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Phase Studies in the Chromium–Manganese–Titanium Oxide System at Different Oxygen Partial Pressures

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Abstract

The phase diagram of the quasi-ternary oxide system Cr–Mn–Ti has been investigated at 1000°C in air and in an Ar–4 vol.% H_2 atmosphere ($p_{O_2} \approx 10^{-21}$ bar). All samples have been water-quenched and investigated by X-ray diffraction. The results can be summarized as follows.

Phase relationships in air:

- *—The spinel $Mn(Mn_xCr_{1-x})_2O_4$, with a cubic structure for $0 \leq x < 0·39$ and tetragonal for $0·39 \leq x < 0·87$, dissolves up to 16% of the spinel phase Mn_2TiO_4.*
- *—The solubility of manganese oxide in Cr_2O_3 is negligible ($\approx 1·6$ at.%).*
- *—In the system Cr_2O_3–TiO_2 only the continuous region of the Andersson phase exists. $Cr_2Ti_3O_9$ is metastable under these conditions.*

Heat treatments under $p_{O_2} \approx 10^{-21}$:

- *—The monoclinic phase $CrTi_2O_5$ was observed in the Cr–Ti oxide system.*
- *—Cr_2O_3 dissolves 18 at.% Ti as oxide, and Ti_4O_7 12 at.% Cr_2O_3.*
- *—The spinels $MnCr_2O_4$ and Mn_2TiO_4 form a complete series of solid solutions and up to 24% Cr^{3+} ions can be replaced by Ti^{3+} ions.*

Das Phasendiagramm des quasi-ternären Oxidsystems Cr–Mn–Ti wurde bei 1000°C in Luft und in einer Ar–4 Vol.% H_2 Atmosphäre ($p_{O_2} \approx 10^{-21}$ bar) untersucht. Alle Proben wurden in Wasser abgeschrekt und röntgenographisch beurteilt. Die Ergebnisse können wie folgt zusammengefaßt werden.

Phasenbeziehungen an Luft:

- *—Der $Mn(Mn_xCr_{1-x})_2O_4$-Spinnell, der im Bereich $0 \leq x < 0·39$ eine kubische Struktur und im Bereich $0·39 \leq x < 0·87$ eine tetragonale Struktur besitzt, kann bis zu 16% der Spinellphase Mn_2TiO_4 lösen.*
- *—Die Löslichkeit von Manganoxid in Cr_2O_3 ist vernachlässigbar ($\approx 1·6$ at.%).*
- *—Im Cr_2O_3–TiO_2-System existiert nur der Bereich der Andersson-Phase. $Cr_2Ti_3O_9$ ist bei diesen Bedingungen metastabil.*

Wärmebehandlungen bei $p_{O_2} \approx 10^{-21}$:

- *—Im Cr–Ti-Oxid-System konnte die monokline Phase $CrTi_2O_5$ beobachtet werden.*
- *—Cr_2O_3 löst 18 at.% Ti als Oxid und Ti_4O_7 12 at.% Cr_2O_3.*
- *—Die Spinelle $MnCr_2O_4$ und Mn_2TiO_4 bilden eine lückenlose Reihe von Mischkristallen und bis zu 24% Cr^{3+} Ionen können durch Ti^{3+} Ionen ersetzt werden.*

On a étudié le diagramme de phases du système oxyde quasi-ternaire Cr–Mn–Ti à 1000°C dans l'air et dans une atmosphère Ar–4% volumiques de H_2 ($p_{O_2} \approx 10^{-21}$ bar). Tous les échantillons subissaient une trempe à l'eau et étaient étudiés par diffraction X. Les résultats peuvent être résumés comme ci-dessous.

Relations de phases dans l'air:

- *—Le spinelle $Mn(Mn_xCr_{1-x})_2O_4$ qui présente une structure cubique pour $0 \leq x < 0·39$ et tétragonale pour $0·39 \leq x < 0·87$ dissout jusqu'à 16% de la phase spinelle Mn_2TiO_4.*
- *—La solubilité de l'oxyde de manganèse dans le Cr_2O_3 est négligeable ($\approx 1·6$% atomiques).*
- *—Dans le système Cr_2O_3–TiO_2, il n'existe que la région continue de la phase d'Andersson. $Cr_2Ti_3O_9$ est métastable dans ces conditions.*

Traitements thermiques sous $p_{O_2} \approx 10^{-21}$:

- *—La phase monoclinique $CrTi_2O_5$ a été observée dans le système oxyde Cr–Ti.*

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—*Cr_2O_3 dissout 18% atomiques de Ti sous forme d'oxyde et Ti_4O_7 12% atomiques de Cr_2O_3.*

—*Les spinelles $MnCr_2O_4$ et Mn_2TiO_4 forment une série complète de solutions solides et les ions Ti^{3+} peuvent remplacer jusqu'à 24% d'ions Cr^{3+}.*

1 Introduction

High-temperature alloys are used for heat exchangers and other components in high-temperature facilities and their use is planned in nuclear heat conversion in high temperature reactors. For the long-term use of these materials the problem of corrosion is of particular significance. The interaction of nickel- and nickel/iron-base alloys with the different gas components of the process gases leads to the formation of oxides, carbides and sulphides of the metallic components of the respective alloys.[1] The oxide layers often lead to a passivation of the alloy, protecting it against further corrosion. On the other hand, carburization changes the ductility of these alloys, while the uptake of sulphur can lead to eutectic compounds, especially with nickel.

The extent to which an oxide layer causes a passivation of these materials depends essentially on the structure and chemical composition of these oxide layers. The detailed characterization of surface oxides and carbides may explain the formation mechanism of such layers, and the high-temperature alloys can then be protected against these corrosive media by selective precautions.

Post-exposure metallurgical examinations were carried out on high-temperature alloys both after a prolonged application period in coal conversion plants and after corrosion tests in the laboratory with a simulated gas atmosphere of such a process gas. It was found that the oxide layer consists in general of a chromium oxide layer on the surface of the alloy and that various spinels and other oxides are present on the outer surface.[2]

Figure 1 shows the variation in concentration of different elements by means of line scans of such a sample (Incoloy 800 H) annealed for 2000 h in a process gas atmosphere at 950°C ($p_{O_2} \approx 10^{-15}$ bar). A microprobe was used for this demonstration. It can be seen that slight amounts of titanium are dissolved in the chromium oxide phase and that a manganese–chromium–titanium compound is present on the surface.[3]

Parallel to these line scans non-destructive X-ray diffraction analysis of the surface of oxidized high-temperature alloys leads to the conclusion that a spinel phase is present within the outer oxidation layer. For a non-destructive characterization of these very thin layers by X-ray diffraction it is often also necessary to know the phase relationship of the corresponding oxide system at an oxygen partial pressure which is substantially lower than in air, i.e. $p_{O_2} \ll 10^{-6}$ bar, and at temperatures as will be encountered during application, i.e. at about 1000°C.

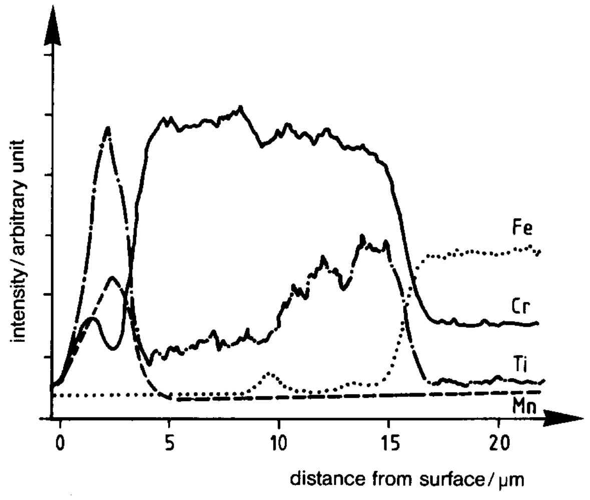

Fig. 1. Line scans observed with the electron microprobe analyser show the variation in concentration of different elements of an Incoloy 800 H sample after 2000 h of exposure in a process gas atmosphere at 950°C ($p_{O_2} \approx 10^{-15}$ bar).

This was the aim of investigations into the quasi-ternary system of the oxides of chromium, manganese and titanium both in air and at a very low oxygen partial pressure of about 10^{-21} bar at 1000°C. In this paper the results of these investigations are presented.

2 Experimental

2.1 Preparation of oxide mixtures

A critical requirement for these studies is the reproducible preparation of a mixed oxide powder which is sufficiently homogeneous and suitable for equilibrium studies.

The preparation of such homogeneous materials has already been reported in the literature.[4] It was found to be difficult to obtain sufficiently homogeneous products from powdered starting materials. The use of solutions with different salts does not necessarily lead automatically to homogeneous salt or oxide mixtures because separation can take place during water removal.

For the purposes of this study, the hot kerosene drying process as reported by Reynen *et al.*[5] has been used to prepare oxide mixtures with different compositions. According to this method, one starts out from an aqueous metal salt solution. The water is removed sufficiently quickly that substantial degrees of segregation are excluded. The solution is a highly concentrated (at least 50%) aqueous metal salt solution which is emulsified in kerosene with the aid of an emulsifier (SPAN 85; Atlas Chemie, Essen) to obtain a material as finely powdered as possible. The volume ratio of aqueous solution to kerosene is 1:3 for a properly flowing emulsion. This emulsion is dropped into hot petroleum at 170–190°C using a hose pump. The water evaporates abruptly in this step and fine salt particles are obtained, which are easily separated from the oil phase by filtration. Adherent kerosene is removed by heating the powder for 15 h in air up to 450°C. The product is a homogeneous powder with a grain size smaller than 1 μm.

This preparation method served to produce a number of oxide mixtures of chromium, manganese and titanium (see Fig. 2) starting from different mixtures of the salts $Cr(NO_3)_3 . 9\,H_2O$, $Mn(NO_3)_3 . 4\,H_2O$ and $TiCl_4$ (dissolved in 10 wt% HCl solution). The obtained homogeneous powder mixtures were used to produce compacted pellets of about 1 g (pellet diameter $\bigcirc = 10$ mm, thickness $h \approx 2$ mm) after having added glycerol (≈ 5 wt%). These compacts were then subjected to several annealing processes at different temperatures and in different gas atmospheres.

The two standard atmospheres were dry air at $p_{O_2} = 0{\cdot}21$ bar and one of Ar with 4 vol.% H_2 and a total oxygen content of 10 ppm as given by a certificate. The residual moisture of this gas mixture then corresponds to a water vapour fraction of about 2×10^{-5}. This gives a calculated oxygen partial pressure of about 10^{-21} bar at 1000°C. In some cases, the oxygen partial pressure was increased by defined moistening of this Ar/H_2 mixture. Saturation with water vapour was effected in each case at a temperature between -30 and $+80$°C. For this purpose, the gas duct to the furnace equipped with a heater winding was kept at a temperature of at least 50°C above the selected saturation temperature. In this way, oxygen partial pressures between 10^{-18} and 10^{-12} bar were established. Similarly, oxygen partial pressures between 10^{-6} and 10^{-4} bar were achieved by moistening technical Ar.

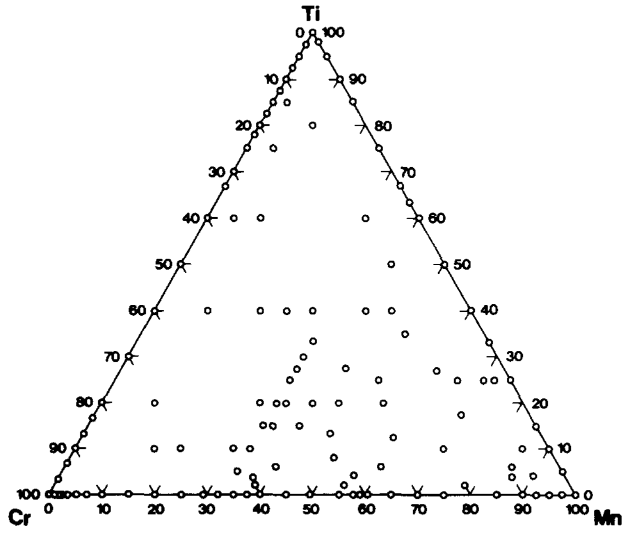

Fig. 2. Compositions of the prepared oxide mixtures.

The oxygen partial pressure was measured up to 10^{-17} bar by means of an oxygen probe using the EMF of the measuring chain Pt/annealing atmosphere/ZrO_2/air/Pt for determination. The values measured were in good agreement with theoretical data when using the Ar/H_2 mixture (factor 0·6 to 1·4). With technical Ar, however, the values determined by the probe were higher by a factor of 4 than those calculated.

The samples were annealed first for 15 h at 1100°C and then for 25 h at 1000°C on the one hand and at 1000°C from the very beginning for periods of up to 660 h on the other hand. Water was used for quenching in all cases. Annealing was effected using an arrangement with a vertical furnace in which the gas flowed from top to bottom so that the annealing atmosphere was contained in the downsection of the sample during quenching and no water vapour could diffuse in.

2.2 Analysis of the products

The metal contents of a few selected samples were determined by emission spectroscopy (inductively coupled plasma) of solutions obtained by dissolving the heat treated oxides.

All the samples were then examined by X-ray diffraction analysis to identify the phases formed and determine the lattice parameters. For this purpose the equilibrated pellets were powdered and from this powder new pellets were formed with 25 mm diameter using a 10% propanone solution of polymethylacrylate binder (2 ml solution with 5 g powder).

A microprocessor-based diffractometer D500 MP system (Siemens AG) in conjunction with a PDP-11/23-plus computer (Digital Equipment Corporation) was used for the measurements. The diffractometer was equipped with a Cu tube, a divergence slit varied automatically with the diffraction angle and a graphite monochromator. The calibration curve was determined by a silicon standard. The Siemens DIFFRAC 11 software was retained for diffractometer control as well as data processing and evaluation.

Table 1. Comparison of the nominal composition of various mixed oxides with that observed by the optical emission spectroscopy (ICP)

Sample number	*Nominal composition (Cr/Mn/Ti atomic ratio)*	*Actual composition (Cr/Mn/Ti atomic ratio)*
H 21a	71/29/—	70·6/29·4/—
H 44	40/60/—	39·5/60·5/—
H 50	56/44/—	55·7/44·3/—
H 51	45/55/—	44·3/55·7/—
H 55	63/37/—	62·7/37·3/—
H 58	68/32/—	67·7/32·3/—
H 71	42/50/08	42·1/49·6/8·3
H 72	28/60/12	28·3/59·3/12·4
H 73	13/70/17	13·2/69·3/17·5
H 74	90/—/10	89·2/—/10·8
H 75	80/—/20	79·1/—/20·9
H 81	—/75/25	—/74·8/25·2
H 83	—/25/75	—/24·5/75·5
H 84	05/70/75	5·2/68·8/26·0
H 85	10/65/25	10·2/63·5/26·3

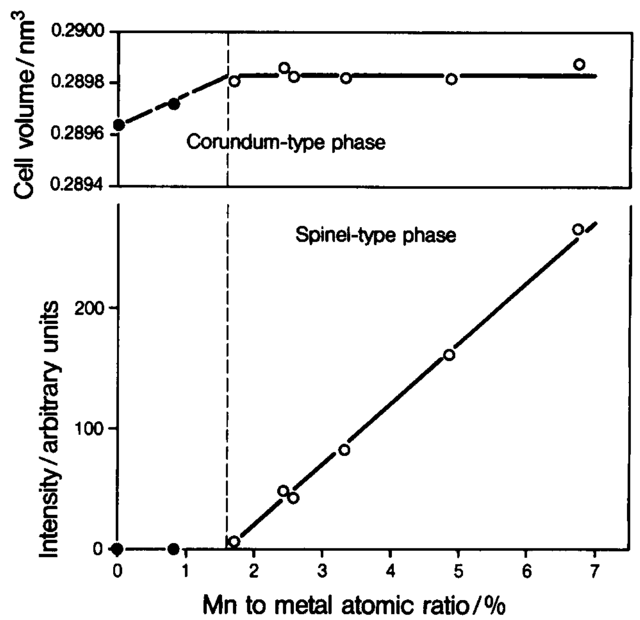

Fig. 3. The volume change of about 0·07% of the hexagonal cell of the corundum-type phase in the chromium–manganese oxide system indicates a manganese solubility in Cr_2O_3 after annealing at 1000°C in air. An amount of about 1·6% chromium ions replaced by manganese ions follows from the intensity slope of the spinel $MnCr_2O_4$ being in equilibrium with the corundum-type phase.

3 Results and Discussion

Only a few samples were selected for chemical analyses. The results are listed in Table 1. This table only comprises information about the nominal and actual composition. The specific analytical values of the metals and oxygen were omitted. A comparison of these values shows that the technique used is suitable for preparing samples with a given composition and accuracy better than 1%.

3.1 Quasi-binary Cr–Mn oxide system

In the quasi-binary chromium–manganese oxide system the corundum-type Cr_2O_3, the spinel $MnCr_2O_4$ and hausmannite Mn_3O_4, also with a spinel structure,[6] are formed in the samples annealed at 1000°C in air.

Some manganese can be dissolved in the Cr_2O_3. Since the change in lattice parameters is too small for determining the solubility (Fig. 3, top), the intensity of the $MnCr_2O_4$ spinel phase was used, which is in equilibrium with Cr_2O_3. The intensities of the coincidence-free interferences 111, 220 and 400 of the cubic spinel were summed and drawn versus the composition (Fig. 3, bottom). By extrapolating the intensity slope a manganese fraction of about 1·6% of the metal ions in Cr_2O_3 follows. This result is in contradiction to the phase diagram published by Speidel & Muan.[7] It is in agreement with the results of studies carried out by Pollert *et al.*[8] The low manganese solubility in Cr_2O_3 was left out of consideration in the further studies.

Only one phase, the $Mn^{2+}(Mn_xCr_{1-x})_2^{3+}O_4$ spinel phase, was found in connection with manganese fractions of the metal ions between 0·33 and 0·91. Based on the $Mn^{2+}Cr_2^{3+}O_4$ spinel, the parameter x specifies the fraction of chromium ions replaced by trivalent manganese ions. The lattice parameter of the cubic spinel increases with rising manganese fraction (Fig. 4). The intersection of the two straight lines averaging the lattice parameters of the spinel in the two-phase range with Cr_2O_3, on the

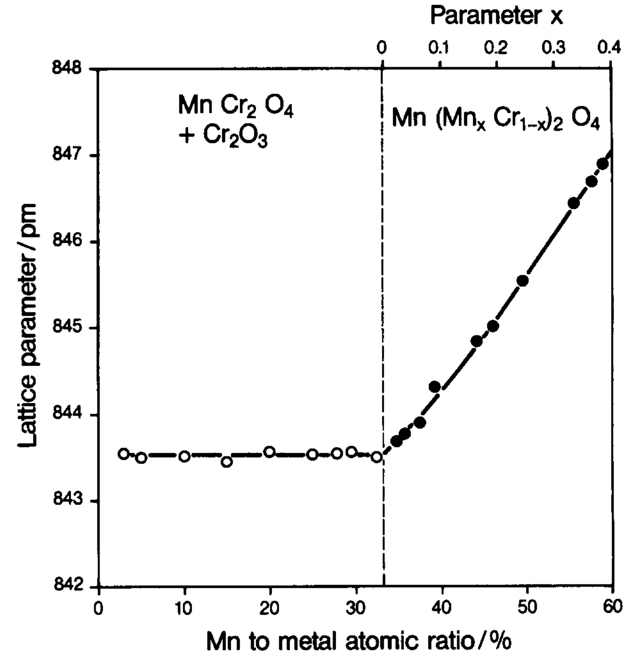

Fig. 4. Lattice parameter of the cubic spinel phase measured in the chromium–manganese oxide system as a function of the composition after annealing at 1000°C in air.

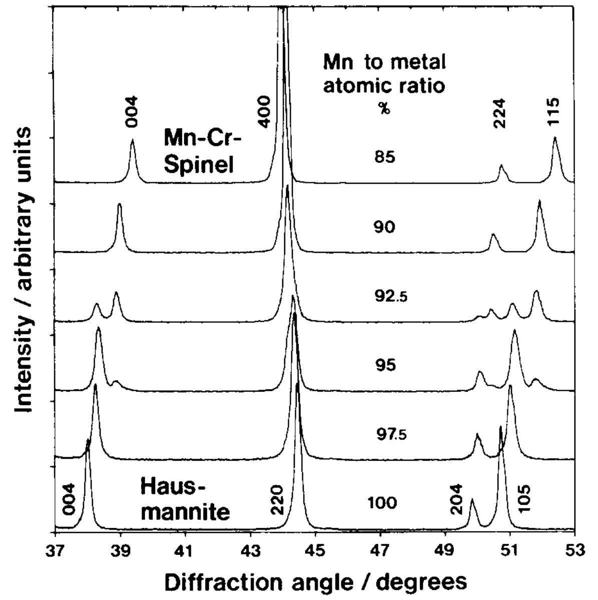

Fig. 5. X-Ray diffraction patterns of the spinels manganese–chromium oxide and hausmannite demonstrate the miscibility gap corresponding to 1000°C in air.

one hand, and in the single-phase cubic spinel-phase range, on the other hand, corresponds to a fraction of 0·33 Mn, i.e. the spinel in the two-phase range is the stoichiometric compound $MnCr_2O_4$. For $x > 0{\cdot}39$ (manganese fraction > 0·59) the spinel becomes tetragonal.

The manganese oxide, hausmannite, also has a tetragonal spinel structure and dissolves up to 3·5 at.% Cr. Figure 5 shows the similarity of the diffraction patterns of both spinels as well as the existence of a miscibility gap, and Fig. 6 shows the lattice parameters plotted as a function of the composition.

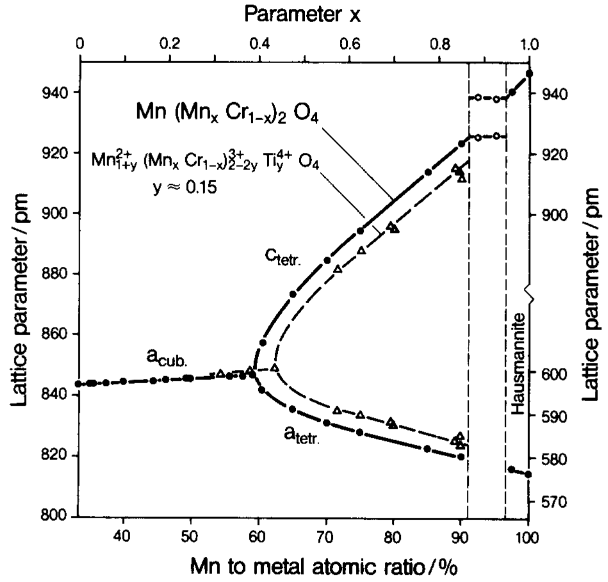

Fig. 6. Lattice parameters of the cubic and the tetragonal manganese–chromium spinels as well as the manganese oxide hausmannite as a function of composition. The miscibility gap corresponds to 1000°C in air. Also drawn are values for the mixed spinel containing 15% Mn_2TiO_4.

The only three compounds present at an oxygen partial pressure of 10^{-21} bar at 1000°C are Cr_2O_3, $MnCr_2O_4$ and MnO (manganosite). Solubilities were not detected. The two-phase region Cr_2O_3–$MnCr_2O_4$ remains unaffected by the annealing atmosphere.

3.2 Quasi-binary Mn–Ti oxide system

Pyrophanite ($MnTiO_3$) and rutile (TiO_2) are formed in addition to hausmannite in the quasi-binary manganese–titanium oxide system after equilibrium annealing at 1000°C in air.

A solubility for manganese in rutile was not detected, but a Mn_2TiO_4 solubility of 25% was found in hausmannite (31% at 1100°C). As a result of this solution the lattice parameter a increases by 1·6%, whereas the lattice parameter c decreases by 2·5%. This leads to a volume expansion of the tetragonal cell by 0·6% (Fig. 7).

The quenching rate must be particularly high for samples with compositions in this region of the phase diagram in order to prevent the formation of Mn_2O_3 at temperatures lower than 870°C. Powder samples were used instead of small pellets followed by quenching in water.

At the low oxygen partial pressure of 10^{-21} bar the four compounds MnO, Mn_2TiO_4, $MnTiO_3$ and Ti_4O_7 were found in the quasi-binary Mn–Ti oxide system. The manganese-rich cubic spinel Mn_2TiO_4 and pyrophanite $MnTiO_3$ were also detected in oxide layers of high-temperature alloys.

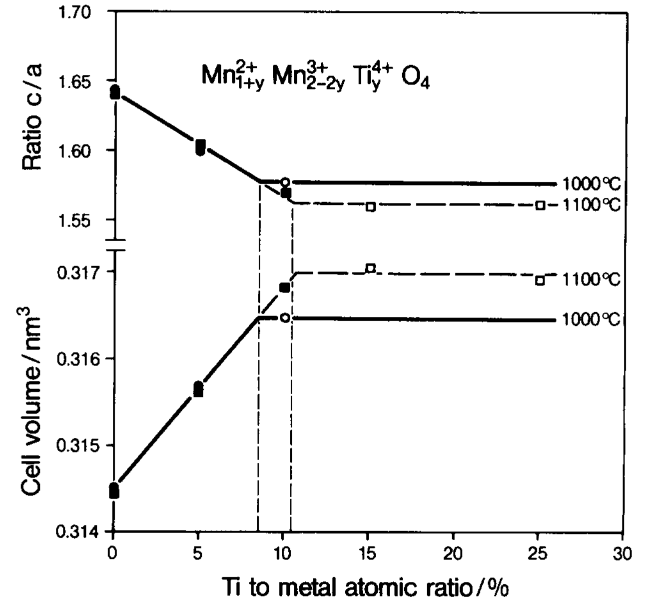

Fig. 7. Solubility of Mn_2TiO_4 in the tetragonal manganese spinel hausmannite determined by X-ray investigation of samples after annealing in air.

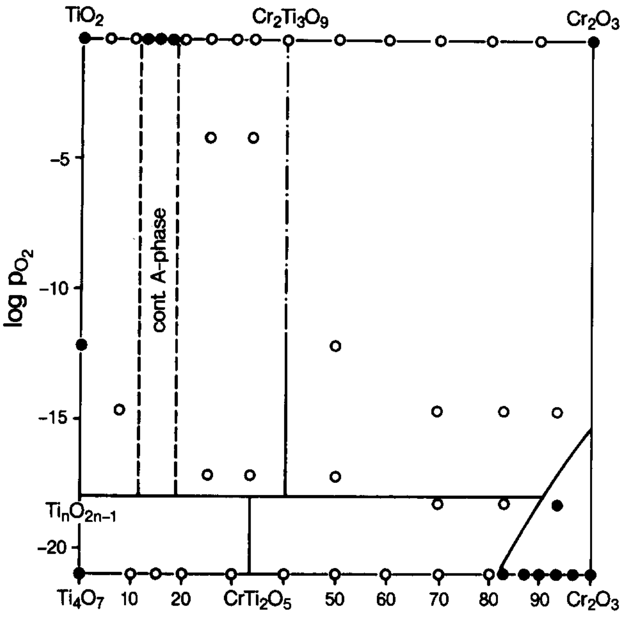

Fig. 8. Phase equilibria in the quasi-binary system titanium oxide–chromium oxide after annealing at 1000°C as a function of the oxygen partial pressure.

3.3 Quasi-binary Ti–Cr oxide system

Annealing at oxygen partial pressures between the standard conditions of 0·21 and 10^{-21} bar were carried out in the quasi-binary titanium–chromium oxide system. The phase diagram derived from the results of the phase and lattice parameter determinations is shown in Fig. 8. A phase limit at about 10^{-18} bar divides this diagram into two partial pressure ranges in which basically those phases appear that were identified under standard conditions.

A Ti solubility was found to exist in Cr_2O_3 after annealing at 1000°C and $p_{O_2} = 10^{-21}$ bar. Figure 9 demonstrates the volume of the unit cell and the c/a ratio of the lattice parameters of the hexagonally indexed corundum-type phase. It may be seen that about 18% of the Cr atoms can be replaced by Ti atoms in the Cr_2O_3 lattice. The volume then increases by 1·7% due to expansion of the lattice by 0·6% in the a direction and 0·5% in the c direction. It may be assumed that titanium is present as a trivalent cation in the mixed oxide, since the solubility decreases with increasing oxygen partial pressure and ends approximately at 10^{-15} bar. The solubility of Ti in Cr_2O_3 was also proved qualitatively in oxide layers of high-temperature alloys.[9]

In the range of $p_{O_2} < 10^{-18}$ bar the compound $CrTi_2O_5$ is formed as well as the Magneli phases Ti_nO_{2n-1} which have not been studied here in detail. The index n has the value 4 at 10^{-21} bar and increases with rising oxygen partial pressure. The compound $CrTi_2O_5$ has a monoclinic crystal lattice.

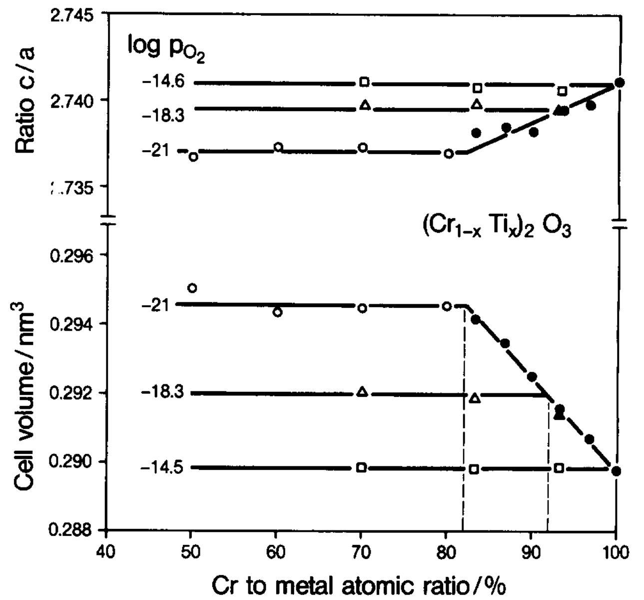

Fig. 9. Solubility of titanium in the corundum-type phase Cr_2O_3 (hexagonally indexed) determined by X-ray measurement after annealing at 1000°C and several oxygen partial pressures.

The following parameters were determined from the X-ray diffractograms present (with Cr_2O_3 and Ti_4O_7 as the second phase): $a = 1005{\cdot}5 \pm 1{\cdot}1$ pm, $b = 503{\cdot}3 \pm 0{\cdot}5$ pm, $c = 706{\cdot}5 \pm 0{\cdot}8$ pm and $\beta = 111{\cdot}67 \pm 0{\cdot}06°$. A more precise determination of the parameters and of the structure of $CrTi_2O_5$ may be found in a paper by Müller-Buschbaum & Bluhm.[10]

The Andersson phases $A_n = Cr_2Ti_{n-2}O_{2n-1}$ and rutile appear above 10^{-18} bar. In contrast to known results at $T > 1200°C$ in air[11–15] the region of the continuous E phase does not exist at 1000°C, but only the A_5 compound $Cr_2Ti_3O_9$ which, however, is only stable at a low O_2 partial pressure. At high O_2 partial pressures it partially disproportionates into Cr_2O_3 and an A_n phase. The region of the continuous A phase is also present at 1000°C. It ends as for higher temperatures at a chromium ion fraction of 12%, but does not begin at $n = 8$ or 9, but probably only at $n = 11$ or 12.

3.4 Quasi-ternary Cr–Mn–Ti oxide system

The results of the X-ray diffraction studies carried out on specimens of the Cr–Mn–Ti oxide system after annealing at 1000°C in the two standard atmospheres are compiled in Fig. 10 (annealing in air) and Fig. 11 (annealing in the Ar/H_2 atmosphere); three-phase regions are white, one-phase regions are dark and two-phase regions are radiate-shaded.

Decisive in the two diagrams are the spinels. They appear halfway on the quasi-binary edges and in all regions of the quasi-ternary system except for region 9 in Fig. 11. The spinel $MnCr_2O_4$ as well as the corundum-type Cr_2O_3 and the ilmenite-type

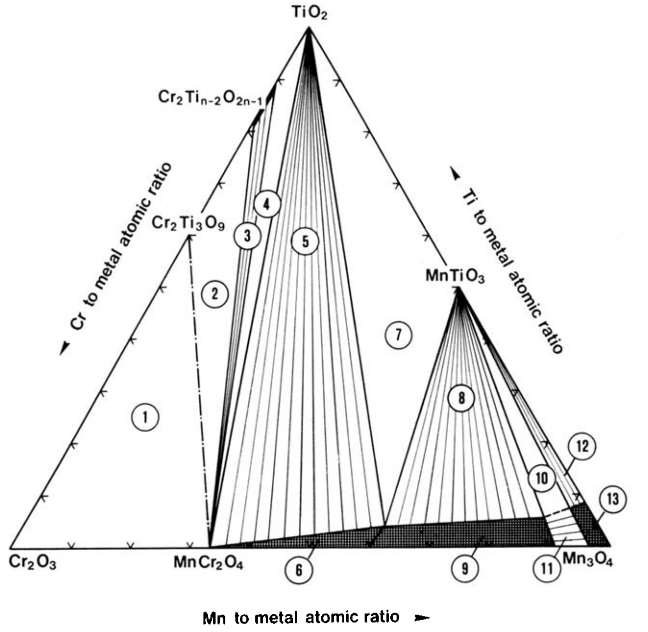

Fig. 10. Phase equilibria in the quasi-ternary system Cr_2O_3–Mn_3O_4–TiO_2 after annealing at 1000°C in air.

$MnTiO_3$ (pyrophanite) are formed independently of the O_2 partial pressure within the used conditions.

Annealing in air (Fig. 10) produces the spinels which can be represented by the formula $Mn(Mn_xCr_{1-x})_2O_4$, i.e. the cubic spinel with $0 \leq x < 0{\cdot}39$, the tetragonal spinel with $0{\cdot}39 \leq x < 0{\cdot}87$ and the tetragonal hausmannite with $0{\cdot}095 < x \leq 1$. These spinels form solid solutions with the cubic spinel Mn_2TiO_4, resulting in the three single-phase regions 6, 9 and 13 respectively. The maximum fraction of Mn_2TiO_4 in these solid solutions increases with decreasing oxygen partial pressure. After annealing in air this fraction has a maximum value of 0·16. The lattice parameters resulting for the upper-phase limit of region 9 are also plotted in Fig. 6 for comparison with those of the lower-phase limit, i.e. those of the binary system.

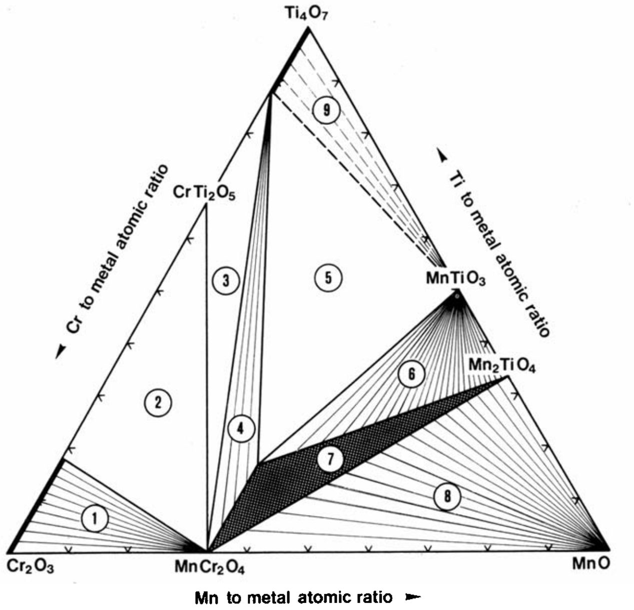

Fig. 11. Phase equilibria in the quasi-ternary system Cr_2O_3–MnO–Ti_4O_7 after annealing at 1000°C and an oxygen partial pressure of 10^{-21} bar (Ar/H_2).

In an Ar/H_2 atmosphere with $p_{O_2} \approx 10^{-21}$ bar (Fig. 11) a mixed spinel is formed by the spinels $MnCr_2O_4$, Mn_2TiO_4 and $MnTi_2O_4$, producing the single-phase region 7. Consequently, the three adjacent regions 4, 6 and 8 are two-phase with 'Ti_4O_7', pyrophanite $MnTiO_3$ and manganosite MnO at the edge. Two further two-phase regions result from the solubility of Ti in chromium oxide (region 1) and of Cr in titanium oxide (region 9). Region 9 was not examined in detail.

The cubic spinel in region 7 can be described by the formula

$$\mathrm{Mn}^{2+}_{1+y}\mathrm{Cr}^{3+}_{2-2y-2u}\mathrm{Ti}^{3+}_{2u}\mathrm{Ti}^{4+}_{y}\mathrm{O}_4$$

where the parameters y and u specify the fractions of the spinels Mn_2TiO_4 and $MnTi_2O_4$ in the mixture. The solid solutions between $MnCr_2O_4$ and Mn_2TiO_4 are characterized by $u = 0$ and are in equilibrium with MnO. The lattice parameters of this solid solution series are plotted in Fig. 12 over the parameter y using the lattice parameters measured on the specimens of region 8. The composition determined by chemical analysis is used to derive the associated parameter y in each case through projection from the MnO corner to the mixed-spinel straight line. The results obtained in this way (Fig. 12) are in good agreement with the values measured by Hagenmüller *et al.*[16]

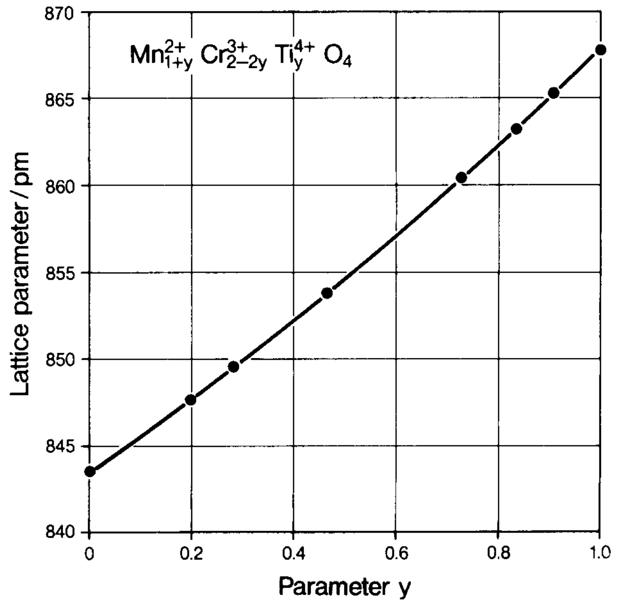

Fig. 12. Lattice parameter of the cubic mixed spinel $Mn_{1+y}Cr_{2-2y}Ti_yO_4$ as a function of the composition parameter y.

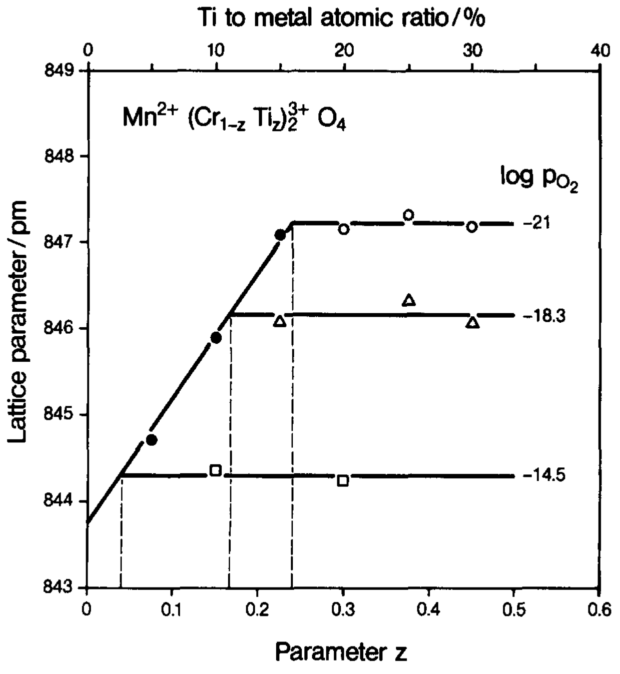

Fig. 13. Solubility of Ti^{3+} ions in the spinel $MnCr_2O_4$ at 1000°C and several oxygen partial pressures.

While $MnCr_2O_4$ and Mn_2TiO_4 can contribute fractions of 0 to 100% to the mixed spinel, there is a limit for the fraction u of the third spinel $Mn^{2+}Ti_2^{3+}O_4$ which, in a first approximation, is proportional to the fraction of the $Mn^{2+}Cr_2^{3+}O_4$ spinel so that $u = z(1 - y)$ can be defined. The single-phase spinel region 7 can therefore also be interpreted as replacement of chromium ions by trivalent titanium ions in the mixed spinel $Mn(Cr_{1-z}Ti_z)_2O_4$–Mn_2TiO_4.

Figure 13 shows the lattice parameter of the spinel $Mn^{2+}(Cr_{1-z}Ti_z)_2^{3+}O_4$ plotted over the parameter z (substitution of Cr^{3+} by Ti^{3+}) for different oxygen partial pressures. $z_{max} = 0{\cdot}24$ for $p_{O_2} = 10^{-21}$ bar. z_{max} becomes smaller with rising oxygen partial pressure, i.e. the solubility for titanium decreases. In this case the single-phase region 7 in Fig. 11 becomes narrower, leaving only the mixed-spinel straight line $MnCr_2O_4$–Mn_2TiO_4 at about 10^{-14} bar, whose region of existence obviously extends up to significantly higher oxygen partial pressures.

4 Conclusions

The spinels play a decisive role in the quasi-ternary Cr–Mn–Ti oxide system. The spinel $MnCr_2O_4$ may be regarded as the central connection. Part of the chromium can be replaced by trivalent manganese at high oxygen partial pressures and by trivalent titanium at low pressures, and the formation of a solid solution with the spinel Mn_2TiO_4 is possible in all cases.

In this way, a coherent single-phase spinel region is observed which extends over the entire oxygen partial pressure range of 0·21 to 10^{-21} bar examined at 1000°C. The lattice parameter of the cubic mixed spinels ranges between 844 and 868 pm for $MnCr_2O_4$ and Mn_2TiO_4 respectively.

A spinel phase whose lattice parameter was within these two values was also identified on the outer surface of oxide layers which had been formed under highly different conditions on the high-temperature alloys INCOLOY 800 H and HASTELLOY X. However, the lattice parameter alone is not sufficient to define the composition, since this system has a higher degree of freedom.

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