X-Ray Studies on Vanadium and Chromium Oxides with Low Oxygen Content

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METALLIC VANADIUM OXIDES

Samples of vanadium oxides with oxygen contents up to the composition $\text{VO}_{1.30}$ were obtained by heating vanadium metal powder (Vanadium Corporation of America, 99.7 % Grade) and dried vanadium pentoxide (Schuchardt, reinst. ca. 100 %) or vanadium trioxide *in vacuo* at a temperature of 1 000° C. V_2O_3 was prepared by the reduction of V_2O_5 in oxygen-free hydrogen at a temperature of 800° C for about three hours. The powder mixtures of metal and oxide were poured into alumina tubes, placed in silica tubes, which were then evacuated, sealed and heated at 1 000° C for about one week. As it proved difficult to achieve equilibrium most of the samples from these reactions were powdered again, moulded into small brickettes and heated in zirconia crucibles in a high frequency vacuum induction furnace¹ up to about 1 600° C. In order to detect the possible presence of high temperature modifications of the oxides, some samples were heated *in vacuo* at temperatures between 600° C and 1 200° C and then quenched in cold water.

X-ray powder photographs of the samples taken in a Guinier focusing camera with monochromatized Cr- K_α radiation revealed the existence of three phases, *viz.* vanadium, the vanadium oxide with the metal atoms in a tetragonally deformed vanadium lattice² and the approximate homogeneity range $\text{VO}_{0.15}$ — $\text{VO}_{0.25}$, and the vanadium oxide ("VO phase")^{3,4} with the sodium chloride structure. The VO phase was found to have a wide range of homogeneity, with the limits $\text{VO}_{0.80}$ and $\text{VO}_{1.20}$.

As the present investigation confirmed in all respects the recently published results about the vanadium phase and the phase $\text{VO}_{0.15}$ — $\text{VO}_{0.25}$ obtained by Seybolt and Sumsion², there is no need to repeat the actual data.

The X-ray patterns of the specimens with the compositions $\text{VO}_{0.80}$ and $\text{VO}_{1.20}$ showed only VO-reflections. But additional lines of the $\text{VO}_{\sim 0.2}$ phase were visible in the photograph when the composition of the oxide was $\text{VO}_{0.75}$, and the pattern of the V_2O_3 phase appeared for the composition $\text{VO}_{1.25}$.

The lattice constant was found to increase from $a = 4.042 \text{ \AA}$ ($\text{VO}_{0.80}$) to $a = 4.126 \text{ \AA}$ ($\text{VO}_{1.20}$). This result is not in agreement with the statement of

Table 1. Calculated and observed densities for the VO phase.

Phase composition	Density (<i>d</i>)		<i>d</i> _{calc.} - <i>d</i> _{obs.}
	calculated	observed	
VO _{0.80}	6.41	6.12	0.29
VO _{0.90}	6.39	6.01	0.38
VO _{1.00}	6.49	5.92	0.37
VO _{1.10}	6.29	5.66	0.63
VO _{1.20}	6.08	5.50	0.58

Klemm and Grimm³, that the cube edge decreases from $a = 4.11$ Å at the composition VO_{0.9} to $a = 4.10$ Å at the composition VO_{1.3}. Also, these authors suggest that the cubic VO phase exists only at high temperatures, and that it decomposes at low temperatures into pure vanadium or a solid solution of oxygen in vanadium and an "X-phase" of undetermined composition and structure (not the V₂O₃ phase). This is contradicted by the fact that samples with the compositions VO_{0.80} and VO_{1.00} did not change their structure on being cooled *in vacuo* from 800° C to room temperature over a period of eight weeks, and the fact that a sample with the composition VO_{1.30} proved to be a mixture of the VO and V₂O₃ phases after the same cooling procedure.

Mathewson, Spire and Samans⁴ and Anderson⁵ report that the unit cell dimensions increase with increasing oxygen content, which is in agreement with the present result.

For a sample with the composition VO_{1.00} the lattice constant was found to be $a = 4.093$ Å. The V-V distances (12-coordination) are 2.89 Å and the O-V distances (6-coordination) 2.05 Å. If the oxygen content is greater than 50 atom-%, this must be due to vanadium atom vacancies in the close-packed metal lattice. It is not possible for oxygen to replace vanadium atoms because the resulting O-O distance would be 2.05 Å. The shortest O-O distances observed in oxides are of the order 2.6 Å, this value being characteristic of oxides with ionic as well as metallic properties.

Table 1 lists the densities calculated on the assumption that all vanadium sites are occupied in samples with an oxygen content up to 50 atom-% and that the vanadium lattice is defective in samples with a greater oxygen content. The accuracy of the density determinations is not great enough to give quantitative information about the percentage of unoccupied atomic positions in the unit cell. But the experimental results seem to indicate a defective lattice even for the composition VO_{1.00}.

It may be of interest to compare the VO phase with the analogous TiO phase. Ehrlich⁶ reports the homogeneity range TiO_{0.58}—TiO_{1.33} for this metallic oxide with the lattice constant varying between 4.184 Å and 4.152 Å. He further states that 15 % of the atomic sites are unoccupied at the composition TiO_{1.00}.

THE METALLIC CHROMIUM OXIDE Cr₂O

In connection with an investigation of metallic double-oxides containing two transition elements, Cr₂O₃ (Baker's Analyzed) was reduced with titanium, vanadium and zirconium in a high frequency vacuum induction furnace¹ at

Table 2. Observed and calculated intensities for the Cr_3O phase.

<i>hkl</i>	<i>I</i> _{calc.}	<i>I</i> _{obs.}
1,1,0	260	200
2,0,0	46	50
2,1,0	532	500
2,1,1	113	130
2,2,0	43	50
3,1,0	75	80
2,2,2	195	200
3,2,0	233	200
3,2,1	107	130
4,0,0	93	80
4,1,1	41	50
3,3,0	21	20
4,2,0	41	50
4,2,1	279	300
3,3,2	32	30
4,2,2	30	30
5,1,0	30	30
4,3,1	61	50
5,2,0	118	100
4,3,2	238	200
5,2,1	65	80
4,4,0	216	200

about 1 500° C. Besides oxides of titanium, vanadium and zirconium, a new phase was obtained with the atoms in a comparatively small cubic unit cell. As the same compound was formed in small amounts in the oxidation of chromium metal powder (Ferrolegeringar, Stockholm, 99.4 %) by steam in a large excess of hydrogen at a temperature of 600° C, this new phase must be a chromium oxide with an oxygen content smaller than that of Cr_2O_3 . In spite of several experiments it was not possible to obtain this oxide in a pure state. The reaction between chromium metal and Cr_2O_3 in an induction furnace only yielded traces of the low-oxygen oxide.

A comparison of the powder photographs of the oxide phase and of Cr_3Si indicated that these two compounds were isomorphous, both having the β -tungsten structure (A 15 type). The probable formula of the oxide is therefore Cr_3O . The cubic lattice constant was found to be 4.544 Å ($V = 93.83 \text{ Å}^3$). The previously known compounds with the β -tungsten structure are V_3Si^7 ($a = 4.71 \text{ Å}$), Cr_3Si^8 ($a = 4.55 \text{ Å}$), Mo_3Si^9 ($a = 4.81 \text{ Å}$), V_3Ge^{10} ($a = 4.76 \text{ Å}$), $\text{Cr}_3\text{Ge}^{10}$ ($a = 4.61 \text{ Å}$) and $\text{Mo}_3\text{Zr}^{11}$ ($a = 4.94 \text{ Å}$) *.

The space-group is $O_h^3\text{—}Pm\bar{3}n$ with 6 Cr in 6(c): $\frac{1}{4}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{4}, 0; 0, \frac{1}{2}, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4}; 0, 0, \frac{1}{2}, \frac{3}{4}$ and 2 O in 2(a): $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

Calculated and observed relative intensities are compared in Table 2, and interatomic distances are listed in Table 3.

* The molybdenum-zirconium system has been investigated by the author, and the only intermediate phase existing in this system was found to be Mo_2Zr of the Laves C15 type. The cubic lattice constant $a = 7.563 \text{ Å}$. The compound Mo_3Zr of A15 type reported by Wallbaum ¹¹ is probably an oxide analogous to Cr_3O .

Table 3. Interatomic distances in the Cr_3O phase.

Atom	Surrounding Atoms	Interatomic Distance, Å
Cr	2 Cr	2.272
	8 Cr	2.779
	4 O	2.520
O	12 Cr	2.520

It is evident from Table 3 that the mean intermetallic distance is 2.68 Å (10-coordination). It is not possible to calculate the accurate oxygen positions from X-ray investigations, but $p|F|^2$ values corresponding to the distribution of two or three oxygen atoms in ordered or disordered 6(c) positions show poor agreement with the observed intensities. Hence the atomic positions given above are the most likely ones.

It is remarkable that the oxygen atoms are surrounded by twelve chromium atoms at abnormally large distances. All metallic oxides previously known have the oxygen atoms at the centres of metal atom octahedra with the interatomic oxygen-metal distance equal to or slightly greater than the sum of the metal atom radius and the oxygen atom radius. In Cr_3O the corresponding distance may be formally written as: chromium atom + oxygen ion.

The existence of an oxide CrO , probably of the wurtzite type, assumed by Lux and Proeschel¹² has not been confirmed.

[SUMMARY

The vanadium-oxygen system has been investigated by X-ray methods up to an oxygen content corresponding to the composition $\text{VO}_{1.30}$ (56.5 atom-% of O). Three phases were found to occur, *viz.* the vanadium phase (α), the vanadium oxide with the metal atoms in a tetragonally deformed vanadium lattice and the approximate homogeneity range $\text{VO}_{0.15}$ — $\text{VO}_{0.25}$ (β), and the VO phase with the sodium chloride structure (γ). The results reported by Seybolt and Sumsion² for the α and the β phases have been confirmed in all respects. The homogeneity limits of the VO phase have been found to be $\text{VO}_{0.80}$ (44.5 atom-% of O) and $\text{VO}_{1.20}$ (54.5 atom-% of O), with the lattice constants $a = 4.042$ Å and $a = 4.126$ Å respectively.

A chromium oxide of the β -tungsten structure has been prepared. The most likely formula is Cr_3O .

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