JOURNAL OF MATERIALS SCIENCE LETTERS 13 (1994) 821–825

Diffusion in oxide scales: application to Cr_2O_3 scales

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The protective character of oxide scales is, at least for a part, related to the self-diffusion phenomena in such scales. Frequently, diffusion data are obtained from measurements performed on massive oxides and these diffusion coefficients are taken into account in order to calculate the parabolic oxidation constants. In the case of Cr_2O_3, Sabioni *et al.* [1–3] recently determined oxygen and chromium diffusion coefficients in the lattice of massive chromia single crystals and in grain boundaries of polycrystalline samples. It appeared that these so-determined diffusion coefficients were too small to account for the oxidation rate [4]. Similar observations were made for other oxides [5].

Over the last few years, attempts have been made to determine the diffusion coefficients directly in oxide scales. In the case of Cr_2O_3 scales, the more recent works are those of Graham *et al.* [6] for oxygen diffusion and Lobnig *et al.* [7] for cationic diffusion. Their results obtained on "thermal" Cr_2O_3 scales (i.e. chromia developed by oxidation) and those of Sabioni are collected in Table I. It must be noted that the given values of Sabioni [1–3] have been extrapolated from his results (he worked at higher temperatures) and sometimes on the basis of only a few points, particularly for grain boundary diffusion. Nevertheless, it appears that the diffusion coefficients obtained on chromia scales are greater by many orders of magnitude than those extrapolated from Sabioni's work on massive Cr_2O_3. The order of magnitude of the lattice diffusion coefficient of both oxygen or chromium in thermal Cr_2O_3 is 10^{-15} $cm^2\,s^{-1}$ at 900 °C, while the value extrapolated from Sabioni's work is about 10^{-19}–10^{-21} $cm^2\,s^{-1}$.

TABLE I Diffusion results at 900 °C in thermal and massive Cr_2O_3

900 °C	D_L (cm^2/s)	D_{gb} (cm^2/s)
Graham *et al.* [6]	1.68×10^{-15}	1×10^{-12}
Cr_2O_3Cr, D^O		
Lobnig *et al.* [7]	4×10^{-15}	1×10^{-10}
Cr_2O_3/FeCrNi, D^{Fe}	7×10^{-16}	
Cr_2O_3/FeCrNi, D^{Cr}	7×10^{-15}	2×10^{-10}
	8×10^{-16}	5×10^{-11}
Cr_2O_3/FeCrNi, D^{Ni}	5×10^{-15}	5×10^{-12}
	4×10^{-16}	1×10^{-12}
Lobnig *et al.* [7]	2×10^{-14}	1×10^{-9}
Cr_2O_3/FeCr, D^{Fe}	3×10^{-15}	
Cr_2O_3/FeCr, D^{Cr}	1×10^{-14}	1×10^{-9}
	4×10^{-16}	2×10^{-10}
Cr_2O_3/FeCr,D^{Ni}	3×10^{-15}	2×10^{-12}
	8×10^{-16}	2×10^{-12}
Sabioni *et al.* [1–4]	2×10^{-21}	1×10^{-21}
D^{Cr}_{Cr2O3}		
$D^{O}_{Cr_2O_3}$	1×10^{-19}	1×10^{-21}

In order to clarify the origin of these differences, diffusion experiments were performed on chromia scales developed by oxidation of a $Ni_{70}Cr_{30}$ alloy which offers the advantage to form only a Cr_2O_3 scale (without spinel or NiO) [8].

The Ni–30Cr alloy was provided by Imphy S.A. (France). Its composition is given in Table II. The oxidation treatments were performed at 900 °C, in oxygen at a pressure 1.013×10^5 Pa for times such that the oxide scale thickness varied between 1 and 4 μm. The scale is compact (Fig. 1), made of Cr_2O_3 only, with a grain size between 0.5 and 1 μm.

For oxygen diffusion, the sample was treated at 900 °C for 15 h in $^{16}O_2$ at 1.013×10^5 Pa, then for 1 h in $^{18}O_2$($pO_2 \approx 5 \times 10^3$ to 1×10^4 Pa).

As chromium stable isotope was not available at this time in our laboratory, either Ni or Fe were deposited on the oxide scale by vacuum evaporation. Note that, according to the results of Lobnig *et al.* (Table I), Fe, Cr and Ni diffuse at the same rate. It was verified that the thickness of the tracer layer was equal to ≈20 nm. The diffusion treatment was then performed in argon for 48 or 69 h.

The diffusion profiles were analysed by secondary ion mass spectroscopy (SIMS), and the sputtering rate was determined by measuring the crater depth with a profilometer.

In the case of thick deposits (cationic diffusion) or

TABLE II Composition (wt %) of the substrate

Element	Ni	Cr	Fe	C	S
wt %	68.4	31.6	0.05	0.0048	0.0022

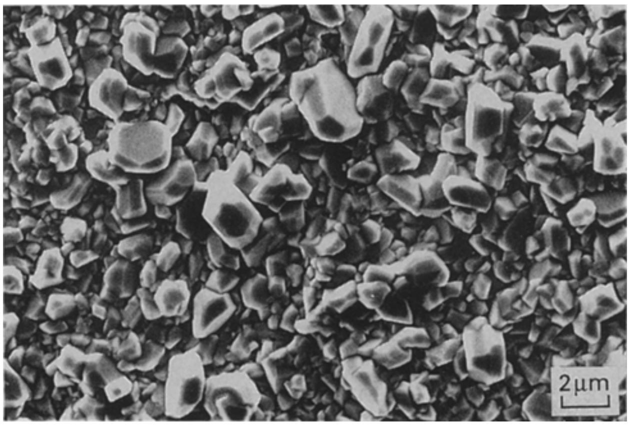

Figure 1 Microstructure of the surface of the oxide scale observed by MEB (oxidation at 900 °C for 15 h in O_2 at 1.013×10^5 Pa).

of a constant superficial concentration (oxygen diffusion), the Fick equation solution is:

$$[C(x) - C_S]/[C_0 - C_S] = \mathrm{erf}\,(x/2(Dt)^{1/2}) \quad (1)$$

with C_0 = the tracer natural concentration in the sample and C_S = the tracer constant superficial concentration.

For the grain boundary diffusion D_{gb}, the Whipple–Le Claire equation was used:

$$D_{gb}\delta = 0.661(-\partial \ln C/\partial x^{6/5})^{-5/3}(4D_L/t)^{1/2} \quad (2)$$

with δ the grain boundary width (taken as 10^{-7} cm) and D_L the lattice diffusion coefficient. It was always verified that the β parameter ($\beta = [D_{gb}/D_L][\delta/2(D_L t)^{-1/2}]$) is higher than 10.

The oxygen penetration profile is given in Fig. 2, and Fig. 3 is related to Ni and Fe penetration profiles.

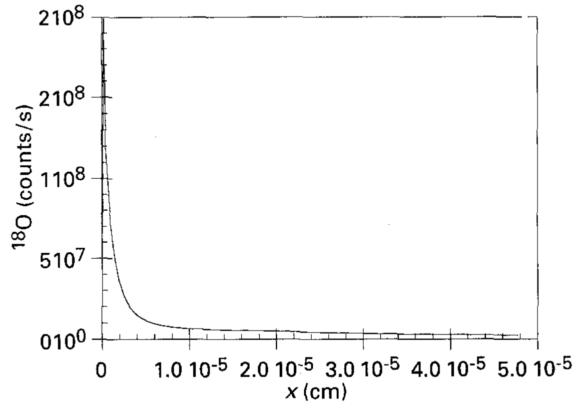

Figure 2 Oxygen penetration profile in Cr_2O_3 scale after 1 h diffusion in $^{18}O_2$ at 900 °C.

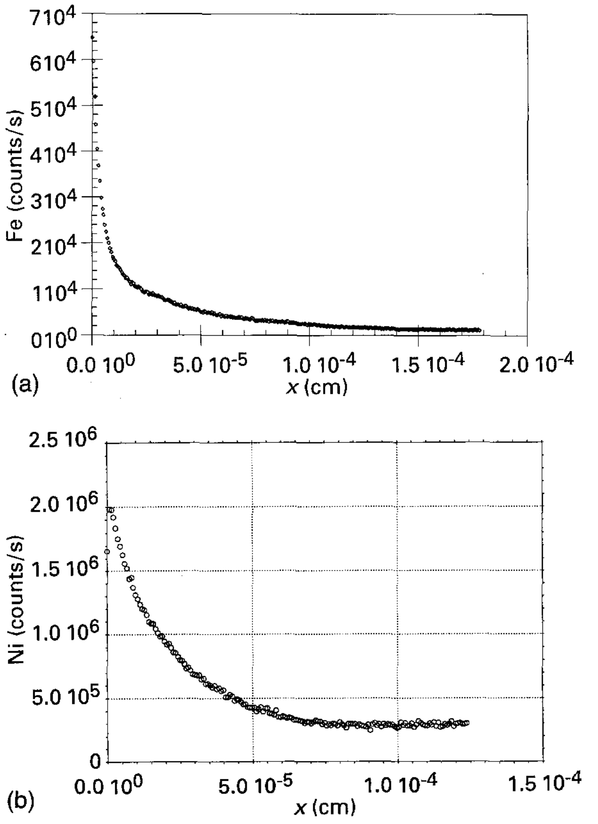

Figure 3 Penetration profile of Fe (a) and Ni (b) in Cr_2O_3 scale after diffusion in argon at 900 °C for 48 h (a) and 69 h (b).

In order to analyse the experimental profiles, it is necessary to determine the diffusion regime in our experiments. Taking into account either the lattice diffusion coefficients given by Sabioni [1, 2] or those that were determined in this study (*a posteriori* verification), it appears that, in our experiments, diffusion in regime C occurs [9]. Indeed:

$$(D_L t)^{1/2} < \delta \ll \Phi$$

where Φ is the grain diameter.

According to the recent work of Mishin *et al.* [10], in such a regime the diffusion coefficient which can be deduced from the ^{18}O profiles is an intergranular diffusion coefficient. But, our profiles (Figs 2 and 3) are different from the profile simulated by [10], as shown in Fig. 4. Consequently, our profiles were considered as being constituted of two domains (Fig. 5), a first short one which corresponds to a combination of diffusion in the lattice and in the grain

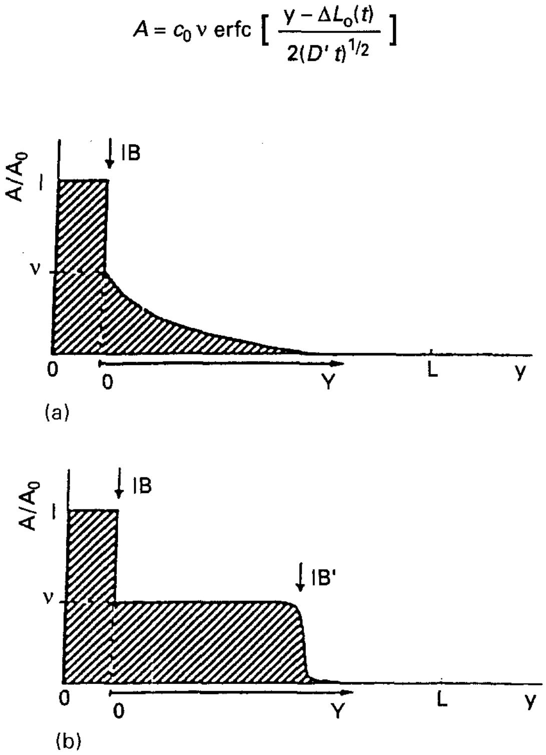

Figure 4 Diffusion profiles in regime C described by Mishin *et al.* [10]: (a) diffusion regime; (b) draft regime.

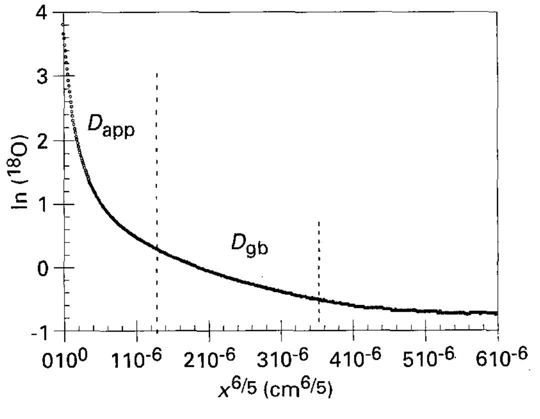

Figure 5 Scheme of the two domains in the penetration profile of ^{18}O (1 h, 900 °C).

boundaries, and a longer, second domain which is relative only to intergranular diffusion. The analysis of the first domain allows determination of an apparent diffusion coefficient D_{app}:

$$D_{\mathrm{app}} = (1 - f)D_{\mathrm{L}} + fD_{\mathrm{gb}} \qquad (3)$$

with $f = 3\delta/\Phi = 0.003$ in our case. In such a case, Equation 1 becomes:

$$[C(x) - C_{\mathrm{S}}]/[C_{\mathrm{O}} - C_{\mathrm{S}}] = \mathrm{erf}\,(x/2(D_{\mathrm{app}}t)^{1/2}) \qquad (1')$$

The values of D_{app} are collected in Table III.

On the basis of Equation 2, D_{gb} can be written as

$$D_{\mathrm{gb}} = 10^7 \times 0.661 \times (P_{\mathrm{gb}})^{-5/3} \times (4D_{\mathrm{L}}/t)^{1/2} \qquad (4)$$

with P_{gb} the slope of the curve $\mathrm{Ln}\,C = f(x^{6/5})$ plotted in the second domain of the experimental curves (see Fig. 6). By combining Equations 3 and 4, D_{L} can be calculated according to

$$0.997D_{\mathrm{L}} + 1.322\,10^7\,ft^{-1/2}(P_{\mathrm{gb}})^{-5/3}(D_{\mathrm{L}})^{1/2} - D_{\mathrm{app}} = 0 \qquad (5)$$

and once D_{L} is determined, Equation 4 allows one to calculate D_{gb}.

The values of P_{gb}, D_{L} and D_{gb} are given in Table III. Figure 6 is one example of the determination of D_{gb} by the analysis of the second domain according to Whipple–Le Claire equation.

If the results obtained in this study (Table III) are compared with those obtained either by Graham *et al.* [6] or Lobnig *et al.* [7] (Table I), it appears that their so-called lattice diffusion coefficients deduced from the slope of the first domain of the experimental diffusion profile correspond to our apparent diffusion coefficients. So, it is suggested that they did not determine lattice diffusion coefficients but *apparent diffusion coefficients*. This could explain why, in the case of the Lobnig *et al.* work [7], the diffusion coefficients vary with time.

On the basis of this suggestion, the results of Lobnig *et al.* were analysed using Equations 1′, 4 and 5. In the case of diffusion of Ni for 15 min in the Cr_2O_3 scale formed on FeCrNi alloy, it is then found that

$D_{\mathrm{app}} = 5 \times 10^{-15}$ cm^2/s (i.e. their given value of D_{L})
$P_{\mathrm{gb}} = 2.39 \times 10^5$ cm$^{-6/5}$ (deduced from Fig. 6 of [7])
$D_{\mathrm{L}} = 1.2 \times 10^{-17}$ cm^2/s
$D_{\mathrm{gb}} = 1.6 \times 10^{-12}$ cm^2/s

It must be considered that first our diffusion time is longer than the diffusion time of the Lobnig experiment, and secondly the purity of the chromia scale must differ according to the substrate nature: in the case of Lobnig *et al.*, the chromia scale must be doped with Fe and Ni, while in our case the chromia scale is doped only with Ni (3000 ppm analysed by EDX). With such considerations, it can be concluded that their values are of the same order of magnitude as ours (see Table III).

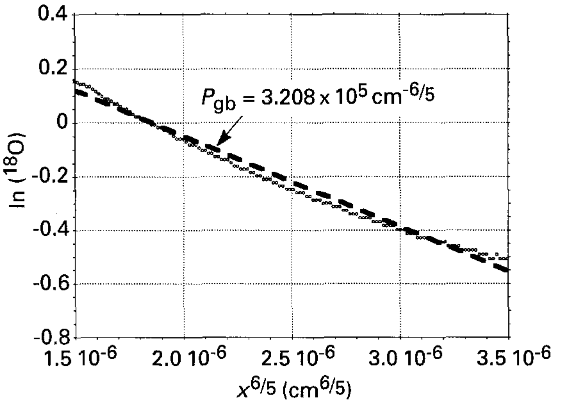

Figure 6 Curve $\mathrm{Ln}\,C = f(x^{6/5})$ in the case of ^{18}O diffusion for 1 h at 900 °C.

These analyses of the diffusion profiles are corroborated by a comparison of diffusion coefficients in chromia scales and in massive chromia. If the results of Graham *et al.* [6] or Lobnig *et al.* [7] are compared to diffusion coefficients obtained by Sabioni *et al.* [1–4] (Table I) it appears that the lattice diffusion coefficients determined in chromia scales are, by about five orders of magnitude, greater than those determined in massive chromia. The comparison for grain boundary diffusion is more audacious because grain boundary diffusion coefficients in massive chromia at 900 °C have been extrapolated from a few points only.

Now, if the first domain of the diffusion profiles obtained on chromia scales is analysed as corresponding to an apparent diffusion coefficient, the deduced lattice diffusion coefficients (using Equations 1′, 4 and 5), given in Table III, are in rather good agreement with those given by Sabioni *et al.* in massive chromia. In the case of oxygen lattice diffusion, there is a very good agreement:

at 900 °C

$$D^{\mathrm{O}}_{Cr_2O_3} = 10^{-19}\ \mathrm{cm^2/s\ in\ massive\ chromia\ [1–4]}$$
$$= 7.8 \times 10^{-19}\ \mathrm{cm^2/s\ in\ our\ case}$$
$$\mathrm{(chromia\ scale\ on\ NiCr\ alloy)}$$

In the case of cationic lattice diffusion, the differences between values in scales and values in massive chromia are greater. But, such differences can be due to many parameters:

TABLE III Values of D_{app} at 900 °C (deduced from the curves arg erf $= f(x)$ in the first domain of our experimental diffusion curves) and of P_{gb}, D_{L} and D_{gb} determined with Equations 1′, 4 and 5, for oxygen and cationic (Fe, Ni) diffusion.

Tracer	t diffusion	D_{app} (cm^2/s)	P_{gb} (cm$^{-6/5}$)	D_{L} (cm^2/s)	D_{gb} (cm^2/s)
^{18}O	3600 s	3.9×10^{-16}	3.208×10^5	7.84×10^{-19}	1.3×10^{-13}
Fe	48 h	2×10^{-16}	1.26×10^5	4.5×10^{-19}	6.6×10^{-14}
Ni	69 h	1.6×10^{-15}	1.78×10^5	1.1×10^{-16}	4.9×10^{-13}

- uncertainty in diffusion coefficient values;
- nature of the cationic species: Cr in the case of Sabioni, Fe or Ni in our case;
- differences in the diffusion gradients: in the case of massive chromia the tracer diffusion is due to a chemical potential gradient only, while in the case of chromia scale, the diffusion is due to an electrochemical potential gradient;
- purity of chromia: in the case of Sabioni, chromia was doped by silicon (1000 ppm), while in our case, the scale is doped with Ni (3000 ppm);
- stresses or/and stress gradient in chromia scale developed by oxidation which is not the case with massive chromia.

It can be observed from the results in Table III that Fe and O lattice and grain boundary diffusions are of the same order of magnitude. In particular, the apparent diffusion coefficients of oxygen and iron can be considered as equal. According to Lobnig *et al.* [7], results which show that Cr and Fe diffusion coefficients are in the same range, it can be said that chromia scale growth is ensured by both oxygen and chromium diffusion. This observation does not agree with most of the results concerning the oxidation of chromia formed alloys: indeed, authors generally consider that chromia scales formed on alloys without active elements grow by preponderant chromium diffusion [11]. Contrarily, Sabioni *et al.* [1–4] observed that oxygen diffusion in massive chromia was faster than chromium diffusion.

It is now possible, with these new values of diffusion coefficients, to calculate the parabolic oxidation constant at 900 °C (it was verified that the oxidation of NiCr alloy obeys a parabolic law). From the classical equation for an oxide MaOb:

$$k_c = (2/kT)\int [D_{\text{anion}} + (b/a)D_{\text{cation}}]^{d\mu}$$

with

$$d\mu = kTd(1/\text{p}2)$$

it can be written

$$k_c = 2[D_{\text{anion}} + (b/a)D_{\text{cation}}]\ln(\text{pO}_2^{\text{ext}}/\text{pO}_2^{\text{int}}) \quad (7)$$

In our case, $a = 2$ and $b = 3$, $\text{pO}_2^{\text{ext}} = 1.013 \times 10^4$ Pa and $\text{pO}_2^{\text{int}} = 1.013 \times 10^{-15}$ Pa.

The oxidation constant was calculated assuming various mechanisms (lattice, grain boundary or both) for the scale growth and the values are given in Table IV. For cationic diffusion, values for iron diffusion were considered (instead of Cr diffusion), as Lobnig *et al.* [7] showed that iron and chromium diffusion rates are in the same range.

The experimental oxidation constant of our alloy oxidized at 900 °C is equal to 10^{-13} cm^2/s, in agreement with literature data for chromia scales [12].

So, it appears clear from the calculations in Table IV, that chromia scale growth is ensured by countercurrent diffusion of oxygen and chromium by both the lattice and the grain boundaries, the main phenomenon being grain boundary diffusion. This good agreement between experimental and calculated kc values also corroborates the diffusion profile analysis that was performed in this study.

Summarizing, anionic and cationic diffusion profiles in chromia scales formed on NiCr alloy were analysed assuming that the first part of these profiles corresponded to an *apparent diffusion coefficient* ($D_L + fD_{gb}$) and the second part to a grain boundary diffusion coefficient. By combining diffusion equations, it has been possible to determine new lattice and grain boundary diffusion coefficients.

Consequently, lattice diffusion coefficients previously determined by authors in chromia scales are, in fact, apparent diffusion coefficients, and this induces errors also on their grain boundary diffusion coefficients.

This analysis is corroborated first by the rather good agreement between diffusion coefficients determined in massive chromia and those calculated in this study in chromia scales, and, secondly, by the very good agreement between the experimental oxidation constant and the calculated one.

The results indicate that chromia scale growth is ensured by both oxygen and chromium diffusion, mainly by grain boundary diffusion, but lattice diffusion is not negligible.

Acknowledgements

The authors are indebted to V. Bousquet for her participation in the experimental work and to C. Monty and C. Dolin for their help in SIMS analyses at CNRS Bellevue.

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TABLE IV Calculations of the parabolic oxidation constant at 900 ch007C assuming various mechanisms for the chromia scale growth. For the cationic diffusion, the values concerning Fe were considered (instead of Cr), as Lobnig *et al.* [7] showed that iron and chromium diffusion rates are in the same range.

Diffusion mechanism	D_{anion} (cm^2 s^{-1})	D_{cation} (cm^2 s^{-1})	k_c (cm^2 s^{-1})
Lattice: D_L	7.84×10^{-19}	4.5×10^{-19}	1.27×10^{-16}
D_{gb}: Grain boundary	1.3×10^{-13}	6.6×10^{-14}	2×10^{-11}
D_{app}: both mechanisms	3.9×10^{-16}	2×10^{-16}	1.02×10^{-13}

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Received 8 September 1993
and accepted 17 January 1994