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Phase Analysis Studies on the Vanadium — Oxygen System within the $VO_{0.25}$—$VO_{1.5}$ Region at 800° C

SVEN WESTMAN and CLAES NORDMARK

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The lower vanadium oxides existing at 800° have been investigated by X-ray methods. Powder diffraction data are given for the two phases $VO_{0.53}$ and $VO_{1.27}$. The homogeneity range and lattice occupancy of the VO phase have been established.

The phase relations of the vanadium-oxygen system have been studied by several investigators, using various methods. The results may be summarized as follows. The solubility limit for oxygen in b.c.c. vanadium (α phase) was found, by Tucker, Seybolt and Sumsion [1], to be 3.2 at. % ($VO_{0.033}$). Rostoker and Yamamoto [2] found this to be valid only above 900°C, the solubility decreasing at lower temperatures.

The tetragonal β phase, "V_4O", obtained by Seybolt and Sumsion [3] was shown to be homogeneous between 15 and 21.8 at. % O (*i.e.* $VO_{0.17}$—$VO_{0.28}$). This was confirmed by Schönberg [4] and by Rostoker and Yamamoto [2].

Klemm and Grimm [5] found X-ray diffractograms of $VO_{0.3}$ to contain weak reflexions in addition to those given by the tetragonal phase. They ascribed this to a continuous deformation of the tetragonal lattice. From metallographic evidence, Rostoker and Yamamoto [2] postulated the existence of a δ phase which they thought to be V_2O. The phase was, however, never obtained in a pure state. The authors gave a tentative indexing of the X-ray pattern of the δ oxide, assuming a hexagonal unit cell.

The homogeneity range of the "VO" phase, which has a structure of the sodium chloride type [6], was found, by Schönberg [4] and Andersson [7], to extend from $VO_{0.80}$ to $VO_{1.20}$ at 900°C. Schönberg [4] assumed the vanadium lattice to be only partly occupied by atoms above the composition $VO_{1.0}$.

The existence of an "X phase" ($VO_{\sim 1.3}$) proposed by Klemm and Grimm [5] has not been confirmed by subsequent work.

The corundum structure of the sesquioxide was established by Goldschmidt *et al.*[8]

Phase analyses by Andersson [7] and Aebi [9] cover the higher vanadium oxides.

In connection with a wider research programme covering the oxide chemistry of several transition metals, a reinvestigation of the lower vanadium oxides was thought desirable, considering the rather incomplete evidence reviewed above.

EXPERIMENTAL

The starting materials for the preparations were vanadium metal (Fairmount Chemical Co. 99.7 % pure) and vanadium pentoxide (LKB-produkter, reagent grade). Vanadium sesquioxide was obtained by reduction of vanadium pentoxide with hydrogen[10].

Preparations of vanadium oxides with compositions between $VO_{0.25}$ — $VO_{1.5}$ were obtained by melting pressed pellets consisting of weighed amounts of vanadium metal and vanadium sesquioxide in an argon atmosphere by means of an electric arc furnace[11]. The samples were subsequently heat-treated in sealed, evacuated silica tubes at 800°C for two weeks and then quenched in water.

The preparations were analyzed for oxygen content by dissolution in cerium(IV) sulphate solution followed by back-titration with iron(II) sulphate solution. The procedure is similar to the one described by Reuter and Siewert[12]. A weighed sample ($\sim$0.1 g) of finely divided oxide was dispersed in 10 ml of 50 % sulphuric acid and dissolved by addition of $Ce(SO_4)_2$ solution in excess, so that all the vanadium was oxidized to the vanadyl state. During the dissolution process the mixture was kept hot and the sample was ground with a glass rod. After cooling and dilution, 5 ml of concentrated phosphoric acid was added, and the small amount of vanadate formed back-titrated to the vanadyl state using ferrous ammonium sulphate solution, with diphenylamine sulphonic acid as indicator.

The phase analysis was performed by means of X-ray powder photographs taken in a Guinier focusing camera of 80 mm diameter with strictly monochromatized $CuK\alpha_1$ radiation. An aluminium foil (35 μ) covering the film served to reduce the background fogging caused by fluorescent radiation from the samples. Potassium chloride (a = 6.2919 Å at 20°C[13]) 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[14].

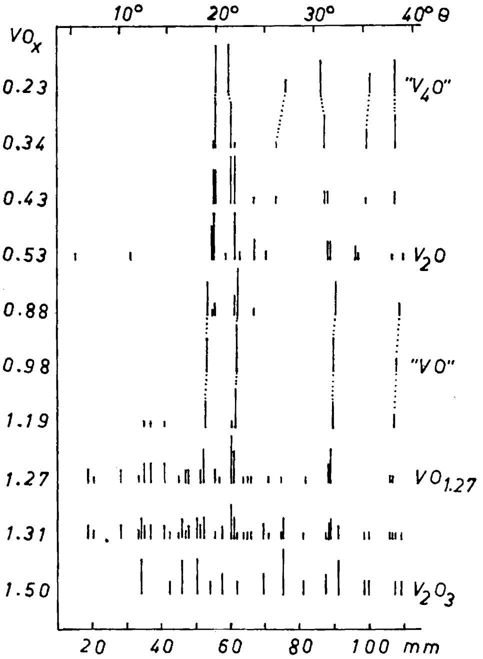

Fig. 1. Powder patterns of VO_x samples.

Table 1. Guinier powder pattern of $VO_{0.53}$. Cu$K\alpha_1$ radiation.

Intensity	$\sin^2\Theta_{obs}$
vw	0.00978
vvw	0.03920
m	0.11386
s	0.11547
vvw	0.12858
vs	0.13802
w	0.14556
m	0.16465
vw	0.18246
w	0.18439
w	0.27441
w	0.27716
w	0.32074
vw	0.32391
vw	0.38823
w	0.39216

RESULTS

The present phase analysis has established the existence of two phases with the approximate compositions $VO_{0.53}$ and $VO_{1.27}$. The results are summarized in Fig. 1. The homogeneity range of the "VO" phase and the occupancy of its vanadium and oxygen lattices have been determined.

The "V_4O" phase appears to be homogeneous up to the composition $VO_{\sim 0.3}$. No accurate determination of the phase boundary has been made however, since the result seemed to be in fairly good agreement with previously published work.

The $VO_{0.53}$ phase (possibly V_2O) seems to have an extremely narrow range of composition. X-Ray powder data are given in Table 1. It is evident from Fig. 1 that the structure of "V_2O" represents a transition between the V_4O and the VO structures. It has not been possible so far to obtain single crystals of this phase.

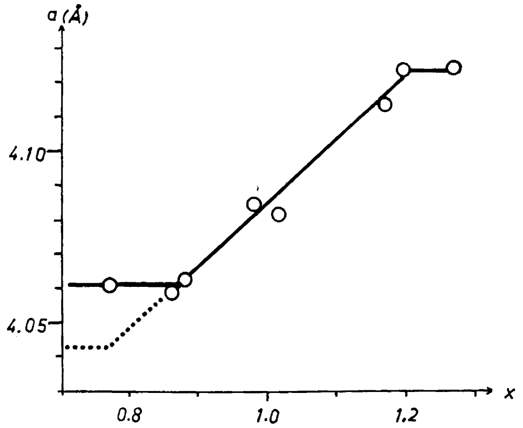

Fig. 2. Lattice parameter of VO_x (800°C).

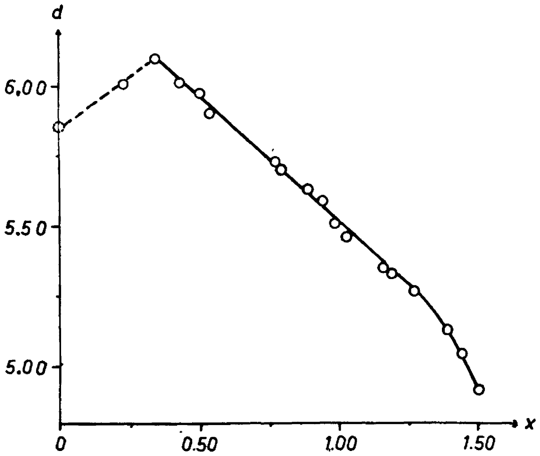

Fig. 3. Density of VO_x samples (g cm^{-3})

The cubic "VO" phase is homogeneous between the limits $VO_{0.89}$ and $VO_{1.20}$. The lattice parameter varies between $a = 4.062$ Å and $a = 4.125$ Å (Fig. 2).

Schönberg[4] found a somewhat extended homogeneity range towards lower oxygen content at 900°C (indicated by the dotted line in Fig. 2). The lattice parameter *vs.* composition curve obtained in the present investigation is, within its limits, in excellent agreement with the results of Schönberg[4] and Andersson[7].

The densities of the oxide preparations have been determined (Fig. 3) and the occupancy of the vanadium and oxygen lattices of the NaCl-type structure calculated for various compositions of the "VO" phase. The result is shown in Fig. 4.

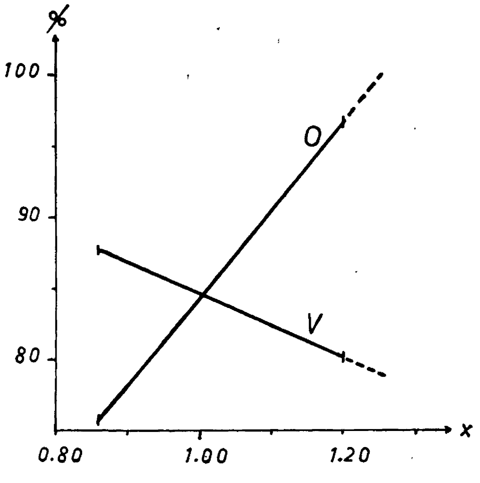

Fig. 4. Percent occupancy of atomic sites in cubic VO_x.

Table 2. Guinier powder pattern of $VO_{1.27}$. $CuK\alpha_1$ radiation. Lattice parameters found: $a = b = 16.623 \pm 0.005$ Å; $c = 16.515 \pm 0.004$ Å.

Intensity	$h\,k\,l$	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	$(\sin^2\Theta_{obs}-\sin^2\Theta_{calc}) \times 10^5$
w	1 1 2	0.01306	0.01300	+ 6
vw	2 0 2	0.01729	0.01729	0
vw	2 1 3	0.03034	0.03031	+ 3
vw	2 0 4	0.04343	0.04339	+ 4
m	3 2 3	0.04750	0.04749	+ 1
m	2 2 4	0.05213	0.05198	+15
s	5 1 2	0.06464	0.06453	+11
vw	4 2 4	0.07780	0.07775	+ 5
vw	1 1 6	0.08283	0.08260	+23
w	6 0 2	0.08596	0.08600	− 4
w	3 1 6	0.09987	0.09978	+ 9
vs	4 4 4	0.01351	0.10351	0
vw	7 1 2	0.11614	0.11606	+ 8
vw	6 2 4	0.12088	0.12069	+19
vw	7 3 2	0.13330	0.13323	+ 7
vs	8 0 0	0.13741	0.13741	0
vs	0 0 8	0.13927	0.13922	+ 5
vw	5 3 6	0.15127	0.15131	− 4
vw	2 2 8	0.15642	0.15640	+ 2
vw	9 1 2	0.18493	0.18476	+17
vw	$\begin{Bmatrix}9\ 2\ 3\\7\ 6\ 3\end{Bmatrix}$	0.20205	0.20208	− 3
vw	6 3 7	0.20310	0.20321	−11
vw	3 1 10	0.23917	0.23900	+17
s	8 8 0	0.27489	0.27483	+ 6
s	8 0 8	0.27646	0.27663	−17
vw	12 4 4	0.37832	0.37834	− 2
vw	4 4 12	0.38185	0.38195	−10
m	8 8 8	0.41389	0.41404	−15

The upper composition limit, $VO_{1.20}$, represents an almost completely occupied oxygen lattice (96 %), whereas no similar relation defines the lower phase boundary. It is noteworthy that the boundaries of the high-temperature "TiO" phase with the same type of structure ($TiO_{0.64}$—$TiO_{1.26}$) are defined by 96 % and 98 % occupancy of the Ti and O lattices, respectively [15].

The $VO_{1.27}$ phase forms below ~ 900°C and appears to have a very narrow range of homogeneity. The X-ray powder diffractogram given in Table 2 has been indexed on the basis of single crystal data. The symmetry of the phase is body-centered tetragonal with

$$\begin{aligned} a = b &= 16.623 \text{ Å} = 4 \times 4.156 \text{ Å} \\ c &= 16.515 \text{ Å} = 4 \times 4.129 \text{ Å} \\ V &= 4\,563 \text{ Å}^3 \end{aligned}$$

The diffraction symmetry is pseudo-cubic with reflexions $h00$, $h \neq 4n$, missing. It is shown, by single crystal as well as powder data, that the crystal structure is a superstructure of a slightly deformed VO (NaCl-type) structure.

The observed density of the phase indicates that the vanadium lattice is only partly occupied. The vacancies should, on the above evidence, be ordered; and the number per unit cell, a multiple of four. If the cell content is assumed to be $V_{204}O_{256}$, observed and calculated values of density and composition agree rather well:

obs.	*calc*
$d = 5.269$	$d = 5.272$
$VO_{1.269}$	$VO_{1.255}$

$VO_{1.27}$ ought to be the "X phase" reported by Klemm and Grimm [5]. Crystal structure studies are in progress.

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