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On the Lower Oxides of Vanadium

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The homogeneity range, at 900°C, and unit cell of V_2O have been established. A survey of the lattice parameters and numbers of atoms per cell of the lower vanadium oxides is given.

A phase analysis study on the lower vanadium oxides, with a survey of the pertinent literature, has been reported in a previous publication [1].

At temperatures below 900°C all of the following phases were found (or confirmed) to exist.

Phase	Composition limits		Reference
V	$(V-VO_{0.033})$	body centered cubic	3
V_4O	$(VO_{0.17}-VO_{0.28})$	body centered tetragonal	3
V_2O	$(\sim VO_{0.5})$		1
VO	$(VO_{0.89}-VO_{1.20})$	face centered cubic	1
$VO_{1.27}$	$VO_{1.27}$	body centered tetragonal	1

The present work was undertaken in order to establish the homogeneity range and unit cell of V_2O phase, and to determine the concentration of vacancies in the structure.

EXPERIMENTAL

The starting materials for the preparation were vanadium metal (Fairmount Chemical Co. 99.7 % pure) and NH_4VO_3 (reagent grade). Vanadium sesquioxide was obtained by reduction of NH_4VO_3 with hydrogen.

Preparations of the compositions to be investigated were obtained by melting pressed pellets consisting of weighed amounts of vanadium metal and vanadium sesquioxide in an electric arc furnace containing an atmosphere of argon.

The samples were subsequently heat-treated in sealed, evacuated silica tubes at 900°C for one week.

The preparations were analyzed by oxidation to V_2O_5. The reaction was carried out by heating a portion of a sample in a platinum crucible over a Meker burner while a stream of oxygen gas was directed into the crucible.

The phase analyses were performed by means of X-ray powder photographs taken in a Guinier focusing camera of 80 mm diameter with monochromatized Cu$K\alpha$ radiation.

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An aluminium foil (35 μ) covering the film served to reduce the background caused by fluorescent radiation from the samples. Potassium chloride was added to the specimens as an internal standard. Details of the techniques employed in the X-ray work have been given in a previous article [2].

RESULTS

The most prominent lines of the X-ray powder diffraction patterns of the V_2O preparations could be indexed by assuming a monoclinic unit cell which is a slightly distorted version of the V_4O cell. The sublattice parameters are nearly equal to those of the oxygen-saturated V_4O phase.

The results of the phase analyses of the heat-treated samples are given in Table 1 and Fig. 1. Most of the raw arc-melted samples contained a mixture of V_4O, V_2O and VO.

The V_2O phase appears to be homogeneous (at 900°C) between the limits $VO_{0.45_5}$—$VO_{0.54_6}$.

A multiplication of all three subcell axes by five allows all diffraction lines to be indexed. The indexing and lattice parameters found from a Guinier photograph of $VO_{0.530}$ are given in Table 2.

In spite of repeated efforts, no single crystals of V_2O have been obtained.

Table 1. Lattice parameters of VO_x (900°C).

x	a (Å)	b (Å)	c (Å)	β°	Phases observed
0.329					V_4O
0.405					$V_4O + (V_2O)$
0.418	2.948	2.934	3.549	90.29	$V_4O + V_2O$
0.434	2.945	2.933	3.550	90.28	$V_4O + V_2O$
0.452	2.946	2.934	3.552	90.27	$(V_4O) + V_2O$
0.469	2.943	2.932	3.558	90.29	V_2O
0.512	2.939	2.929	3.573	90.40	V_2O
0.530	2.942	2.926	3.585	90.38	V_2O
0.562					$V_2O + VO$
0.588	2.942	2.925	3.586	90.39	$V_2O + VO$

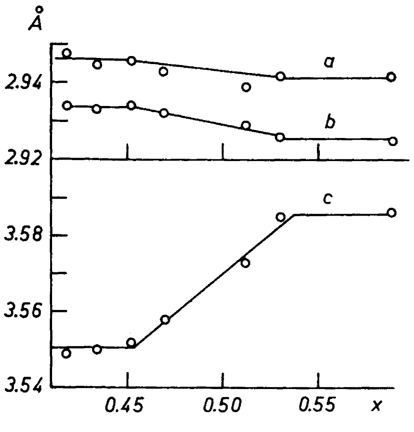

Fig. 1. Lattice parameter variation with composition (VO_x) in the V_2O phase.

Table 2. Guinier powder pattern of $VO_{0.530}$. Cu$K\alpha$ radiation. Lattice parameters found:

$a = 14.710 = 5 \times 2.942$ Å
$b = 14.630 = 5 \times 2.926$ Å
$c = 17.925 = 5 \times 3.585$ Å
$\beta = 90.38°$

Intensity	h	k	l	$\sin^2\Theta_{obs.}$	$\sin^2\Theta_{calc.}$	$(\sin^2\Theta_{obs.} - \sin^2\Theta_{calc.}) \times 10^5$
vvw	$\bar{1}$	0	2	0.01005	0.01011	− 4
m	$\bar{5}$	0	5	0.11459	0.11458	+ 1
s	5	0	5	0.11607	0.11606	+ 1
	0	5	5		0.11604	+ 3
vvw	$\bar{2}$	0	8	0.12920	0.12938	− 18
(vvw	2	1	8	0.13352	0.13311	+ 41)
vvs	5	5	0	0.13862	0.13852	+ 10
vw	$\bar{1}$	3	8	0.14641	0.14641	0
w	7	0	4	0.16562	0.16558	+ 4
vw	8	0	2	0.18348	0.18334	+ 14
w	0	0	10	0.18567	0.18567	0
vvw	4	1	10	0.23370	0.23373	− 3
w	10	0	0	0.27561	0.27561	0
vw	0	10	0	0.27847	0.27847	0

A survey of the change in lattice parameters over the composition range $V - VO_{1.27}$ is given in Fig. 2. The diagram shows clearly the progressive deformation of the unit cell from b.c.c. in vanadium to f.c.c. in VO (and its continuation to $VO_{1.27}$).

The data for V and V_4O are taken from Seybolt and Sumsion [3]. The body-centered tetragonal (sub-)lattice parameters for VO and $VO_{1.27}$ are calculated from the figures given in Ref.[1] for the corresponding face-centered lattices.

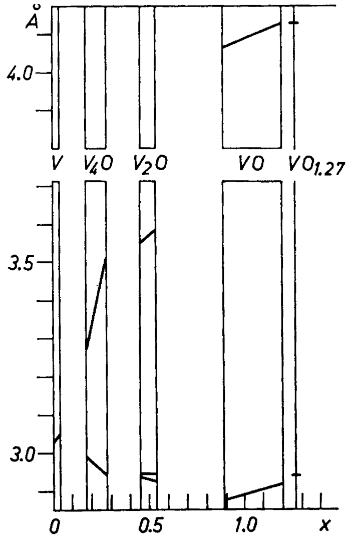

Fig. 2. Lattice parameters of body-centered subcell of VO_x.

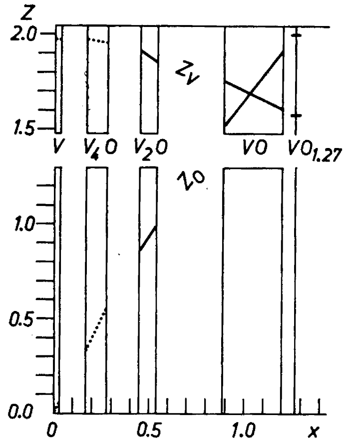

Fig. 3. Number of atoms per body-centered subcell of VO_x.

Using the density data from Ref.[1], the number of oxygen and vanadium atoms per subcell have been calculated and plotted in Fig. 3. The density of vanadium metal, 5.98 g cm^{-3}, has been taken from Ref.[4] The data do not allow an accurate determination of the lattice occupancies in V and V_4O. The corresponding lines are dotted in the diagram.

The most notable features in the diagram are the indications that the subcell contains exactly one oxygen atom in $VO_{0.54}$ and exactly two oxygen atoms in $VO_{1.27}$.

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