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A Homologous Series of Mixed Titanium Chromium Oxides $Ti_{n-2}Cr_2O_{2n-1}$ Isomorphous with the Series Ti_nO_{2n-1} and V_nO_{2n-1}

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By heating mixtures of titanium(IV)oxide and chromium(III)oxide at 1 300°—1 400°C in an inert atmosphere, mixed oxides $Ti_{n-2}Cr_2O_{2n-1}$ (n = 6, 7, 8, and 9) are obtained. These phases are isomorphous with the members of the homologous series Ti_nO_{2n-1} and V_nO_{2n-1}. Some structural data are given for the mixed oxide homologues. When heated at still higher temperatures, the structures seem to undergo a partial disordering.

From a consideration of an X-ray phase analysis of the vanadium-oxygen system carried out by Georg Andersson, it was suggested by one of the present authors (A.M.) that the phases occurring in the composition region $VO_{1.75-1.87}$ form a "homologous series" based structurally on the rutile-type structure[1]. The evidence constituting the grounds for this suggestion was the following:

1) The compositions of the phases, none of which shows an extended range of homogeneity, are all in good agreement with the general formula V_nO_{2n-1}, n being an integer. The phases prepared by Andersson correspond to values of n equal to 4, 5, 6, 7 and 8.

2) The powder photographs of the various phases are of a closely related appearance and are similar to the pattern of a structure of rutile type. Thus, all the strong reflexions of the former occur as doublets or triplets close to the positions of the rutile type lines. With increasing n, the distribution of the reflexions converges towards that of the rutile-type pattern.

Recent studies on the titanium-oxygen system have revealed the existence of an analogous family of oxides with the general formula Ti_nO_{2n-1}[2-4]. The members of this series ($4 \leq n \leq 10$) should, as indicated by the analogous appearance of the powder diagrams, in every case be isomorphous with the corresponding vanadium oxides.

An alternative formulation of a series M_nO_{2n-1} is $(n-2)MO_2 \cdot M_2O_3$. The latter formula suggests the possibility of preparing an oxide series from appropriate mixtures of oxides of tetravalent and trivalent metals. This article will give results obtained in this way using titanium(IV) and chromium(III) oxides.

The TiO_2-Cr_2O_3 system has previously been studied by Hamelin[5] who found a wide region of solid solubility in preparations rich in titanium. A phase transition was observed for this region at temperatures rising from about 1 440° to 1 500°C with increasing contents of chromium. It was pointed out that the X-ray powder patterns of the low temperature form were very similar to those given by products obtained by reducing rutile. The existence of a phase with the stoichiometric composition $2TiO_2 \cdot Cr_2O_3$ was also stated.

A different picture resulted from the studies on this system by Dietzel and Flörke[6,7] who found that the rutile-type structure broke down when the chromium content was raised above 3—5 %, giving rise to a series of new phases structurally related to the rutile type.

EXPERIMENTAL

The starting materials for preparing the mixed titanium chromium oxides were titanium dioxide (Baker analyzed, anatase modification, about 99.97 % pure) and dichromium trioxide (Matheson Coleman and Bell, reagent grade). Intimate mixtures of weighed amounts of the oxides were pressed into tablets and then heated at temperatures between 1 200° and 1 450°C for periods of time ranging from a few hours to ten days. In several cases, the samples had to be refired after grinding. The heating was performed in a glowbar furnace provided with a horizontal heating tube made of pythagoras mass. The tablets were always placed on a thin sheet of platinum which prevented the sample from reacting with the corundum boat carrying the specimen. The heating was performed in air or a stream of oxygen or argon. After completion of the period of heating, the boat was quickly moved out of the hot zone in order to ensure a fairly rapid cooling of the sample. In a few instances, the mixed oxide tablets were melted in an electric arc furnace under argon atmosphere.

X-Ray powder photographs were taken of all the samples using a Guinier set-up with monochromatized $CuK\alpha_1$ radiation. An aluminium foil (35 μ) covering the film served to reduce the back-ground fogging caused by the fluorescent radiation from the samples. Potassium chloride (a = 6.2919 Å at 20°C[8]) was always added to the specimens as an internal standard. Details about the techniques employed in the X-ray work have been given in a previous article[9].

Table 1 gives a survey of several of the experiments performed during this investigation. The colour of the samples listed was always graphite grey after the heat-treatment but, upon grinding, it turned to a dark brown. Density data for several preparations are given in Table 5.

PHASE ANALYSIS

Most of the synthesis experiments were carried out in an argon atomsphere. It is obvious from Table 1 that the attainment of a state of equilibrium requires a more intense heat-treatment of the reaction mixture at low titanium contents than at higher ones. Fig. 1 gives a schematic representation of the powder patterns of several equilibrium samples.

The non-existence of a compound $TiO_2 \cdot Cr_2O_3$ and the existence of the phase $2TiO_2 \cdot Cr_2O_3$ ($Ti_2Cr_2O_7$) reported by Hamelin[5] are clearly demonstrated by our results. For higher contents of titanium dioxide, the powder patterns

Table 1. Survey of some preparations and results of phase analyses.

Starting composition of reacted mixture	Heating conditions			X-ray evidence
	Temperature °C	Time	Atmosphere	
1–6 $TiO_2 \cdot Cr_2O_3$	1 200	4 + 2 days	air or oxygen or argon	non-equilibrium
1–4 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 »	–»–	incomplete equilibrium
5 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 »	argon	M_7O_{13}
5 $TiO_2 \cdot Cr_2O_3$	1 300	2 days	air	M_7O_{13} + M_8O_{15}
5 $TiO_2 \cdot Cr_2O_3$	1 300	2 + 5 days	»	M_8O_{15}
5.5 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 days	argon	M_7O_{13} + M_8O_{15}
5.5 $TiO_2 \cdot Cr_2O_3$	1 300	1 day	air	M_8O_{15}
6 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 days	argon	M_8O_{15}
7 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 »	»	M_9O_{17}
8–15 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 »	»	M_nO_{2n-1}-type
16 $TiO_2 \cdot Cr_2O_3$	1 300	4 + 2 »	»	M_nO_{2n-1}-type + rutile
$TiO_2 \cdot Cr_2O_3$	1 450	4 + 2 »	»	$Ti_2Cr_2O_7$ + Cr_2O_3
2 $TiO_2 \cdot Cr_2O_3$	1 450	4 + 2 »	»	$Ti_2Cr_2O_7$
3 $TiO_2 \cdot Cr_2O_3$	1 450	4 + 2 »	»	$Ti_2Cr_2O_7$ + M_6O_{11}
4 $TiO_2 \cdot Cr_2O_3$	1 450	4 + 2 »	»	M_6O_{11}
5– 7 $TiO_2 \cdot Cr_2O_3$	1 450	4 + 2 »	»	M_nO_{2n-1}-type pattern with several lines absent.

are of a mutually related appearance and the whole of this region could easily be mistaken for being one sigle phase of a composition varying within wide limits. A careful study, however, reveals the existence, at least up to the composition $7TiO_2 \cdot Cr_2O_3$, of a regular alternation of one-phase and two-phase regions. The compositions of the former are underlined in Fig. 1. The ranges of homogeneity should be very narrow since the positions of the X-ray reflexions of the various phases do not change appreciably with the composition of the samples. The discontinuous character thus demonstrated for this region of the titanium chromium oxide system is in agreement with the opinion put forward independently by Dietzel and Flörke [6,7] but conflicts with the results reported by Hamelin [5].

For titanium dioxide contents exceeding $7TiO_2 \cdot Cr_2O_3$, the powder patterns still maintained the same general appearance. It was not, however, possible to observe the existence of any two-phase regions or to demonstrate a discontinuous character in this range of composition. This may indicate either that there is actually a continuos series of solid solutions or that the series of discrete oxide phases observed at lower titanium dioxide contents is continued up into this range of composition. In the latter case, the failure to demonstrate the existence of two-phase regions would be due to an inadequate resolving power of the powder camera. The upper limit of this range of composition is at about $15TiO_2 \cdot Cr_2O_3$, where the first indications of another two-phase region show up, rutile being the additional phase.

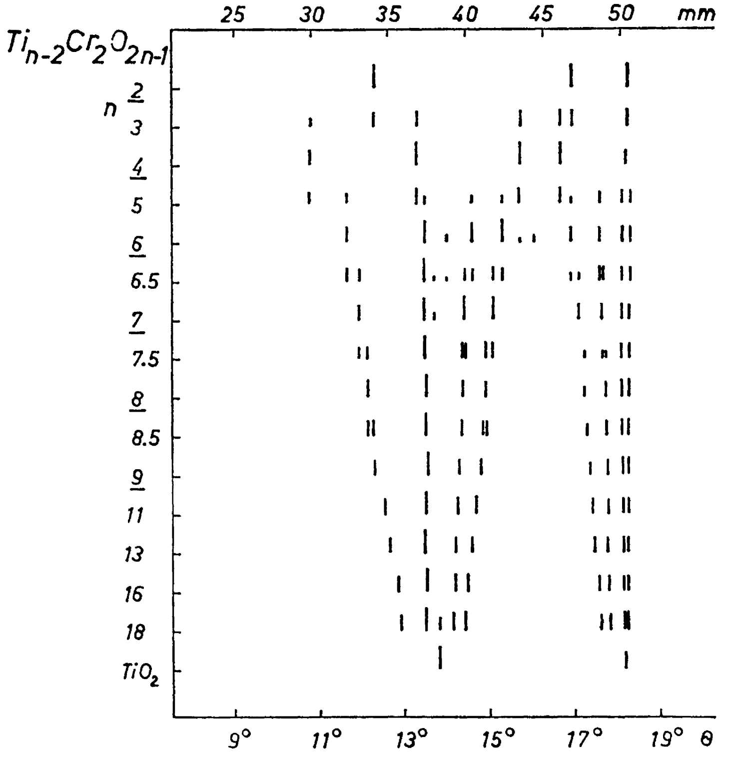

Fig. 1. Powder patterns of samples $Ti_{n-2}Cr_2O_{2n-1}$.

The phase analysis evidently demonstrates the existence of at least four discrete, related phases of compositions xTiO$_2$ · Cr$_2$O$_3$, x having values close to the integers 4, 5, 6, and 7. An alternative way of expressing these compositions is $Ti_{n-2}Cr_2O_{2n-1}$, where n stands for $x + 2$. The powder patterns of the four phases show pronounced similarities and approach that of a rutile-type pattern with increasing values of n. The results obtained for the series of mixed titanium chromium oxides thus suggest that a far-reaching analogy exists with the homologous series Ti_nO_{2n-1} and V_nO_{2n-1}. Actually, a comparison of the powder photographs of all these phases reveals that the pattern of a member of the mixed oxide series may generally be described as something intermediate between the patterns of the titanium and vanadium oxide phases with the same value for n. The isomorphism of the three series has been further elucidated by the detailed interpretation of the powder photographs (*v. infra*).

The identification of the phases of the series $Ti_{n-2}Cr_2O_{2n-1}$ made possible the phase analysis of preparations obtained by heating the mixed oxide samples in air or in oxygen (*cf.* Table 1). Preparations heat-treated in this way give X-ray powder patterns showing phases of higher n values than those corresponding to the compositions of the starting mixtures. These starting mixtures

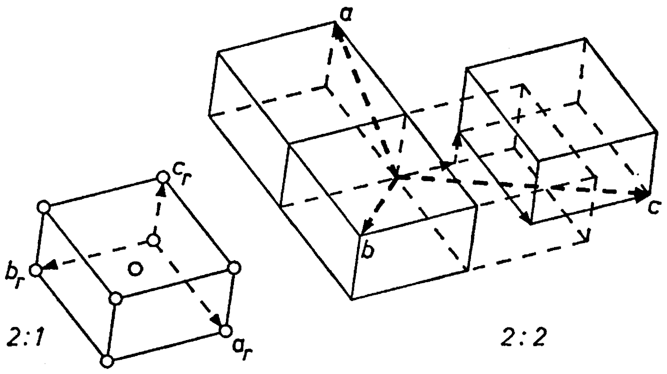

Fig. 2. 1) Unit cell of rutile with positions of metal atoms indicated. 2) Interrelation of basic rutile-type structure of adjacent slabs of Ti_5O_9. Unit cell axes of the latter indicated by dashed heavily-drawn arrows.

have therefore evidently been partly oxidized during the firing. This process is accompanied by a slight loss of weight of the sample. This phenomenon has so far not been further investigated. An oxidation of chromium(III)oxide when it was heated together with titanium(IV)oxide in air at 700°C was observed by Dietzel and Flörke. They also found that chromium(III)oxide when heated in air at 1 000°C is slightly volatile, forming a higher oxide [6,7].

Upon heating members of the series $Ti_{n-2}Cr_2O_{2n-1}$ at sufficiently high temperatures (*cf.* Table 1), preparations are obtained which give powder patterns that differ in a characteristic way from those shown in Fig. 1. Thus, while part of the reflexions are unchanged, several appear diffuse and with reduced intensities while others are not even visible after the high-temperature firing. This phenomenon, which is probably associated with the phase-transition reported by Hamelin [5], may indicate a partial disordering of the structures of the homologues. Further studies on this matter are in progress.

STRUCTURAL DATA OF THE SERIES $Ti_{n-2}Cr_2O_{2n-1}$

Crystals of the members of the homologous titanium chromium oxide series grow only very slowly and this of course made X-ray studies of these compounds with single-crystal methods impracticable. The deduction of detailed structural data of the homologues under such circumstances had to be based on information now available for the Ti_nO_{2n-1} series and especially for its second member, *i.e.* Ti_5O_9.

The crystal structure of Ti_5O_9 has recently been determined by one of the present authors (S.A.)[10] and is now being refined. (A detailed account of this investigation will, in due time, appear elsewhere.) The structure may be described as being built up of slabs of a rutile-structure type, *i.e.* TiO_6 octahedra joined by edges and corners as in the rutile structure. The slabs are of infinite extension in two dimensions and have a characteristic finite width corresponding to five TiO_6 octahedra in a third direction. The mutual connection of the slabs takes place by means of TiO_6 octahedra sharing faces. If the axes of the rutile-type subunit cell ($\boldsymbol{a}_r$, $\boldsymbol{b}_r$ ($\boldsymbol{b}_r = \boldsymbol{a}_r$) and $\boldsymbol{c}_r$) are used to define the coordinate system, then the axes of the "ideal" Ti_5O_9 unit cell will be $\boldsymbol{a} = \boldsymbol{c}_r - \boldsymbol{a}_r$, $\boldsymbol{b} = \boldsymbol{a}_r + \boldsymbol{b}_r + \boldsymbol{c}_r$ and $\boldsymbol{c} = \boldsymbol{a}_r - \frac{3}{2}\boldsymbol{b}_r + \frac{1}{2}\boldsymbol{c}_r$. (The term, "ideal" cell, is used here to imply that no deformation of the geometry of the rutile subunit takes place.) The infinite extension of the slabs is parallel to the *ab* plane. The rutile arrangements of adjacent slabs are out of step by $\frac{1}{2}(\boldsymbol{b}_r + \boldsymbol{c}_r)$ (*cf.* Fig. 2).

Assuming the structural principles found for Ti_5O_9 to be valid also for the other members of the series, general expressions may be derived for the characteristics of the "ideal" structures of all the homologues. This is done in a way similar to that applied when deducing general structural data for the homologous series of molybdenum wolfram oxides M_nO_{3n-1} [11]. A detailed account of this investigation will be presented elsewhere. For the present discussion, the following vectorial expressions for the unit cell parameters will suffice.

$$\boldsymbol{a} = \boldsymbol{c}_r - \boldsymbol{a}_r$$

$$\boldsymbol{b} = \boldsymbol{a}_r + \boldsymbol{b}_r + \boldsymbol{c}_r$$

$$\boldsymbol{c} = \frac{n-3}{2}\boldsymbol{a}_r - \frac{n-2}{2}\boldsymbol{b}_r - \frac{n-6}{2}\boldsymbol{c}_r$$

The fundamental role of the rutile-type subcell in the structures of the various homologues shows itself in the character of the X-ray patterns. Thus, the latter only show strong reflexions when the reciprocal lattice points are situated close to those of the strong rutile reflexions. The indices of the strong reflexions of a homologue M_nO_{2n-1} may thus be found by means of the following matrix giving the relations between the homologue and rutile.

$$\begin{array}{c|ccc|}
 & & \rightarrow \text{rutile} & \\
 & \bar{1} & 0 & 1 \\
M_nO_{2n-1} & 1 & 1 & 1 \\
 & \frac{n-3}{2} & \frac{2-n}{2} & \frac{6-n}{2}
\end{array}$$

Thus the reciprocal point of the strong rutile reflexion 110 corresponds, for all the homologues, to the point $1\bar{2}\frac{1}{2}$, which implies that the reflexions of the adjacent points $1\bar{2}0$ and $1\bar{2}1$ should always be strong. On the other hand, the rutile point $1\bar{1}0$ corresponds, for the various homologues, to $1\ 0\ \frac{5-2n}{2}$. The reflexions generated by the strong $1\bar{1}0$ reflexion of rutile should thus be $10\bar{3}$ and $10\bar{4}$ for M_6O_{11}, $10\bar{4}$ and $10\bar{5}$ for M_7O_{13} *etc.*

Such considerations should in principle make it possible to index the powder pattern of any member of a homologous series M_nO_{2n-1} possessing the structural characteristics given above. Actually all well resolved patterns of members

Table 2. Powder patterns of the phases $Ti_{n-2}Cr_2O_{2n-1}$. Guinier camera. $CuK\alpha_1$ radiation.

Compound	*I*	$\sin^2\Theta_{obs}$	*h k l*	$\sin^2\Theta_{calc}$
$Ti_4Cr_2O_{11}$	w	0.02468	$10\bar{2}$	0.02467
	m	0.04017	$10\bar{3}$	0.04011
	st	0.05347	$1\bar{2}0$	0.05343
	w	0.05771	$\bar{1}21$	0.05769
	m	0.06232	$1\bar{2}1$	0.06237
	m	0.06870	$10\bar{4}$	0.06875
	w	0.07517	$02\bar{3}$	0.07518
	m	0.08325	021	0.08326
	w	0.08758	$20\bar{3}$	0.08760
	m	0.08968	$20\bar{2}$	0.08972
	m	0.09494	102	0.09491
	m	0.09707	$12\bar{2}$	0.09707
$Ti_5Cr_2O_{13}$	m	0.04214	$10\bar{4}$	0.04214
	st	0.05347	$1\bar{2}0$	0.05346
	w	0.05535	$\bar{1}21$	0.05527
	m	0.06115	$1\bar{2}1$	0.06115
	m	0.06656	$10\bar{5}$	0.06659
	m	0.08491	021	0.08491
	m	0.09029	$20\bar{3}$	0.09031
	m	0.09494	102	0.09494
	m	0.09656	$12\bar{3}$	0.09659
$Ti_6Cr_2O_{15}$	m	0.04376	$10\bar{5}$	0.04375
	st	0.05386	$1\bar{2}0$	0.05383
	m	0.06055	$1\bar{2}1$	0.06057
	m	0.06516	$10\bar{6}$	0.06507
	m	0.08631	021	0.08632
	m	0.09104	$20\bar{4}$	0.09100
	m	0.09501	102	0.09499
	m	0.09648	$12\bar{4}$	0.09639
$Ti_7Cr_2O_{17}$	m	0.04510	$10\bar{6}$	0.04509
	st	0.05395	$1\bar{2}0$	0.05395
	m	0.06001	$1\bar{2}1$	0.06000
	m	0.06399	$10\bar{7}$	0.06404
	m	0.08723	021	0.08724
	m	0.09148	$20\bar{5}$	0.09146
	m	0.09508	102	0.09509
	m	0.09630	$12\bar{5}$	0.09626

of the series Ti_nO_{2n-1}, V_nO_{2n-1} and $Ti_{n-2}Cr_2O_{2n-1}$, have been indexed in this way *. Parts of the powder diagrams of the latter homologues are given in Table 2. The good agreement between the calculated and the observed diffraction data may be taken as a confirmation of the structural character discussed above for these phases.

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* According to a private communication Mr. Jørgen Villadsen of F:a Haldor Topsøe, Hillerup, Denmark, has indexed the powder patterns of Ti_4O_7 and V_4O_7 by applying a procedure according to De Wolff [12] and has found parameter values in perfect agreement with those derived in this investigation.

Table 3. Observed and calculated unit cell parameters and densities of the members of the $Ti_{n-2}Cr_2O_{2n-1}$ series.

Phase	Unit cell parameters						Density
	a_{obs} a_{calc}	b_{obs} b_{calc}	c_{obs} c_{calc}	α_{obs} α_{calc}	β_{obs} β_{calc}	γ_{obs} γ_{calc}	obs calc
$Ti_4Cr_2O_{11}$	5.50 Å	7.07 Å	11.89 Å	98.6°	120.6°	107.4°	4.42
	5.46	7.14	11.48	97.4°	120.3°	108.5°	4.47
$Ti_5Cr_2O_{13}$	5.50	7.09	15.24	99.1°	125.3°	108.2°	4.36
	5.46	7.14	14.78	98.1°	125.2°	108.5°	4.42
$Ti_6Cr_2O_{15}$	5.49	7.08	18.64	99.5°	128.2°	108.1°	4.33
	5.46	7.14	18.18	98.6°	128.3°	108.5°	4.40
$Ti_7Cr_2O_{17}$	5.49	7.09	22.13	99.5°	130.3°	107.3°	4.24
	5.46	7.14	21.40	98.9°	130.8°	108.5°	4.38

Table 3 gives a comparison between the unit cell parameters of the members of the $Ti_{n-2}Cr_2O_{2n-1}$ series derived from the experimentally obtained X-ray data and parameter values calculated from the expressions given above. For simplicity, the parameters a_r and c_r are taken here to be equal to those of rutile, *viz.* 4.59 and 2.96 Å, respectively. The agreement between the observed and calculated data is satisfactory when considering the simplifying assumptions involved in the derivation of the latter. Thus, for the a and b axes, which should be constant for all the homologues, the deviation does not exceed 1 %. The observed length of the c axis, which increases with increasing n, is throughout larger than the calculated value by about 4 %. This difference is, however, easily accounted for by the repulsion between the metal atoms of octahedra sharing faces. The resulting expansion of the structure, which was not considered when deriving the ideal lattice parameters, has its largest component in the c direction. The agreement is satisfactory also for the angle parameters.

Further developments of the expressions giving the structural characteristics of »ideal» and eventually also real members of a series M_nO_{2n-1} should make it possible to calculate rather accurate positions for the metal and oxygen atoms of the various phases. The distribution of the titanium and chromium atoms on the metal atom sites might possibly be derived from comparisons of detailed structural data, including interatomic distances, obtained from single-crystal studies of titanium chromium and titanium oxides.

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