JOURNAL OF SOLID STATE CHEMISTRY 4, 351–356 (1972)

Interdiffusion and the Solubility Limits of Cr_2O_3 in the Rutile Phase of TiO_2

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Received May 26, 1971

The interdiffusion of Cr_2O_3 and TiO_2 has been studied between 990 and 1520°C in the range of concentrations for which the solid phase is a rutile solid solution. The concentration limits of this phase have been determined. At low concentrations the interdiffusion coefficient varies approximately as chromium concentration but decreases again at higher concentration. The ratio of the diffusion coefficients parallel and perpendicular to the rutile *c*-axis decreases from 4.0 at 990°C to 1.75 at 1520°C. Attention is drawn to some features of the problem of evaluation of interdiffusion coefficients in systems of variable molar volume.

Introduction

The interdiffusion of oxides has been the subject of an increasing amount of attention in recent years. Studies so far have been confined mainly to systems in which transport is believed to occur by a point defect mechanism; however, evidence is accumulating that, in a number of oxide systems, mass transport might occur by migration of extended defects such as crystallographic shear (CS) planes which are planes containing a higher density of cations and which may be considered as formally derived from the parent crystal by removal of a plane of anions and then closing up the crystal by displacement of the two parts relative to each other. This evidence, largely from electron microscope and other structural studies, has been the subject of recent reviews (*1*).

Electron microscope studies of the TiO_2–Cr_2O_3 system by Bursill, Hyde, and Philp (*2*) have led us to investigate interdiffusion of these oxides, using an electron microprobe. In this paper, we describe first our methods and then our measurements in the region of rutile structure solid solution (low chromium concentration).

Sample Preparation

Small cubes of TiO_2 (~1 mm^3) were cut from a boule of pure TiO_2 supplied by the National Lead Company. The cube edges were parallel to the crystal axes. One face of the cube was highly polished (diamond paste then gamma alumina). In all the work to be reported here, the other half of the diffusion couple was dense polycrystalline $Ti_2Cr_2O_7$. This was made by intimately mixing appropriate proportions of the pure oxides, prefiring at 4–5 kbar at about 1000°C in a sealed tube, and then sintering in air at 1300°C for 7 days. This procedure gave a dense material which accepted a high polish.

Diffusion Anneals and Analysis

In each diffusion run two TiO_2 cubes, one with polished face perpendicular to the *c*-axis and one with polished face containing the *c*-axis, were placed on a polished face of a $Ti_2Cr_2O_7$ pellet. After the diffusion anneal (in air), cuts with a wire saw were made parallel to the diffusion direction through the TiO_2 cubes and the underlying pellet. The pieces were then mounted and the cut faces polished with great care being taken to preserve a flat surface To this end final polishing consisted of only a brief polish with a 6- and a 3-micron diamond powder in an oil medium. Although the resulting surface retained fine scratches, it could be kept sufficiently flat for electron microprobe analysis of the highest accuracy.

Analyses were made with CAMECA MS46 electron microprobe utilizing two pairs of opposed spectrometers. Simultaneous recording of chromium $K\alpha$ radiation from opposed spectrometers allows one to spot any artefacts due to irregularities or curvature of the sample surface. Titanium and chromium analyses were made at 20 μm intervals along the diffusion path. The counting rate for each element was standardized by comparison with counts from $Ti_2Cr_2O_7$. The composition at each point was then calculated using a modified version of Rucklidge's data reduction program (*3*).

We have found that under our operating conditions the relative count rate is not strictly linear with concentration over the whole range of composition. However, for the low chromium concentrations of interest, it was found that within experimental error the chromium concentration measured as mole fraction of $Ti_{2/7}Cr_{2/7}O$ in $Ti_{1/2}O$ was equal to 1.11 times the relative count rate; the relative count rate being defined as count rate, corrected for background, from the sample divided by the similarly corrected count rate from the $Ti_2Cr_2O_7$ standard. The reason for the unusual formula units chosen for the two components is explained below.

Determination of the Interdiffusion Coefficient

The operational definition of the interdiffusion coefficient has been discussed recently by Wagner (*4*), with particular reference to diffusion couples such as under study in this work. He emphasizes that there is but one interdiffusion coefficient in a binary system and that this must be invariant with choice of the frame of reference. The diffusion coefficient is given by

$$\tilde{D} = V(X_2 J_1 - X_1 J_2)/\partial X_2/\partial x. \quad (1)$$

Here V is the molar volume, X_1 and X_2 are the mole fractions and J_1 and J_2 the molar fluxes of components 1 and 2, respectively. x is the coordinate in the diffusion direction and may be chosen with respect to any suitable reference plane.

Sauer and Freise (*5*), Wagner (*4*), and more recently, van Loo (*6*) have discussed at length the procedure for evaluating $\tilde{D}(X_2)$ from data for a diffusion couple in the case that V is not constant. Their result may be written

$$D = \frac{V}{2t}\left(\frac{\partial x}{\partial Y}\right)\left[(1-Y)\int_{-\infty}^{x}\frac{Y}{V}dx + Y\int_{x}^{\infty}\frac{(1-Y)}{V}dx\right], \quad (2)$$

where Y is defined by

$$Y = (X_2 - X_2^-)/X_2^+ - X_2^-), \quad (3)$$

and in turn X_2^+, X_2^- are the mole fractions of component 2 at $x = \pm\infty$.

In our experiments reported here, we have been exclusively concerned with the interdiffusion of $Ti_{1/2}O$ (i.e., TiO_2) considered to be component 1 and $Ti_{2/7}Cr_{2/7}O$ (i.e., $Ti_2Cr_2O_7$) considered to be component 2. The formula units of the two components are referred to one atom of oxygen, as *with this choice* the molar volume is only a very weak function of composition. It transpires also that this is also a very convenient choice of components in microprobe work with many oxide systems. Equation (3) now becomes

$$Y = 1 - X_2. \quad (4)$$

For the variation of V with concentration, we have utilized the lattice parameter measurements of Flörke and Lee (*7*). These authors found that within experimental error c_0 was independent of concentration. We considered, therefore, for diffusion anneals with $x \parallel c_0$, we should carry out the calculation as if the molar volume were constant. Equation (2) then becomes simply

$$\tilde{D} = \frac{1}{2t}\frac{\partial x}{\partial Y}\left[(1-Y)\int_{-\infty}^{x} Y\,dx + Y\int_{x}^{\infty}(1-Y)\,dx\right]. \quad (5)$$

This expression is conveniently evaluated graphically from a plot of $1 - Y$ (i.e., X_2) vs x.

When the molar volume is a function of concentration, it is convenient to introduce two new variables $v = V(X_2 = 0)/V(X_2)$ and $y = v(1 - Y)$. Equation (2) may then be written

$$\tilde{D} = \frac{-1}{2t[\partial y/\partial x - (y/v)\partial v/\partial x]} \times \left[(y/v)\int_{-\infty}^{x}(v-y)\,dx + (1-y/v)\int_{x}^{\infty} y\,dx\right]. \quad (7)$$

This expression may then be evaluated from one graph on which y and v are plotted as a function of x as is shown schematically in Fig. 1.

In the case of diffusion with $x \perp c$, we have considered that the appropriate volume is now proportional to a_0^3. The molar volume is only a weak function of concentration and within experimental error linear with concentration so that we may write, if α is a constant,

$$1/v = V(X_2)/V(X_2 = 0) = 1 + \alpha X_2. \quad (7)$$

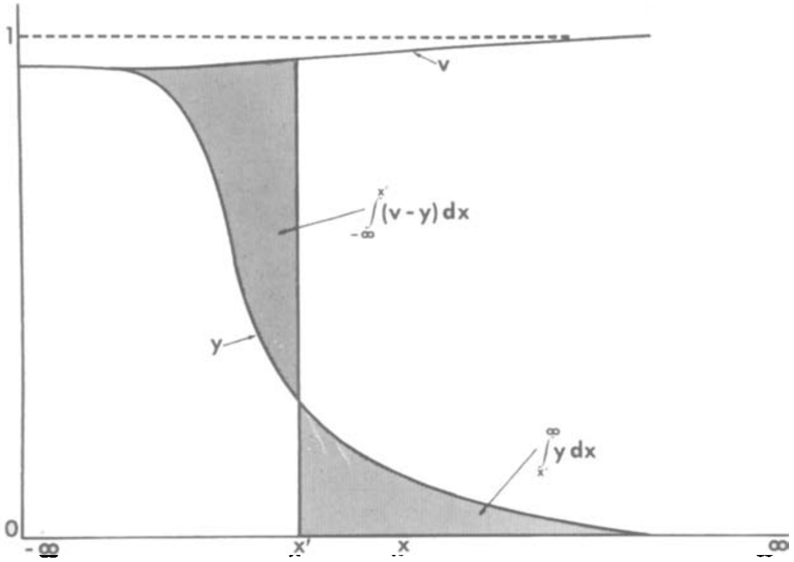

FIG. 1. Illustrating the graphical evaluation of the integrals needed for the evaluation of the interdiffusion coefficient from Eq. (7).

Equation (6) may be simplified a little to read in this case:

$$\tilde{D} = \frac{-v}{2t}\frac{\partial x}{\partial y}\left[(y/v)\int_{\infty}^{x} (y-v)\,dx + (1-y/v)\int_{x}^{\infty} y\,dx\right]. \tag{8}$$

Utilizing again the data of Flörke and Lee (7), we find that the appropriate value of α in Eq. (7) is $\alpha = 0.0625$ for $Ti_{1/2}O$–$Ti_{2/7}Cr_{2/7}O$. The correction for variation of molar volume with composition is barely greater than the experimental error in determining $\tilde{D}$.

Diffusion in the Rutile "Solid Solution" Region

Flörke and Lee (7) have determined part of the phase diagram of the TiO_2–Cr_2O_3 system. In agreement with earlier work, their results indicate a wide region of apparent primary solid solution of Cr_2O_3 in TiO_2. Expressed in terms of $N =$ mole fraction $Cr_{1.5}O_2$ in TiO_2, this solubility is as large as $N = 0.1$ at 1500°C. In the notation of the present paper, this corresponds to $1 - Y = 0.17$.[1] Our results confirm this behavior, although we are well aware that apparently single-phase solid solutions often resolve into biphasic mixtures under sufficient close scrutiny.

Specifically, we found in our experiments that after short diffusion anneals (such as illustrated by Fig. 2), a sharp interface persisted between $Ti_2Cr_2O_7$ and this primary solid solution. Only after very long diffusion anneals (to be discussed in a subsequent communication) did the intermediate Magnéli (8) phases $Ti_{n-2}Cr_2O_{2n-1}$ become evident. The limiting solubility determined from the interface concentration in these experiments was in good agreement with the data of Flörke and Lee and is shown in Fig. 3.

The concentration profiles of the type shown in Fig. 2 were analyzed according to Eq. (5) or Eq. (8) to obtain the interdiffusion coefficient in the direction perpendicular ($D_\perp$) or parallel ($D_\parallel$) to the rutile c-axis. In all our experiments, we found that $D_\perp < D_\parallel$ although the anisotropy is not large and only very weakly dependent on concentration. The results are displayed as $\log D$ as a function of concentration at constant temperature in Fig. 4 and as $\log D$ as a function of $1/T$ at constant concentration in Fig. 5. As temperature increases, $D_\parallel/D_\perp$ decreases from approximately 4.0 at 990°C to 1.75 at 1520°C. Interestingly, extrapolation to the melting point of TiO_2 ($\approx$1850°C in air) yields $D_\parallel \approx D_\perp \approx 10^{-11}$ m^2 sec^{-1} at this temperature.

Discussion

There are several features of the diffusion data that merit attention. These are:

(1) At low chromium concentrations the interdiffusion coefficient is very roughly proportional to chromium concentration, but at higher chromium

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[1] It is elementary to show that $N = 4(1 - Y)/(8 - Y)$.

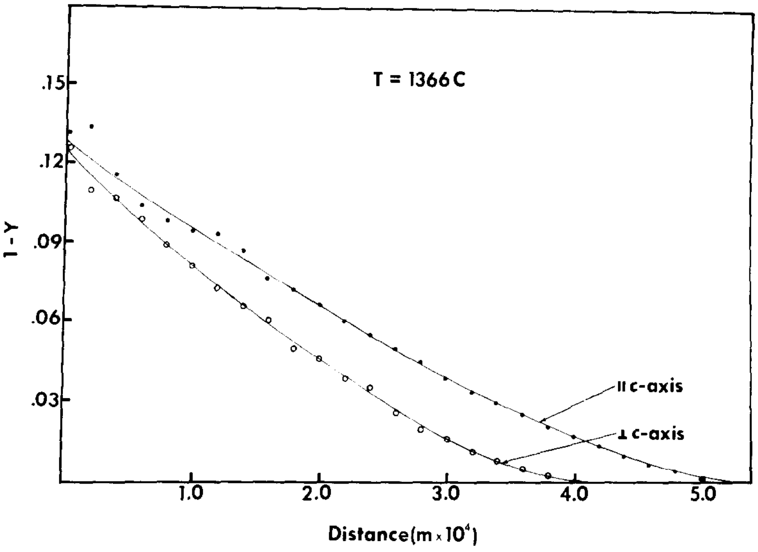

FIG. 2. Representative concentration profiles obtained for diffusion perpendicular and parallel to the rutile c-axis after 3 hr at 1366°C. $1 - Y$ is the mole fraction of $Ti_{2/7}Cr_{2/7}O$ in $Ti_{1/2}O$.

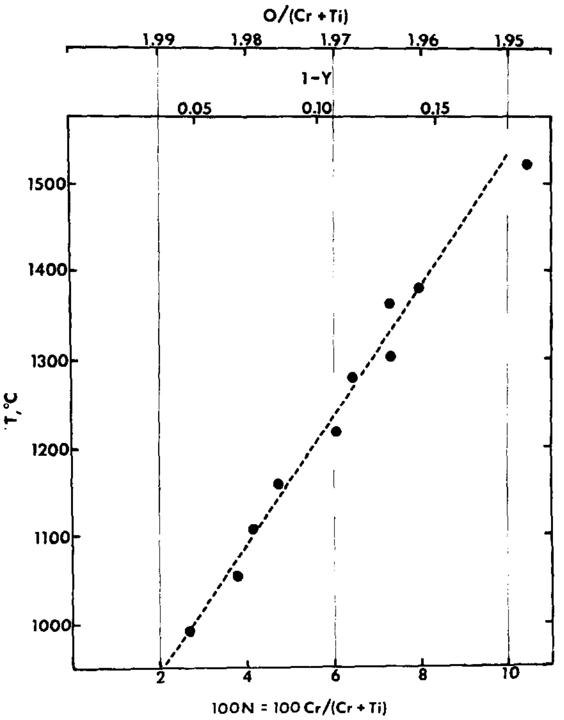

FIG. 3. Limiting concentration of chromium in the "rutile solid solution" phase of TiO_2-Cr_2O_3. Each point represents the average of data from diffusion runs in directions perpendicular and parallel to the c-axis (such as shown in Fig. 2).

concentration $\tilde{D}$ shows a broad maximum and, thereafter, a small decrease before the chromium solubility limit is reached. The simplest interpretation of this behavior is probably that, at low concentrations, mobile defects are introduced in a number proportional to the number of added chromium atoms. At higher concentrations, defect aggregates are presumably forming and it is tempting to interpret this behavior as premonitory of the formation of crystallographic shear planes observed (*2*) at higher chromium concentrations. Certainly the interdiffusion is very much slower in the concentration range embracing the known Magnéli phases.

(2) The anisotropy of interdiffusion is small. In unpublished work, we have noticed for rutile coupled with several other oxides very pronounced anisotropy in interdiffusion ($D_{\parallel} \gg D_{\perp}$) and Johnson (*9*) and Steele and McCartney (*10*) have made similar observations for lithium and iron, respectively. The anisotropy of interdiffusion of TiO_2 and Cr_2O_3 is only a weak function of composition in the region we have studied and decreases with increasing temperature. The simplest interpretation of results, and the one that we adopt tentatively, is that cation displacements are between adjacent octahedral sites of the (approximately) close-packed oxygen lattice. Referred to a rutile unit cell these displacements are $\langle 00c \rangle$ and $\frac{1}{2}\langle a0c \rangle$. The first of these would contribute only to $D_{\parallel}$ whereas the

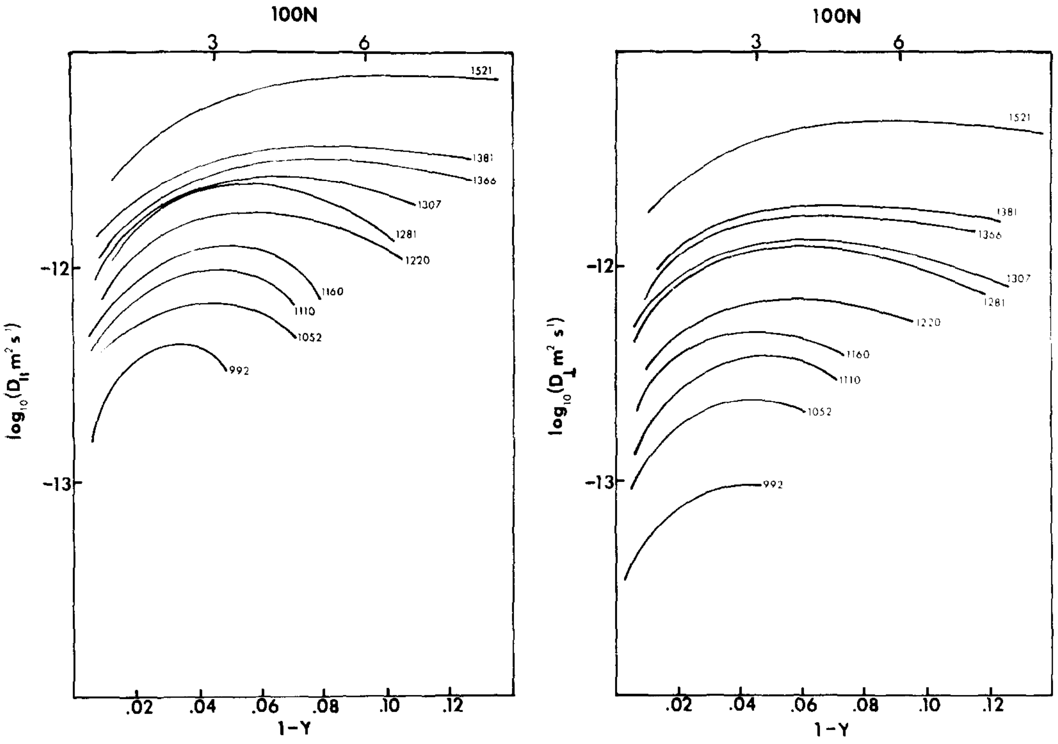

FIG. 4. Coefficient of interdiffusion of Cr_2O_3 and TiO_2 perpendicular ($D_\perp$) and parallel ($D_\parallel$) to the c-axis in the rutile solid solution. $1 - Y$ is the mole fraction of $Ti_{2/7}Cr_{2/7}O$ in $Ti_{1/2}O$.

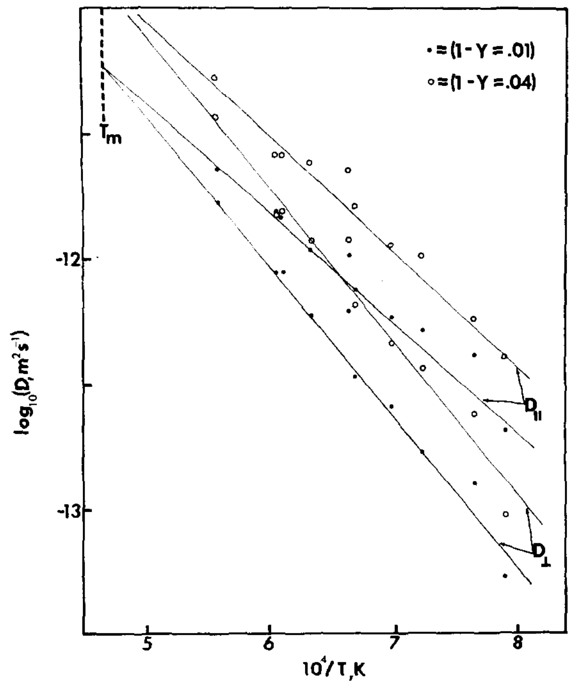

FIG. 5. Logarithm of the interdiffusion coefficient parallel ($D_\parallel$) and perpendicular ($D_\perp$) to the rutile c-axis at two concentrations as a function of reciprocal temperature. T_m is the melting point of TiO_2 in air (~1850°C).

second would contribute approximately equally to $D_\perp$ and $D_\parallel$[2]. One must conclude in this case that jumps along ⟨101⟩ contribute substantially to mass transport. Interestingly, these are the jumps required for lateral displacement of crystallographic shear planes in, e.g., the reduced titanium oxides (*11*). By way of contrast simple interstitial diffusion (such as almost certainly occurs, e.g., for lithium in dilute solution) involves only jumps along ⟨001⟩ with the result that $D_\parallel \gg D_\perp$.

(3) It is customary to report activation energies for diffusion. These can be derived readily from the data reported in Fig. 5. The results are for diffusion at constant composition perpendicular to the c-axis, $E_\parallel = 116$ kJ mol^{-1} and parallel to the c-axis $E_\perp = 86$ kJ mol^{-1}. At the highest concentrations, E appears to increase a little.

Acknowledgments

Discussions with B. G. Hyde and a preprint of Ref. (*2*) has provided much inspiration for this work which was made possible by a grant from the National Science Foundation.

[2] The argument is that on average jumps of the second kind have a displacement along a given a-axis of $a/4 \approx 0.115$ nm and along the c-axis of $c/2 \approx 0.14$ nm.

The National Science Foundation through its chemistry instruments program also provided substantial support for the establishment of the electron microprobe laboratory.

References

1. B. G. Hyde and L. Bursill *in* "Chemistry of Extended Defects in Nonmetallic Solids" (L. Eyring and M. O'Keeffe, Eds.), North-Holland, Amsterdam, (1970); M. O'Keeffe, *Proc. Brit. Ceram. Soc.* **19**, 1 (1971); L. E. Nagel and M. O'Keeffe, *Int. Rev. Sci.* in press (1971).
2. L. A. Bursill, B. G. Hyde, and D. K. Philp, *Phil. Mag.* **23**, 1501 (1971).
3. J. Rucklidge, thesis, Dept. of Geology, University of Toronto, Toronto, Ontario, Canada.
4. C. Wagner, *Acta Met.* **17**, 99 (1969).
5. F. Sauer and V. Freise, *Z. Elektrochem.* **66**, 353 (1962).
6. F. J. J. van Loo, *Acta Met.* **18**, 1107 (1970).
7. O. W. Flörke and C. W. Lee, *J. Solid State Chem.* **1**, 445 (1970).
8. S. Andersson, A. Sundholm, and A. Magnéli, *Acta Chem. Scand.* **13**, 989 (1959); S. Andersson and L. Jahnberg, *Ark. Kemi* **21**, 413 (1963).
9. O. W. Johnson, *Phys. Rev.* **136**, 284 (1964).
10. J. L. Steele and E. R. McCartney, *Nature* **222**, 79 (1969).
11. S. Andersson and A. D. Wadsley, *Nature* **211**, 581 (1966).