Self-diffusion in Cr_2O_3

II. Oxygen diffusion in single crystals

By A. C. S. SABIONI†, A. M. HUNTZ

Laboratoire de Métallurgie Structurale, Institut de Science des Matériaux,
Unité de Recherche associée au CNRS 1107, Batiment 413,
Université Paris-XI, F-91405 Orsay Cedex, France

F. MILLOT

Laboratoire des Composés Non Stoechiométriques,
Unité de Recherche associée au CNRS 449, Batiment 415,
Université Paris-XI, F-91405 Orsay Cedex, France

and C. MONTY

Laboratoire de Physique des Matériaux, CNRS,
Bellevue, F-92195 Meudon Cedex, France

ABSTRACT

Oxygen self-diffusion in chromia (Cr_2O_3) single crystals was studied as a function of oxygen pressure at 1100°C, using the gas–solid isotope exchange method. The diffusion experiments were performed in H_2–$H_2{}^{18}O$ atmospheres. After the diffusion anneal, the ^{18}O diffusion profiles were determined by secondary ion mass spectrometry and the diffusion coefficients were computed using a general solution for the Fick's second law, taking into account evaporation and exchange at the surface.

Our results show that oxygen diffusion coefficients at 1100°C do not depend on the oxygen pressure and are smaller than values given in the literature. Comparison with results concerning chromium self-diffusion in the same Cr_2O_3 single crystals clearly indicates that oxygen diffusion is faster than chromium diffusion.

§1. INTRODUCTION

Chromia (Cr_2O_3) scales are of high interest for protecting many metallic materials against corrosive gases at temperatures up to 1000–1100°C, this limit in temperature, being related to the evaporation phenomena of chromium oxides. Most researchers working on oxidation indicate that Cr_2O_3 scales grow mainly by outward chromium diffusion (Atkinson 1985). However, as discussed in part I (Sabioni *et al.* 1992), at this time, the relative diffusion rates of chromium and oxygen in Cr_2O_3 do not appear to be clear and problems remain about the understanding of the growth mechanism of Cr_2O_3 scales on chromium-rich alloys.

Such problems are related to the fact that there is a lack of data about the self-diffusion coefficients in Cr_2O_3, particularly for oxygen self-diffusion. Anionic self-diffusion was studied by Hagel (1965) and then by King and Park (1988). Hagel worked

---

† Present address: Departamento de Fisica, Universidade Federal de Ouro Preto, 35400, Minas Gerais, Brazil.
‡ Received in final form 31 October 1991.

on Cr_2O_2 samples formed of three or four porous grains (density greater than 95% of the theoretical density) obtained from polycrystals which had been milled and thermally treated, and King and Park worked on polycrystalline specimens. The lack of data is due to the difficulties encountered in measuring diffusion in chromia as explained in part I (Sabioni et al. 1992).

Thus it appeared necessary to perform new diffusion experiments of both cation and anion on the same Cr_2O_3 samples, treated in conditions which were as similar as possible. This was our objective. In part I (Sabioni et al. 1992), the results concerning the chromium self-diffusion were presented. Diffusion experiments were carried out in CO–CO_2 mixtures. In this paper, the results for oxygen lattice self-diffusion in Cr_2O_3 will be presented. Diffusion anneals were performed in H_2–H_2O mixtures. It is the first time that such measurements were carried out on Cr_2O_3 single crystals.

§ 2. Experimental
2.1. Material

Cr_2O_3 single crystals of 99·9% purity, prepared by the flame fusion method, were obtained from Labelcomat (Belgium). It must be noted that the anionic diffusion coefficients were determined on the same samples and with the same preparation conditions as for the determination of the chromium self-diffusion coefficients (Sabioni et al. 1992). This allows us to obtain a correct comparison between anionic and cationic self-diffusion.

For the diffusion experiments, samples 2 mm thick and 5 mm in diameter were cut, their large face being parallel to $(01\bar{1}2)$ plane which is at 57·7° from the (0001) plane.

The diffusion surface was diamond polished and then the samples were pre-annealed at pressures and temperatures corresponding to the diffusion test conditions, the diffusion treatment being conducted without interruption. The pre-annealing times were always greater than the diffusion times. It is expected that such a procedure permits the equilibration of at least the diffusion zone.

2.2. Diffusion experiments

Two types of diffusion experiment were performed depending on the way in which the tracer was introduced.
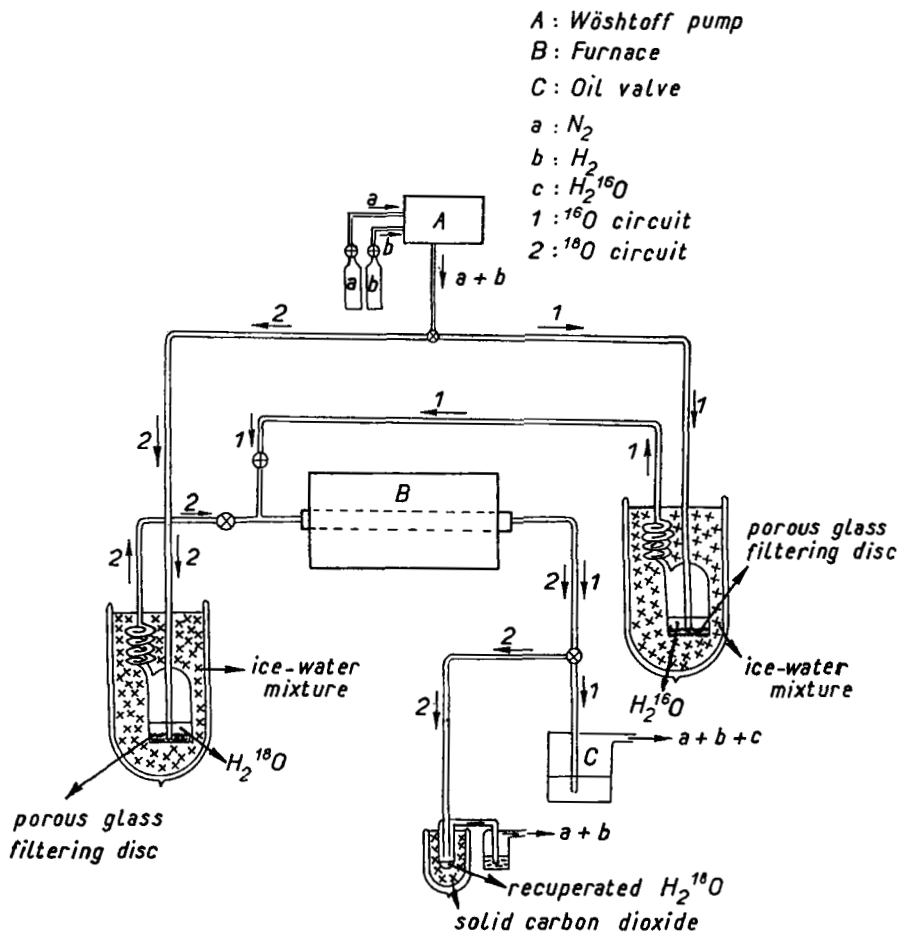
2.2.1. Gas–solid isotope exchange method (p_{O_2} ranging from 10^{-9} to $1·6 \times 10^{-16}$ atm at 1100°C)

The experimental set-up for heat treatments is shown in fig. 1. The atmospheres consisted of N_2–H_2–$H_2{}^{16}O$ and N_2–H_2–$H_2{}^{18}O$ mixtures for the pre-annealing and the diffusion treatments respectively. These atmospheres were obtained as follows: the N_2–H_2 mixtures ($0·1 > p_{H_2}/(p_{H_2} + p_{N_2}) > 10^{-4}$) at a flow rate of 221 h^{-1} were obtained from two Wöshtoff pumps connected in series. Such mixtures then circulated through $H_2{}^{16}O$ or $H_2{}^{18}O$ at 0°C. To recover the $H_2{}^{18}O$, the gases going out of the diffusion furnace were condensed in a trap cooled with solid CO_2.

2.2.2. Superficial film method

In such an experiment, the stable isotope ^{50}Cr was deposited on the sample surface by vacuum evaporation and then oxidized at 700°C for 15 min in an oxygen atmosphere enriched in $^{18}O_2$ in order to obtain a $^{50}Cr_2{}^{18}O_3$ film on the sample surface. Then the sample was annealed at 1300°C in an oxygen pressure of $3·8 \times 10^{-13}$ atm obtained by a CO–CO_2 mixture.

Fig. 1

A : *Wöshtoff pump*
B : *Furnace*
C : *Oil valve*
a : N_2
b : H_2
c : $H_2^{16}O$
1 : ^{16}O *circuit*
2 : ^{18}O *circuit*

Schematic diagram of the heat treatment arrangement used for diffusion experiments by oxygen exchange in controlled oxygen pressure.

The purpose of the first experiments was to establish the oxygen pressure dependence of the oxygen diffusion in Cr_2O_3 at 1100°C, whereas the second experiment was an attempt to obtain a direct comparison of the oxygen and chromium diffusivities in the same Cr_2O_3 sample and in the same atmosphere as for the chromium diffusion experiments described in part I (Sabioni *et al.* 1992).

2.3. *Depth profiling by secondary-ion spectrometry*

For all experiments, the concentration profiles were established by secondary-ion mass spectrometry (SIMS), using a 10 keV Cs^+ ion source. The scanned area was 250×250 μm and the analysed zone was 62 μm in diameter. The oxygen concentration was determined from the ^{16}O- and ^{18}O-signals using the expression

$$C = \frac{I_{18}^c}{I_{16} + I_{18}},$$

where the I values are the count numbers of each isotope, I^c_{18} is the count number for mass 18 corrected for a background obtained by calibrating the signal far from the diffusion zone (natural abundance, 2%). The penetration depths were obtained assuming a constant sputtering rate and measuring the final depth of the crater. For the second experiment the chromium concentration was determined as shown in part I (Sabioni *et al.* 1992).

2.4. *Determination of the diffusion coefficient*

The diffusion coefficients were computed using a solution of Fick's law with three parameters, which for the gas–solid isotope exchange method is given by (Routbort and Rothman 1985)

$$\frac{C_{(x,t)}-C_\infty}{C_1-C_\infty} = \frac{H}{2(H+v/D)}\exp\left(-\frac{vx}{D}\right)\mathrm{erfc}\left(\frac{x-vt}{2(Dt)^{1/2}}\right)+\frac{1}{2}\mathrm{erfc}\left(\frac{x+vt}{2(Dt)^{1/2}}\right)$$
$$-\frac{H+v/2D}{H+v/D}\exp\left[H^2Dt+H(x+vt)\right]\mathrm{erfc}\left(\frac{x+vt}{2(Dt)^{1/2}}+H(D)^{1/2}\right),$$

where $H=K/D$ and K is a transmission coefficient defined by the boundary condition

$$D\frac{\partial C(0,t)}{\partial x}=K[C(0,t)-C_1],$$

while the erfc function is given by

$$\mathrm{erfc}\,u=1-\frac{2}{\pi^{1/2}}\int_0^u \exp(-u^2)\,\mathrm{d}u,$$

where C_∞ is the concentration of ^{18}O far from the diffusion zone, and C_1 is the concentration of ^{18}O in the atmosphere.

In this model, the three fitting parameters are the diffusion coefficient D, the evaporation rate v and the exchange coefficient K through the surface.

§3. RESULTS AND DISCUSSION
3.1. *Oxygen pressure dependence*

The experimental conditions and results obtained for the oxygen self-diffusion in Cr_2O_3 as a function of the oxygen pressure at 1100°C are listed in the table. Figures 2 and 3 show examples of the oxygen profiles obtained at 1100°C in 3.7×10^{-12} and 1.6×10^{-16} atm respectively as well as the theoretical fits taking into account the evaporation and exchange phenomena at the surface of the sample. The sensitivity of the fits has already been discussed in part I (Sabioni *et al.* 1992).

Oxygen diffusion by the isotopic exchange method at 1100°C.

p_{O_2} (atm)	t (s)	D (cm^2 s^{-1})	v (cm s^{-1})	H (cm^{-1})
10^{-9}	8.64×10^4	8.4×10^{-18}	4.9×10^{-12}	1.071×10^5
3.7×10^{-12}	1.775×10^5	4.4×10^{-18}	2.2×10^{-12}	2.045×10^5
3.7×10^{-14}	1.75×10^5	3.8×10^{-18}	4.22×10^{-12}	1.394×10^5
1.6×10^{-16}	8.64×10^4	7.4×10^{-18}	2.7×10^{-12}	1.351×10^5
1.6×10^{-16}	1.728×10^5	3.2×10^{-18}	1.78×10^{-12}	2.531×10^5

Fig. 2
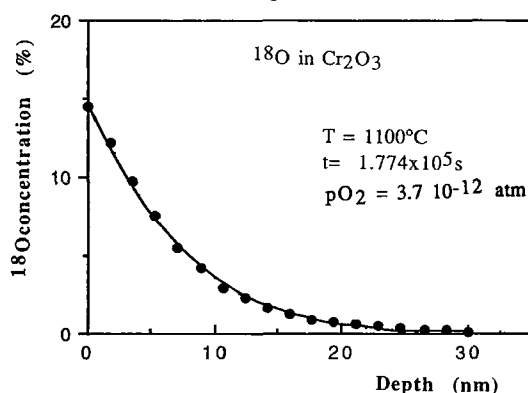
Concentration profiles of ^{18}O after a diffusion treatment at 1100°C in oxygen at 3.7×10^{-12} atm for 1.774×10^5 s: (●), experimental profile; (——), theoretical fit.

Fig. 3
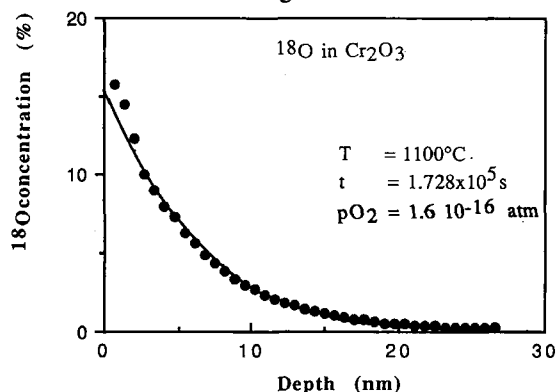
Concentration profiles of ^{18}O after a diffusion treatment at 1100°C in oxygen at 1.6×10^{-16} atm for 1.728×10^5 s: (●), experimental profile: (——), theoretical fit.

Figure 4 shows the oxygen pressure dependence of oxygen self-diffusion in Cr_2O_3 single crystals. The oxygen diffusion coefficients do not seem to vary with the oxygen pressure. Nevertheless, as can be seen in the table, the dependence of D_O on p_{O_2} is not easy to assess. There are apparently two sets of data $(7-8 \times 10^{-18}$ and $3-4 \times 10^{-18}$ cm^2 s^{-1}) corresponding to the two different times of isotopic exchange used. It should be mentioned that both H and v contribute significantly to the final form of the ^{18}O distribution, therefore making D values not so accurate as they should be. However, it is observed that with the same diffusion time there is no important variation in D_O with p_{O_2}. Besides, our oxygen self-diffusion coefficients are lower than those given by Hagel (1965) or King and Park (1988) at different oxygen pressures.

The independence of the lattice self-diffusion coefficients with respect to the oxygen pressure could be due to several reasons, as discussed in part I (Sabioni *et al.* 1992).

(1) It could be that the samples of chromia are difficult to equilibrate (Kofstad 1988). However, we did not observe any influence of the pre-annealing

Fig. 4
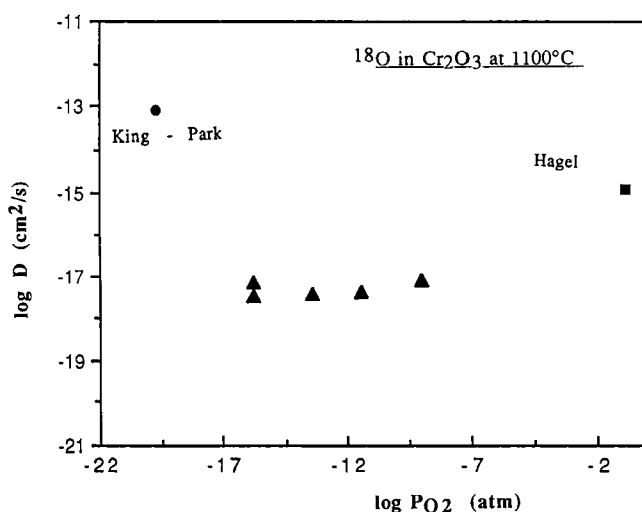
Variation in the oxygen self-diffusion coefficients in Cr_2O_3 as a function of the oxygen pressure
$(T = 1100°C)$, showing a comparison with data from the literature.

on the self-diffusion coefficients; a sample was pre-annealed at 1100°C at
$p_{O_2} = 1.6 \times 10^{-16}$ atm and then subjected to a diffusion anneal at the same
temperature, but at $p_{O_2} = 10^{-9}$ atm. No difference was seen between the values
of the oxygen diffusion coefficient and that obtained for a sample for which the
pre-anneal and the diffusion treatment were made in the same conditions of
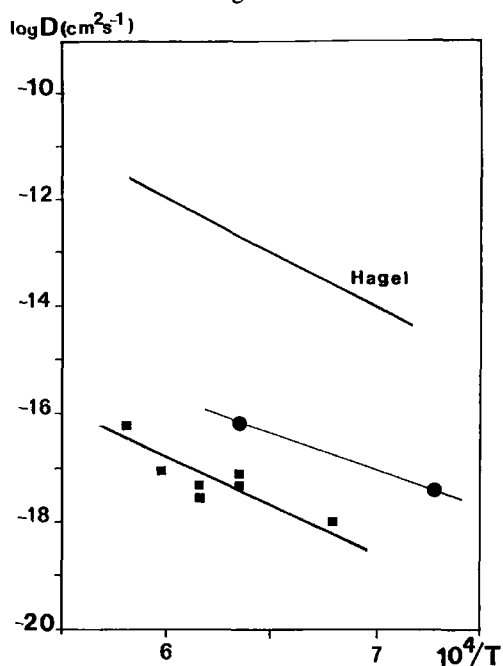oxygen pressure.

(2) It is possible that Cr_2O_3 behaves as⁴ an ionic stoichiometric compound
(Kofstad 1988). Because of the impurity content in our Cr_2O_2 samples
(1000 ppm), such a situation would imply a large concentration of intrinsic
point defects which does not seem to be suggested by the data in the literature.

(3) Because of this impurity content, the most probable explanation is to consider
that *extrinsic diffusion* occurs, as discussed in part I (Sabioni *et al.* 1992); indeed,
table 3 of part I indicates that independence of the oxygen pressure occurs for
extrinsic behaviour.

3.2. *Temperature dependence of the diffusion coefficients*

Figure 5, relative to an Arrhenius plot of the oxygen self-diffusion in Cr_2O_3 single
crystals, treated in oxygen at 10^{-13} atm in our case and in oxygen at 0.164 atm in
Hagel's work, again shows that our oxygen self-diffusion coefficients are smaller than
those found by Hagel (1965). The same observation can be made if our diffusion
coefficients are compared with the oxygen diffusion coefficients found by King and
Park (1988). However, King and Park worked on polycrystals and their results
ascribed to lattice diffusion are probably not representative of bulk diffusion alone. In
the case of Hagel's work, as mentioned before, his samples were not really of a single-
crystal nature and contained about 5% porosity. We consider that our values, obtained
on single crystals, are representative of lattice diffusion for the following reasons.

(1) A diffusion tail was never observed in our various profiles, as is frequently
observed when diffusion measurements are performed on polycrystals and

Fig. 5

Arrhenius plot of the oxygen lattice self-diffusion coefficients in Cr_2O_3 single crystals. Each point is an average value deduced from the oxygen partial pressure dependence study (see fig. 4), showing a comparison with Hagel's results on oxygen diffusion, (———) and with chromium lattice self-diffusion determined in part I (■).

sometimes on single crystals, either of Al_2O_3 (Prot, Miloche and Monty 1990, Prot 1991), or of Cr_2O_3 (Atkinson and Taylor 1984), which excludes subgrain-boundary effects in the diffusion zone in our case.

(2) It must also be noted that evaporation of chromium oxide has not been neglected in analysing the profiles (Sabioni *et al.* 1992), as it was in other studies. If the activation energy is roughly estimated, the value obtained is equal to $230 \, kJ \, mol^{-1}$.

3.3. Comparison of oxygen and chromium diffusion

Figure 6 compares the ^{50}Cr and ^{18}O diffusion profiles obtained from a $^{50}Cr_2^{18}O_3$ superficial film after annealing at 1300°C, in oxygen at 3.8×10^{-13} atm for 1.9×10^5 s (the second experiment). The plot in fig. 6 clearly shows that oxygen diffusion is faster than chromium diffusion in the same conditions. The chromium self-diffusion coefficient was found equal to $5.8 \times 10^{-18} \, cm^2 \, s^{-1}$ by calculating this coefficient as described in part I (Sabioni *et al.* 1992). The ^{18}O initial concentration in the deposited film was, in this case, unknown. So, it was inaccurate to apply the same analytical model to calculate the oxygen self-diffusion coefficient. For this reason, the thin-film solution was used, and the oxygen diffusion coefficient was found to be equal to $6.7 \times 10^{-17} \, cm^2 \, s^{-1}$. The penetration plot (ln C against x^2) for the oxygen diffusion is given in fig. 7. Figure 8 is a comparison of the oxygen pressure dependence of chromium

Fig. 6
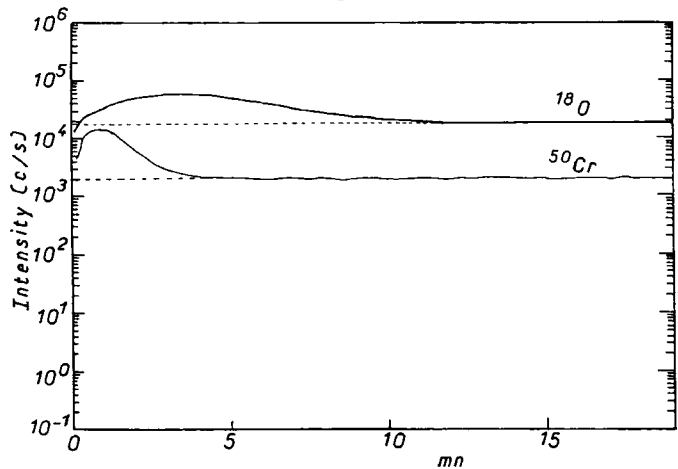
SIMS spectra of the ^{18}O and ^{50}Cr isotopes after diffusion (at 1300°C and $3\cdot8 \times 10^{-13}$ atm) from a superficial film of $^{50}Cr_2^{18}O_3$.

and oxygen self-diffusion coefficients in Cr_2O_3. All these results were obtained on similar samples prepared and treated in the same conditions.

Two remarks can be made. Firstly, as for oxygen diffusion, the chromium diffusion coefficients do not vary with the oxygen pressure (fig. 8), and it was suggested that this is due to extrinsic behaviour on account of the impurity content in our Cr_2O_3 samples. This suggestion is strengthened by the fact that the order of magnitude of the activation energy seems to be in good agreement with the expected values for the migration enthalpy of the involved defects. Secondly, it can be observed that, in our Cr_2O_3 single

Fig. 7
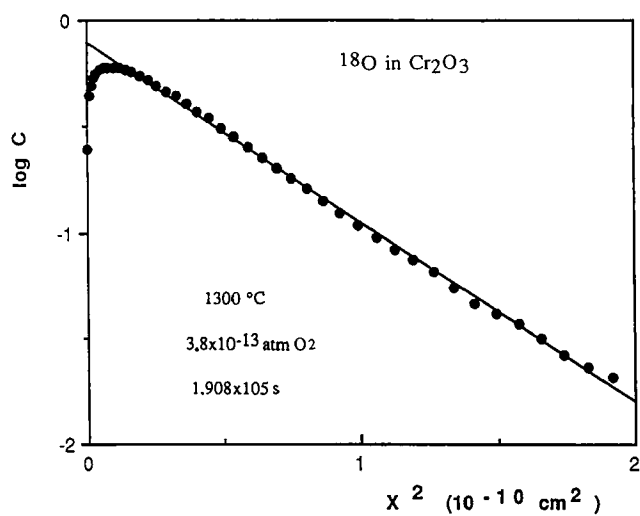
Penetration plot of ^{18}O after a diffusion treatment at 1300°C in oxygen at $3\cdot8 \times 10^{-13}$ atm for $1\cdot908 \times 10^5$ s (the second experiment); the oxygen profile is determined using the thin-film method.

Fig. 8
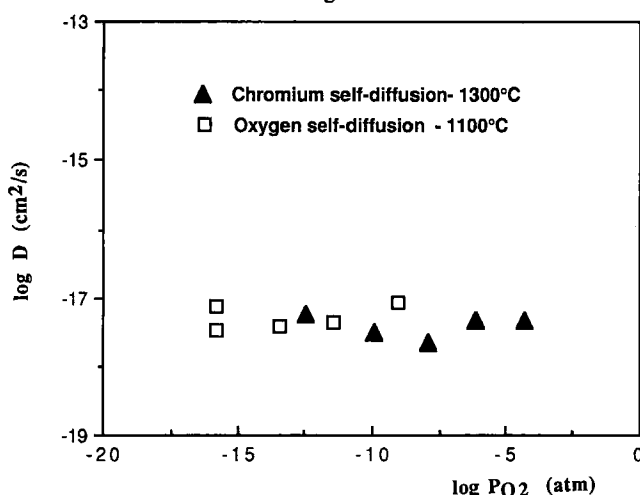
Oxygen pressure dependence of oxygen and chromium self-diffusion in Cr$_2$O$_3$ single crystals. The chromium results were presented in part I (Sabioni *et al.* 1992).

crystals, the oxygen volume self-diffusion is faster than chromium diffusion. This conclusion was already drawn by King and Park, but their results were obtained on polycrystals.

The fact that oxygen diffusion is faster than chromium diffusion could appear as to be opposite to the oxidation results; in most cases, the growth of Cr$_2$O$_3$ scales formed by oxidation of chromium or chromium-enriched alloys is controlled by cationic diffusion. Such a result indicates that the direct comparison of the volume diffusion coefficients in dense oxide samples and of the kinetics of the transport phenomena involved in oxide scales developed by oxidation may not be straightforward. This is due to many phenomena, such as the non-equilibrium of oxide scales, which are subject to other constraints (impurity concentration, stress gradient, chemical potential gradient, etc.). However, the fact that the Cr$_2$O$_3$ scales are polycrystalline is probably the main parameter responsible for the above-mentioned difference: grain boundaries and other short circuits (dislocations, microcracks, etc.) must have a great influence on the growth rate of Cr$_2$O$_3$ scales. Moreover, the natures and amounts of the doping element may differ notably between oxide scales and dense oxide samples.

§4. Conclusions

Oxygen self-diffusion coefficients in Cr$_2$O$_3$ single crystals were determined using the gas–solid isotope exchange method (with H$_2$–H$_2$^{18}O atmospheres), and depth profiling by SIMS. The diffusion coefficients were studied at 1100°C as a function of oxygen pressure (10^{-9}–$1·6 \times 10^{-16}$ atm). The diffusion coefficients were computed using a solution of Fick's second law with evaporation and exchange at the surface.

(1) It is the first time that volume oxygen self-diffusion coefficients have been obtained in dense single crystals. Our oxygen diffusion coefficients are smaller than those found by other researchers either in porous Cr$_2$O$_3$ single crystals or in polycrystals.

(2) In the same conditions of temperature and oxygen pressure and on the same samples, *oxygen diffusion is faster than chromium diffusion*, in case of the single crystals used in this study. This was verified on a direct experiment where both ^{50}Cr and ^{18}O diffused in the same Cr_2O_3 single crystal.

(3) That neither anion self-diffusion nor cation self-diffusion depend on the oxygen pressure has been attributed to an extrinsic diffusion behaviour.

(4) A study of self-diffusion in intentionally doped Cr_2O_3 should improve this defect model. Moreover calculations of the migration energies of defects would be very useful.

REFERENCES

ATKINSON, A., 1985, *Rev. mod. Phys.*, **57**, 437.
ATKINSON, A., and TAYLOR, R. I., 1984, *NATO Adv. Study Inst. Ser.*, B, **129**, 285.
HAGEL, W. C., 1965, *J. Am. Ceram. Soc.*, **48**, 70.
KING, W. E., and PARK, J. H., 1988, *Proceedings of the Materials Research Society Spring Meeting*, edited by M. H. Yoo, W. A. T. Clark, C. L. Briant (Reno, Nevada: Materials Research Society), p. 193.
KOFSTAD, P., 1988, *High Temperature Corrosion* (Barking, Essex: Elsevier Applied Science).
LAWRENCE, P. J., 1988, Ph.D. Thesis, University of Bath; 1989, Theoretical Physics Division, AEA Technology, Harwell Laboratory, Report No. TP1330.
PROT, D., 1991, Doctoral Thesis, University Paris VI.
PROT, D., MILOCHE, M., and MONTY, C., 1990, *J. Phys., Paris*, **51**, Suppl. 1, 1027.
ROUTBORT, J. L., and ROTHMAN, S. J., 1985, *Diffusion and Defects Data*, Vol. 40 (Aedersmannsdorf: Trans. Tech.), pp. 1–17.
SABIONI, A. C. S., LESAGE, B., HUNTZ, A. M., PIVIN, J. C., and MONTY, C., 1992, *Phil. Mag. A*, **66**, 333.