygen (static or dynamic air) this process is scarcely probable. The formation of cubic $Ca_2Os_2O_{6.5}$ becomes a bit clearer for investigators if one assumes that the disproportion reaction $2\ Os^{V} \rightarrow Os^{IV} + Os^{VI}$ occurs on heating orthorhombic $Ca_2Os_2O_7$. However we have no evidence for osmium (V) in the starting material $Ca_2Os_2O_7$ (see Part I).

All that concerns eqn. (1) can be explained by some deviation from the stoichiometric relation $CaO:Os = 2:1$ for a solid residue because part of the osmium is oxidized by oxygen in the air to osmium tetroxide and the latter escapes into the gaseous phase. Therefore, the precise form of eqn. (1) is

$$Ca_2Os_2O_{6.45 \pm x} \rightarrow 2\ CaO + (1 - x)\ Os + (1 + x)\ OsO_4\uparrow + (0.45 \pm x)/2\ O_2\uparrow$$

The calculated mass value for the solid residue on thermal decomposition according to (1) is 54.31 % mass from $Ca_2Os_2O_{6.45}$ as a precursor. From derivatographic data we have obtained the value 54.22 ± 0.12 % mass. The result is convincing evidence that eqn. (1) describes the thermal decomposition in air of $Ca_2Os_2O_{6.45}$ above 1005 ± 5 °C.

REFERENCES

1 I. S. Shaplygin and V. B. Lazarev, *Thermochim. Acta*, 20 (1977) 381.