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Mixed Oxides Prepared with an Induction Plasma Torch

Part 2 *Chromia/Titania*

T. I. BARRY, R. K. BAYLISS, L. A. LAY
Inorganic and Metallic Structure Division, National Physical Laboratory, Teddington, Middx, UK

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Pure and mixed titania and chromia have been prepared and characterised by methods described in the previous paper [1]. The titania and chromia/titania contained mostly spherical particles in the size range 0.01 to 0.15 μm. The pure titania was mainly the metastable phase, anatase, but the proportions of rutile and of stacking faults in the rutile structure increased with increasing chromium concentration.

A high degree of solid solution was achieved for the mixed oxides, a result which accords with the proximity of the temperature ranges for condensation, predictable from thermodynamic data. This is the chief factor which distinguishes the behaviour of the chromia/titania from that of the chromia/alumina system. It is concluded that reference to such data should enable processes in the gas phase to be predicted and controlled. Processes in the condensed phase are governed as much by kinetic as equilibrium factors.

1. Introduction

This work is a companion study to that reported in the preceding paper on the preparation of mixed chromium/aluminium oxides [1]. Under equilibrium conditions, titania and chromia do not have a wide range of solid solution; instead there is a homologous series of mixed metal oxides of general formula $Ti_{n-2}Cr_2O_{2n-1}$ each with a narrow range of composition [2]. The purpose of this paper is to examine whether preparation of the oxides with the plasma torch leads to solid solution or to phase separation, and in this way to determine the factors that control the nature of the product. Finely-divided TiO_2 is widely used in paints, fillers and delustrants. It has undesirable photochemical activity which can to some extent be controlled by additives.

2. Experimental

The experimental methods were as reported for chromia/alumina [1] except that the susceptibility measurements were confined to the temperature range -196 to $+50°$ C. No observations of the effect of pretreatment in oxygen or hydrogen were attempted.

3. Results

3.1. Physical Characteristics

The products were fine light powders. The colours and compositions are collected in table I together with X-ray data.

3.2. Electron Microscopy and Diffraction

In pure titania and mixed oxide specimens the majority of the particles were spherical, but a fraction had angular shapes. Some of these were found by electron diffraction to be single crystals, with diffraction spots elongated into lines. This suggests the presence of stacking faults which are discussed more fully under X-ray diffraction. The particle size ranged from 0.01 to 0.15 μm.

3.3. X-ray Diffraction

At zero concentration of chromia the TiO_2 phase produced was predominantly anatase, whereas rutile is the stable phase at all temperatures.

TABLE I Details of chromia/titania preparations.

Sample no.	Cr at. % of total cations	Colour	X-ray evidence
100% Ti (3 specimens)	0.00	white	anatase, trace of rutile, sharp lines, normal intensities
1% Cr/99% Ti	0.87	pale yellow	anatase, a little rutile, sharp lines, normal intensities
8% Cr/92% Ti	7.55	pale yellow brown	anatase with rutile, broader lines, abnormal intensities
11% Cr/89% Ti	10.60	dirty yellow	rutile with anatase, still broader lines, abnormal intensities
13% Cr/87% Ti	12.90	dirty yellow	similar to 11% Cr/89% Ti
46% Cr/54% Ti	45.60	khaki green	rutile with very broad lines 1 1 0 line weak, α-Cr_2O_3 with very broad lines, some additional lines
83% Cr/17% Ti	82.70	dark green	α-Cr_2O_3, 1 1 0 line relatively strong, broad lines
100% Cr	100.00	dark green	α-Cr_2O_3, 1 1 0 line relatively strong, broad lines

When the chromium fraction was increased, the proportion of rutile also increased, and when the Cr-cation fraction reached 0.1, the proportion of rutile exceeded anatase and some changes in line intensity could be seen. The 1 1 0 reflection of rutile was broadened and weakened. Andersson, Sundholm and Magnéli [2] observed that in ordered titanium chromium oxides of general formula $Ti_{n-2}Cr_2O_{2n-1}$, the crystal structure is made up of slabs of rutile, infinite in the *a* and *b* crystal directions. The stacking arrangement of the slabs in the *c* direction depends on the composition of the phase. No ordered phases were found in the present work, but the weakness of the 1 1 0 reflection suggests a misalignment of the slabs in such a way that the *d*-spacing was not well defined in the 1 1 0 direction. The increasing presence of stacking faults with increasing chromium content showed that chromium was indeed incorporated into the rutile structure.

For 46% Cr/54% Ti the α-Cr_2O_3 pattern was just discernible, and for 83% Cr/17% Ti it was the only phase apparent on the powder photograph. Again, line intensity changes occurred, but these were not due to solid solution of titanium-ions in the Cr_2O_3 lattice, since they occurred almost equally for 100% Cr. Probably these intensity changes were connected with the platelike habit of the larger Cr_2O_3 particles. Evidence of solid solution comes from enhanced line broadening from 83% Cr/17% Ti. The line broadening was so marked that it was not possible to say whether any changes in unit cell had occurred.

In summary, the evidence from X-ray diffraction is that solid solution of chromium-ions in TiO_2 and titanium-ions in Cr_2O_3 was extensive. Phase separation was noticeable only for the specimen containing almost equal proportions of chromium and titanium.

3.4. Electron Spin Resonance

Esr spectra were obtained from specimens at 25° C. The nominally pure TiO_2 showed a low intensity spectrum including some sharp features, indicating Cu^{2+} and V^{4+} impurities, and some weak broad signals, which were probably due to impurity iron oxides from laboratory dust. The specimens containing chromium showed five types of spectra from Cr^{3+} as listed below; no Cr^{5+} was detected.

(i) Sharp peaks at 3320 and 3420 Oe arising from Cr^{3+}-ions in Ti^{4+} sites in anatase [3]. The line width of this spectrum became progressively greater with increasing chromium content due to spin dipole broadening. The signal was strongest in 8% Cr/92% Ti, and very weak in 13% Cr/87% Ti.

(ii) Peaks at 1170 and 1335 Oe arising from Cr^{3+} ions in Ti^{4+} sites in rutile [4]. These signals were visible only in 8% Cr/92% Ti and 11% Cr/89% Ti. They were weak partly because the proportion of rutile was low at low chromium concentrations, and partly because the sensitivity of esr for Cr^{3+} in rutile is relatively poor.

(iii) A broad signal centred at 3100 Oe with a peak-to-peak line width of 1200 Oe. This spectrum is equivalent to the β_W resonance in chromia/alumina, and arises from weakly coupled Cr^{3+}-ions.

(iv) A broad signal centred at 3300 Oe with a peak-to-peak line width of 900 Oe. This type of signal is equivalent to the β_N resonance in chromia/alumina, and arises from magnetically ordered regions of composition approaching that of Cr_2O_3 [1]. The line width is greater than normal for Cr_2O_3, probably because of the small particle size.

(v) A group of signals of average line width 100 Oe in the region 1750 to 2200 Oe. These could arise from magnetically dilute Cr^{3+}-ions near lattice defects in rutile or anatase. These signals occur only in 11% Cr/89% Ti.

The type of spectrum found for each specimen is shown in table II. The increasing concentration of Cr^{3+}-ions in solid solution in the TiO_2 matrix is shown first by the broadening of the peaks due to Cr^{3+} in anatase, and then by the increasing dominance of spectrum C, which is due to weakly coupled pairs or groups. However, some phase separation does occur. Spectrum D sensitively indicates a Cr_2O_3-like magnetic structure which occurs to a small extent even in 8% Cr/92% Ti.

TABLE II Character of esr spectra of chromia/titania specimens.

Specimen	Character of spectrum
1% Cr/99% Ti	A (sharp spectrum), C
8% Cr/92% Ti	C, A (broad peaks), some D and B
11% Cr/89% Ti	C, A (very broad peaks), E, some D and B
13% Cr/87% Ti	C, D, A (very broad peaks)
46% Cr/54% Ti	D
83% Cr/17% Ti	D
100% Cr	D

3.5. Magnetic Susceptibility Measurements

A comparison of the susceptibility data of 8% Cr/92% Ti and 5% Cr/95% Al [1] shows that a greater degree of solid solution was achieved in the chromia/titania than in the chromia/alumina system. If the results for 8% Cr/92% Ti are calculated by the same methods as were used in the preceding paper, the value of the fraction of dispersed Cr^{3+}-ions is 0.49, compared with 0.42 for 5% Cr/95% Al. Thus, for a higher total fraction of chromium atoms in the chromia/titania, the proportion of well dispersed Cr^{3+}-ions is greater.

4. Discussion

A comparison of the results obtained for the chromia/titania preparations with those for chromia/alumina [1] shows that despite some similarities, there is a distinction in the degree of solid solution achieved. The chromia/titania specimens show a wide range of solid solution, as revealed by broad X-ray reflections with changed intensities, and by the fact that the TiO_2 and α-Cr_2O_3 phases exist separately only where the concentrations of both titanium and chromium are high. In contrast, phase separation is marked in the chromia/alumina specimens even at low chromium concentrations. However, it must be pointed out that observations of X-ray diffraction should be used with caution. In the chromia/alumina system most of the ions are trivalent, and so can exchange sites without charge compensation, whereas in the chromia/titania system point defects or stacking faults must be incorporated during solid solution because of the charge difference between the two cations. For this reason, chromia particles containing titania would necessarily have broader X-ray lines than chromia particles containing the same percentage of alumina. This line broadening for chromia particles containing titania could make them undetectable by X-ray diffraction in a preparation containing mostly titania particles. Thus phase separation must be to some extent obscured. Despite these qualifications, there appears to be a real difference in the degree of solid solution in the two systems. This conclusion is supported by the observations of esr and magnetic susceptibility. Thermodynamic considerations discussed below suggest that the difference in behaviour may be ascribed to variations in the time and temperature sequence of the condensation process. Data from the JANAF tables [5] are used as a basis for this discussion.

4.1. Titania

The temperature of the plasma exceeds 5000° K. However, even at this temperature $TiCl_4$ is not completely dissociated; Ti, TiCl and possibly $TiCl_2$ coexist in the gas phase. In the presence of a large excess of oxygen over chlorine, rapid reaction to form TiO occurs. As the temperature of the gas emerging from the plasma falls below 4000° K, TiO_2 becomes the dominant species.

At temperatures less than 2500° K, the vapour pressure of liquid TiO_2 falls below the partial pressure of TiO_2 gas, and condensation can occur. The immediate question is whether titania condenses to a liquid or a solid. The maximum temperature at which condensation to a solid could occur would be the melting point of rutile, i.e. 2143° K. Even at this temperature the supersaturation would be very high unless condensation had previously occurred; (the vapour pressure of TiO_2 at 2143° K is 4×10^{-7} atm; the partial pressure of TiO_2 gas is approximately 10^{-5} atm) thus the most probable temperature range for condensation is 2400 to 2200° K, with the production of liquid droplets.

The predominant phase of pure titania found experimentally is anatase which is metastable with respect to rutile at all temperatures. The hypothetical melting point of anatase calculated from the free energy data is only 1096° K, so that if this value is correct, anatase cannot exist above 1096° K, nor can it be formed from rutile below this temperature. The conclusion is that TiO_2 condenses as a liquid, which converts to anatase at 1096° K, or lower temperatures. As already discussed, liquid droplets probably form in the temperature range 2400 to 2200° K, and yet rutile does not crystallise from the liquid in the temperature interval 2200 to 1096° K. In both the rutile and anatase structures, the Ti^{4+} ions are surrounded by distorted octahedra of oxygen-ions. In anatase, the TiO bonds are shorter, but the octahedra are less efficiently packed, so that its density is lower than that of rutile. In rutile, octahedra are joined into chains by sharing of their shortest edges, and probably it is the stacking of the octahedra which makes nucleation of the rutile structure difficult.

According to Brauer and Littke [6], rutile becomes oxygen-deficient compared with TiO_2 when heated at its melting point, 2143° K, if the partial pressure of oxygen is less than 0.4 atm. In the plasma tail flame, the oxygen pressure is about 0.8 atm but, even at this pressure, liquid titania droplets condensing at over 2200° K are likely to be oxygen-deficient. During cooling of the liquid and solid particles, adsorption and incorporation of oxygen should occur. A glow in the tail of the oxygen plasma shows that excited states of oxygen have a lifetime in the system of the order of 0.3 sec. These excited species may make a contribution to the modification of the particles as they fall rapidly through the temperature range 2000 to 1000° K. All these factors must have an influence on the final composition of the particles which is $TiO_{1.97}$ according to magnetic susceptibility measurements [7]. The Ti/O system has recently been reviewed by Wahlbeck and Gilles [8] who have also made vaporisation studies [9]. $TiO_{1.97}$ lies outside the stability range of rutile, which extends only to $TiO_{1.992}$. The defect structure of anatase has not yet been made the subject of a detailed study.

4.2. The Condensation of Chromia/Titania

In the preceding paper [1] it was argued that the pure chromia condenses as solid particles, probably in the temperature range 2100 to 1900° K, whereas the most probable temperature range for condensation of titania is 2400 to 2200° K. The discrepancy between these two temperature ranges is much smaller than for alumina and chromia. The gap will be reduced when both oxides are present, because the vapour pressure of a solution of Cr_2O_3 in TiO_2 liquid must be lower than that for Cr_2O_3 itself. TiO_2 has a high dielectric constant, and is therefore a good ionising solvent. Thus the relatively high degree of solid solution found for the chromia/titania specimens is readily accounted for.

In the liquid, and in the solid quenched from the liquid, ordering of Cr^{3+}-ions in TiO_2 is likely to be limited, and it is not surprising that no evidence of ordered chromia/titania phases was found. Nevertheless, the specimens containing 8 to 46% chromium showed abnormal X-ray intensities consistent with the existence of stacking faults. Thus it seems improbable that there was an entirely random distribution of the oxygen vacancies or interstitial metal ions which must have been incorporated with the Cr^{3+} ions. The esr spectrum E, observed only for 11% Cr/89% Ti may have arisen from the change of symmetry of Cr^{3+}-ions caused by their location at these stacking faults. At lower concentrations, the Cr^{3+}-ions were not charge compensated locally, probably because of the high quenching rate, and because the high dielectric constant of TiO_2 lowers the dissociation energy of defect pairs.

The increasing Cr^{3+} concentration also has the effect of increasing the proportion of rutile. Although this probably occurs because of the greater ease of reorganisation of a structure containing some oxygen vacancies, there is insufficient evidence for further comment.

It is clear from the nature of the pure aluminium and titanium oxides, and of the mixed oxides with chromia, that neither the crystalline phases nor the degree of solid solution are determined by normal solid state equilibria. The crystallisation processes are governed to a large degree by kinetic factors, especially the rate of nucleation [10]. On the other hand, there is good evidence that processes in the gas phase do approach equilibrium. Thus the nature of the product is influenced by the gas phase equilibria which determine the partial pressures of the various gaseous species and by the vapour pressures of the possible condensed phases.

An understanding of these factors should make it possible not only to predict the behaviour for a particular system, but also to exercise some control on this behaviour. For example, the vapour pressure of incongruently vaporising products can be changed by control of the gaseous components of the plasma, and processes in the condensed phase can be influenced by the rate of quenching.

5. Conclusions

(i) The preparation of titania in an induction plasma leads principally to anatase rather than to the stable phase rutile.

(ii) A relatively high degree of solid solution was achieved for the chromia/titania system, as compared with the chromia/alumina system. The result is consistent with a closer similarity of vapour pressures for chromia and titania.

(iii) An increasing concentration of chromia in the titania leads to a greater proportion of rutile, and to stacking faults in the rutile phase, but none of the ordered, equilibrium phases, $Ti_{n-2}Cr_2O_{2n-1}$, were found.

(iv) The conclusions above and those for the preceding paper indicate that under the conditions in the tail of the plasma, processes in the solid phase are governed by kinetic factors and seldom reach equilibrium, whereas processes occurring in the gas phase and during condensation do approach equilibrium.

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