Formation of Chromium Oxides in the Cr_2O_3 — CrO_3 Region at Elevated Pressures up to 4 Kilobar

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The formation of intermediary chromium oxides has been studied by heating chromium trioxide or mixtures of chromium trioxide and lower chromium oxides at elevated pressures. The experimental equipment is described. Pressure and temperature regions of formation are given for five intermediary phases observed, *viz.* β-oxide ($CrO_{2.65}$), γ-oxide ($CrO_{2.44}$), Cr_6O_{15}, Cr_5O_{12} and CrO_2. None of these phases seems to have an extended range of homogeneity.

The literature on the phase conditions and structural chemistry of chromium oxides has for several decades reflected a rather incomplete and confusing state of knowledge. This is obviously a consequence of the thermodynamic properties of the Cr—O system and in particular of the tendency of some oxygen rich chromium oxides to dissociate at elevated temperatures. So far these oxides have only been obtained at relatively low temperatures (200—350°C at atmospheric pressure), at low rates and as poorly defined products.

During the past few years the introduction of high pressure techniques has provided a new successful line of attack on this problem. The development of new alloys with greatly increased strengths at elevated temperatures has made possible the construction of simple pressure vessels that can be used for investigating equilibrium relations at high temperatures and pressures. Research which previously required expensive and cumbersome equipment can now be carried out much more readily with the aid of the new alloy tools and at considerably less expense. It was thought worth-while to reinvestigate the system and in particular to extend the phase analysis to the wider oxygen pressure range now excessible.

EXPERIMENTAL

The starting material was chromium trioxide, CrO_3 ("Baker's Analyzed"), dried at 150°C and stored over phosphorus pentoxide. In several experiments, lower-oxide preparations were used as starting materials, *viz.* CrO_2 and Cr_2O_3. These samples were obtained from CrO_3 by heating at elevated oxygen pressures.

The *heat-treatment* of the samples was performed at normal pressure (Method A) or at elevated oxygen pressures (Method B). The "open air" experiments were carried out in platinum crucibles with 3—5 g charges of CrO_3 in electric resistance furnaces. The heating was extended over considerable periods of time (5—7 days) which in general were found to be necessary in order to obtain constant chromium/oxygen ratios in the products.

The high-pressure experiments were performed using an apparatus built at this Institute. The autoclave, shown in Fig. 1, is a cylinder of Stellite 25 or Nimonic 115 with a 5 mm axial hole drilled from one end to within 30 mm of the other end. The closed end is placed downwards in Kanthal-wound tube furnace, the water-cooled pressure connection of the autoclave being outside the furnace. The seal is made against a conical seat at the top of the vessel by the pressure induced by torque applied to the cap on the cone-shaped end of the high-pressure water line.

The samples are kept in platinum or gold capsules made from 3 mm wide and 0.1 mm thick metal tubes. The end of the tube is squeezed shut and welded with a micro-welder. The charge (100-200 mg in the case of CrO_3) is then inserted and the tube is sealed at the top with the microwelder while held in a vice to avoid any harmful heating of the charge.

The capsule is then placed within the hole of the autoclave. The pressure applied outside the capsule is obtained by a simple water pressure intensifier (*cf.* Fig. 2) and controlled with a needle valve and a high pressure Bourdon gauge.

The furnace temperature is kept constant by a regulator. A calibrated chromel-alumel thermocouple is inserted into a hole at the bottom of the autoclave and the temperature is measured with at potentiometer bridge at the beginning and end of the heat treatment and is, furthermore, continually registered during the treatment by a recorder. The total variations observed are within ±3°C. The autoclave is usually quenched in water from the reaction temperature.

The oxygen needed for stabilizing the phases formed in the sample is supplied by the partial decomposition of the oxide charge. The flexibility of the thin-walled capsules makes possible an automatic control of the internal oxygen pressure over the partly decomposed sample with respect to the external water pressure.
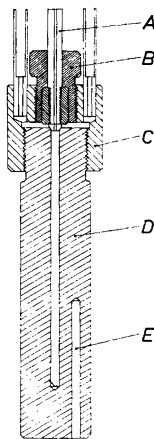

Fig. 1. Autoclave made of Nimonic 115 with a cold cone seat closure. A, High pressure tubing with a threaded collar. B, Glandnut. C, Water-cooled cover. D, Vessel. E, Thermocouple hole.
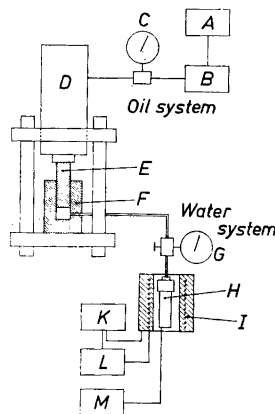
Fig. 2. Schematic diagram of apparatus having a working range up to 900°C and 5000 bars. A, Oil reservoir. B, Pump. C, Low-pressure manometer. D, Ram. E, Piston. F, Steel cylinder with high-pressure tubing. G, Bourdon gauge with valve. H, Autoclave. J, Furnace. K, Power supply. L, Regulator. M, Temperature recorder.
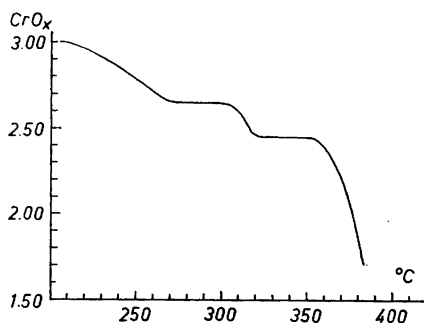
Fig. 3. Composition *versus* formation temperature for chromium oxides obtained by the thermal decomposition of CrO_3 at atmospheric pressure.
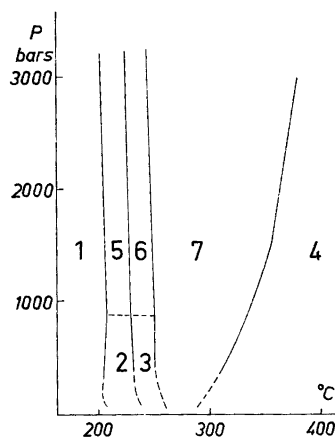
Fig. 4. Pressure-temperature diagram for formation of chromium oxides. The areas 1—7 represent the following compounds. 1, CrO_3. 2, β-Oxide. 3, γ-Oxide. 4, Cr_2O_3. 5, Cr_6O_{15}. 6, Cr_5O_{12}. 7, CrO_2.

The technique described above was applied in the phase analysis studies on the chromium-oxygen system. It was also used for the preparation of single crystals for X-ray analysis of two new binary oxides Cr_5O_{12}[1,2] and Cr_6O_{15}[1,3]. In all these syntheses, the pressure medium in direct contact with the samples was oxygen formed from the CrO_3 content in the charge. Some experiments were also made with small additions of water to the charge.

The chromium contents of all samples prepared by method (A) were determined by chemical analysis. After drying in an oven at 150°C, the sample was dissolved in hot concentrated sulphuric acid or in water (β-oxide). The chromium content was determined using Mohr's salt and standard permanganate solution after oxidation by peroxodisulphate in the presence of silver ions. The reproducibility of the analyses was found to be good.

The densities of several samples were determined from the loss of weight in benzene.

Powder photographs obtained at room temperature have been used in order to identify the phase composition of quenched samples and to determine accurate lattice dimensions.

The powder photographs were taken in a Guinier focusing camera of 80 mm diameter with monochromatized $CuK\alpha_1$ radiation. In order to depress the back-ground fogging caused by the fluorescence radiation, an aluminium filter foil of 35 μ thickness was placed in contact with the photographic film. Potassium chloride (Analar, BDH, ground and recrystallized) was added to the powder specimens as an internal standard, and its lattice parameter was taken to be $a = 6.2919$ Å (20°C) according to Hambling.[4]

The calculations of the cell parameters were carried out on a Facit EDB digital computer by means of a program written by Werner and designed to determine accurate dimensions by the method of least squares.

PHASE ANALYSIS

In Fig. 3 the results of 54 decomposition experiments with CrO_3 at atmospheric pressure covering the temperature range 200—400°C are summarized. The appearance of the diagram corrresponds essentially to those given earlier

Table 1. Products of heat treatment of mixtures of chromium oxides.

Starting composition	Pressure bars	Reaction temperature °C	Results of phase analysis
a) *Mixtures of CrO_3 and CrO_2*			
$CrO_{2.20}$	2000	300	CrO_2
$CrO_{2.40}$	2000	240	$Cr_5O_{12}+CrO_2$
$CrO_{2.50}$	2000	230	Cr_5O_{12}
$CrO_{2.60}$	2000	220	$Cr_5O_{12}+Cr_6O_{15}$
$CrO_{2.70}$	2000	220	Cr_6O_{15}
$CrO_{2.80}$	2000	220	$CrO_3+Cr_6O_{15}$
b) *Mixtures of CrO_3 and Cr_2O_3*			
$CrO_{1.80}$	2000	350	$Cr_2O_3+CrO_2$
$CrO_{2.00}$	2000	300	CrO_2
$CrO_{2.50}$	2000	250	$CrO_2+Cr_5O_{12}$
$CrO_{2.50}$	1500	220	Cr_5O_{12}
$CrO_{2.50}$	1200	220	Cr_5O_{12}
$CrO_{2.50}$	900	220	$Cr_5O_{12}+\gamma$-oxide
$CrO_{2.50}$	700	220	γ-oxide $(+Cr_5O_{12})$
$CrO_{2.50}$	600	220	γ-oxide
$CrO_{2.70}$	1200	250	Cr_6O_{15}
$CrO_{2.70}$	900	250	$Cr_6O_{15}+\beta$-oxide
$CrO_{2.70}$	700	250	β-oxide $(+Cr_6O_{15})$
$CrO_{2.70}$	600	250	β-oxide

by Simon and Schmidt,[5] Glemser *et al.*[6] and Lorthioir and Michel,[7] if the relatively longer heat-treatments applied in this investigation are taken into account. Two intermediary oxides were observed. Following a suggestion in Ref. 6, the phases are called β-oxide and γ-oxide. For a further discussion of these oxides, see the description of the phases.

The high-pressure experiments were conducted using charges consisting of CrO_3 or mixtures of CrO_3 with lower chromium oxides. The results of 36 runs with CrO_3 (above 200 bars) are schematically summarized in Fig. 4 where the formation pressures *versus* temperatures are indicated for the five intermediary oxide phases found. These comprise, in addition to the β- and γ-oxides mentioned above, CrO_2 and two new oxide species denoted here by the formulae Cr_6O_{15} and Cr_5O_{12} (*cf.* below). It must be emphasized that the (p,T)-data given in Fig. 4 represent the formation conditions observed in this study which are not necessarily the true stability regions of the observed phases.

The results of a series of 18 runs with mixtures of CrO_3 and lower oxides (*cf.* Table 1) are consistent with those shown in Fig. 4.

Tables 3—9 list the powder patterns. Careful inspections of the powder photographs have given no evidence for the existence of ranges of homogeneity.

Some properties of the five intermediary phases obtained in these experiments are given below.

Table 2. Summary of earlier works on the β- and γ-oxides.

Oxide	Formation temperature °C	Reaction time hours	Oxygen pressure bars	O/Cr ratio	Suggested formulae	Ref.
β-Oxide	322	2	~50	2.67	Cr_3O_8	8
	267—304	6	1	2.60	Cr_5O_{13}	6
	230—293	4	90— 60	2.75—2.58	Cr_3O_8	9
	268—360	(1°C/min DTA)	0.2	2.63	Cr_8O_{21}	7
γ-Oxide	545	0.2	50	2.50	Cr_2O_5	8
	320—360	6	1	2.40—2.48	Cr_2O_{5-x}	6
	280—380	4	150—400	2.40	Cr_2O_5	9
	420—440	(1°C/min DTA)	0.2	2.44	$Cr_{16}O_{39}$ or $Cr_{11}O_{27}$	7

DESCRIPTION OF THE PHASES

β-Oxide. In Table 2, data on the β-oxide reported by some recent investigators are summarized. The formulae given to this oxide are mainly based on chemical analyses. Lorthioir and Michel [7] have concluded from magnetic measurements that the Cr(III)/Cr(VI) ratio in this oxide is 1:3. The analytical data obtained by the present author indicate that the composition of the β-oxide is close to $CrO_{2.65}$. The β-oxide was in this investigation prepared by decomposing CrO_3 in "open air" experiments in the temperature range 270—300°C. In the pressure experiments the formation of the oxide was observed in the temperature range 210—230°C at 200—600 bars. Higher pressures made the β-oxide disappear and resulted in the formation of the oxide Cr_6O_{15}.

The β-oxide forms dark-brown, very small crystallites, readily decomposed by water giving a solution containing chromium(III) and chromate(VI) ions.

γ-Oxide. The γ-oxide was observed by the present author in "open air" decomposition experiments with CrO_3 in the temperature range 320—350°C. It is formed in a pure state at 600 bars in the temperature range 235—250°C. At 1000 bars, however, the reaction product is Cr_5O_{12}.

The γ-oxide phase forms very small black needles, insoluble in water but soluble in dilute mineral acids to give chromate(VI) and chromium(III) ions. The analytical data of the γ-oxide obtained by the present author are in good agreement with those given by Lorthioir and Michel [7] (see Table 2), the O/Cr ratio being close to 2.44.

Cr_6O_{15}. The oxide Cr_6O_{15} was obtained in a pure state at pressures above 1000 bars and in the temperature range 210—230°C. It forms almost black, very thin plates, insoluble in water or dilute acids but soluble in conc. sulphuric acid at room temperature. The material is in general poorly crystallized. The powder pattern was indexed with the aid of single crystal data. The unit cell dimensions of the orthorhombic cell are $a=8.47$ Å, $b=12.90$ Å, $c=10.08$ Å, $V=1101$ Å³. The observed density 3.34 g cm⁻³, corresponds to a cell content of 4 units of Cr_6O_{15},[1] this formula being supported by the structure determination.[3]

Table 3. Powder photograph of CrO_3. Dimensions of the orthorhombic unit cell: $a=4.789$ Å, $b=8.557$ Å, $c=5.743$ Å.

I_{obs}	$10^4\sin^2\theta_{obs}$	$h\ k\ l$	$10^4\sin^2\theta_{calc}$
w	0328	0 2 0	0324
v st	0343	1 1 0	0340
v st	0506	0 2 1	0504
v st	0524	1 1 1	0520
st	0721	0 0 2	0720
v v w	0994	1 3 0	0988
st	1036	$\begin{cases} 2\ 0\ 0 \\ 0\ 2\ 2 \end{cases}$	1036 \\ 1044
st	1062	1 1 2	1060
st	1174	1 3 1	1168
m	1481	0 4 1	1477
st	1536	2 2 1	1540
v v w	1756	2 0 2	1756
m	1948	$\begin{cases} 0\ 2\ 3 \\ 1\ 1\ 3 \end{cases}$	1949 \\ 1961
w	2021	0 4 2	2017
w+	2080	2 2 2	2080
v w	2294	1 5 0	2285
v w	2337	2 4 0	2332
v w	2414	3 1 0	2412
v w	2514	2 4 1	2512

Table 4. Powder photograph of β-oxide ($CrO_{2.65}$).

I_{obs}	$10^4\sin^2\theta_{obs}$	I_{obs}	$10^4\sin^2\theta_{obs}$
m	42	v w	683
w	155	v v w	751
w	174	v w	832
v w	242	v w	878
v w	294	v v w	1307
st	393	v v w	1463
m	429	v v w	1580
m st	532	v w	1722
w	576	v v w	2010
m st	625		

Table 5. Powder photograph of γ-oxide ($CrO_{2.44}$).

I_{obs}	$10^4\sin^2\theta_{obs}$
m st	83
m	153
m	168
v v w	226
v w	396
w	490
st	558
v v w	625
w	751
v w	784

Table 6. Powder photograph of Cr_6O_{15}. Dimensions of the orthorhombic unit cell: $a=$ 8.47 Å, $b=12.90$ Å, $c=10.08$ Å.

I_{obs}	$10^5\sin^2\theta_{obs}$	$h\ k\ l$	$10^5\sin^2\theta_{calc}$
m	1 435	0 2 0	1 429
st	2 344	0 0 2	2 337
w	3 537	1 1 2	3 524
v w	3 782	0 2 2	3 766
m	4 054	1 3 0	4 044
m	4 753	2 2 0	4 745
st	5 654	2 0 2	5 653
m	5 718	0 4 0	5 717
st	6 453	1 1 3	6 446
w	7 088	2 2 2	7 083
m	7 821	3 1 0	7 818
m	8 408	3 1 1	8 403
v v w	9 322	1 3 3	9 298
v v w	9 370	0 0 4	9 344
v v w	10 036	2 2 3	10 000
v w	11 382	2 4 2	11 370
v v w	12 678	2 0 4	12 660
w	13 045	3 3 2	13 015
w	13 082	3 1 3	13 078
v v w	13 256	4 0 0	13 264
v v w	13 421	0 6 1	13 436
v v w	15 028	1 5 3	15 010
v v w	15 577	4 0 2	15 600
v v w	15 737	1 1 5	15 786
v w	16 389	3 5 0	16 394

Table 7. Powder photograph of Cr_5O_{12}. Dimensions of the orthorhombic unit cell: $a=$ 12.04 Å, $b=8.21$ Å, $c=8.18$ Å.

I_{obs}	$10^5\sin^2\theta_{obs}$	$h\ k\ l$	$10^5\sin^2\theta_{calc}$
v w	1 645	2 0 0	1 639
v w	2 183	1 1 1	2 180
v w	3 533	0 2 0	3 525
v w	3 559	0 0 2	3 555
v v w	3 971	1 0 2	3 695
w	4 415	0 2 1	4 414
m	4 563	3 1 0	4 568
st	4 817	1 2 1	4 824
v w	4 841	1 1 2	4 846
w	5 193	2 0 2	5 194
v w	5 472	3 1 1	5 457
v v w	6 058	2 2 1	6 053
v w	7 249	3 0 2	7 242
v w	7 491	1 2 2	7 490
m	8 325	4 1 1	8 325
w	9 231	1 3 1	9 231
w	9 282	1 1 3	9 289
v w	10 116	4 0 2	10 110
w	10 454	2 3 1	10 460
v w	10 523	2 1 3	10 518
v w	10 762	3 2 2	10 767

Table 8. Powder photograph of CrO_2. Dimensions of the tetragonal unit cell: $a = 4.423$ Å, $c = 2.917$ Å.

I_{obs}	$10^5 \sin^2\theta_{obs}$	$h\ k\ l$	$10^5 \sin^2\theta_{calc}$
v st	6 066	1 1 0	6 067
v st	10 002	1 0 1	10 003
v w	12 133	2 0 0	12 137
m	13 036	1 1 1	13 038
v w	15 166	2 1 0	15 167
v st	22 135	2 1 1	22 137
m	24 266	2 2 0	24 255
w	27 876	0 0 2	27 869
w	30 332	3 1 0	30 330
w	33 943	1 1 2	33 931
w	34 268	3 0 1	34 269
v w	46 401	3 2 1	46 399

Table 9. Powder photograph of Cr_2O_3. Dimensions of the hexagonal unit cell: $a = 4.959$ Å, $c = 13.60$ Å.

I_{obs}	$10^5 \sin^2\theta_{obs}$	$h\ k\ l$	$10^5 \sin^2\theta_{calc}$
st	4 508	0 1 2	4 504
v st	8 353	1 0 4	8 364
v st	9 663	1 1 0	9 651
v v w	11 567	0 0 6	11 560
m	12 545	1 1 3	12 541
w	14 153	2 0 2	14 152
v v st	21 229	1 1 6	21 211
w	23 734	1 2 2	23 803
st	27 657	2 1 4	27 657
st	28 959	3 0 0	28 953
w	35 307	1,0.10	35 327
w	38 612	2 2 0	38 604
w	40 509	3 0 6	40 513
w	43 046	1 2 8 3 1 2	43 069 43 105
m	44 985	0.2.10	44 978
m	46 950	1 3 4	46 959

Cr_5O_{12}. This oxide was formed in a pure state between 230—240°C above 1000 bars. The reaction product consists of black non-ferromagnetic well developed crystals of octahedral shape, readily distinguishable from the other chromium oxides. The phase is decomposed by boiling with concentrated sulphur acid. The dimensions of the orthorhombic cell are $a = 12.04$ Å, $b = 8.21$ Å, $c = 8.18$ Å, $V = 808$ Å. The observed density, 3.68 g cm^{-3}, corresponds to a cell content of 4 units of Cr_5O_{12}. The composition $CrO_{2.40}$ was verified by the chemical analysis and by a complete structure determination.[2]

CrO_2. Pure ferromagnetic CrO_2 has been obtained from thermal decomposition of CrO_3 in the presence of water at high pressure by several investigators.

A review of the methods of preparation of CrO_2 has recently been given by Chamberland.[10] Experiments by the present author have produced chromium dioxide either by thermal decomposition of CrO_3 or by heating a mixture of the stoichiometry $CrO_3+Cr_2O_3$. These reactions were conducted at temperatures above 250°C and pressures above 2000 bars.

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