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Some aspects of diffusion in ceramics

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Résumé. — Les expériences de diffusion sont plus délicates dans les céramiques que dans les métaux, en raison des propriétés physiques, chimiques et mécaniques particulières aux matériaux céramiques. A cause de leur point de fusion élevé, la concentration en défauts ponctuels est généralement beaucoup plus faible dans les céramiques que dans les métaux, à température égale. Cela entraîne des valeurs faibles de coefficients de diffusion beaucoup plus faibles que celles déterminées dans les métaux. La nature de la liaison chimique dans les céramiques donne lieu à des liaisons interatomiques plus fortes que dans les métaux et à une capacité plus faible de dissoudre les impuretés. Dans ces conditions, on peut s'attendre à plus d'effets de ségrégation et de précipitation dans les céramiques, effets qui peuvent avoir une influence sur les valeurs des coefficients de diffusion. L'interprétation des valeurs des coefficients de diffusion nécessite une bonne connaissance de la nature et de la quantité des défauts, qui ne sont pas faciles à contrôler et qui dépendent du moyen utilisé pour préparer les échantillons destinés aux expériences de diffusion. Le but de ce papier n'est pas de donner une revue de toutes les valeurs des coefficients de diffusion obtenues dans toutes les céramiques, mais de souligner quelques problèmes rencontrés dans la détermination des coefficients de diffusion dans ces matériaux : faibles profondeurs de pénétration, taux de dopant et d'impureté relativement élevés par rapport aux faibles teneurs en défauts et ségrégation d'impuretés aux joints de grains ou à la surface. Des exemples sont donnés pour l'alumine α -Al₂O₃ et l'oxyde de chrome α -Cr₂O₃.

Abstract. — Experiments of diffusion are more difficult in ceramics than in metals, because of specific physical, chemical and mechanical properties of ceramic materials. Due to their high melting point, the amount of point defects is generally much less than in metals at the same temperature. That implies very low diffusion coefficients, comparatively to diffusion coefficients measured in metals. The nature of the chemical bond of ceramics gives rise to stronger bonding than in metals and less ability to solve impurities. In these conditions, more segregation and precipitation effects are to be expected in ceramics and these effects may have an influence on the values of the diffusion coefficients. The interpretation of diffusion coefficient values needs a good knowledge of the nature and amount of defects, which are not so easy to control and which depend on the way used to prepare the samples destined to diffusion tests. The aim of this paper is not to give a review of all the values of diffusion coefficients obtained in all ceramics, but to point out some difficulties encountered in determination of diffusion coefficients : penetration depths, comparatively high level of impurity or dopant content in regard with the low amount of intrinsic defects and segregation of impurities to the grain boundaries and to the surface. Examples are given for alpha alumina and chromia.

Introduction.

It can be said that « ceramics » are inorganic compounds that contain mainly several chemical elements and whose properties are generally different from properties of metallic compounds. Diffusion in ceramics is at the present time mainly studied in the so-called « fine ceramics », such as alumina, zirconia, silicon carbide, silicon nitride, superconductors..., which are high technological materials. Knowledge of diffusion coefficients in ceramic materials is needed for interpretation of transport mechanisms involved in creep, sintering and corrosion processes.

What is the composition of a ceramic material ? Essentially one or several metallic elements associated with one or several light non-metallic elements such as hydrogen, boron, carbon, nitrogen or oxygen, giving rise respectively to hydrides, borides, carbides, nitrides or oxides. These compounds can be crystalline or amorphous compounds (glasses).

Several different own networks of atoms imply of course several different types of point defects : metallic defects and non-metallic defects, without forgetting potential defects associations. Moreover, non metallic elements such as oxygen, nitrogen and hydrogen are present in the surrounding atmosphere, giving rise to equilibria between the atmosphere and the non metallic defects.

Interpretation of diffusion data for ceramics is less easy than for metals, due to the complexity of the defects network in the bulk and also in the grain boundaries, whose structure is more difficult to define than in metals.

The essential difference between metals and ceramics lies in the nature of the bonding : bonds in a ceramic compound are either ionic (NaCl), covalent (SiC) or for the majority ionic-covalent. In all cases the cohesion energies are stronger for ceramic than for metals. The nature of these bonds increases the melting point, the hardness and the ability to brittleness and decreases the plasticity. In these conditions, synthetic ceramic materials are sometimes difficult to produce.

One other difference with metals is in almost all cases the very low solubility of ceramics into each other. Because of the strong bonds, localization of atoms are very precise and additions of impurities or dopants give rise to segregation or/and precipitation effects. The major difficulty with studying diffusion in ceramics lies in the control of the impurity or dopant content.

It is not the purpose of this paper to list all diffusion results in ceramics. There are lots of papers about these topics. For diffusion in oxides, it can be referred to papers written by Monty [1, 2], for carbides and nitrides by Matzke [3, 4], for superconductors by Rothman [5], for oxides glasses by Greaves *et al.* [6], for halides by Laskar [7] and Bénéière *et al.* [8]. A compilation of diffusion data in minerals is given by Freer [9]. New experimental techniques for studying diffusion in minerals are given by Jaoul *et al.* [10].

We have rather to expose some problems encountered during the whole process of determination of diffusion coefficients in ceramics : ceramic powders, single crystals and polycrystals achievement, preparation of the samples for diffusion tests, tracer deposition, obtaining and interpretation of penetration profiles.

Materials.

CERAMIC POWDERS. — The starting material needed for the elaboration of single crystals or polycrystals, doped or undoped is the ceramic powder, whose characteristics have a great influence on the characteristics and properties of the further elaborated materials. At the present time, some investigations are carried out on ceramic powders, particularly on so-called « submicronic powders » in order to find the best way to obtain high quality single crystals or sintered polycrystals mainly without adjuvant, with reproducible properties and characteristics, and of course at the least cost.

One of these studies was undertaken by Petot-Ervas *et al.* [17] on submicronic alumina powders provided by Baibowski Chimie, France. These authors found, by XPS and Raman analyses and observation by transmission electron microscopy, that even in the powders some segregation phenomena occurred and that, when the segregation is large enough near the surface, precipitation could also occur.

Doping of a ceramic powder can be made by mixing the element either in liquid phase or in the solid phase. Loudjani [18] studied the doping of alpha alumina and showed that the last way led to less homogeneous powders.

Chemical analysis of the powder is easy and gives generally a good reproducibility. The main impurities encountered in alumina powders are typically : silicon (50 ppm), potassium (40 ppm), calcium (15 ppm), magnesium (10 ppm). As it can be shown, the valency of these impurities can be either less or more than the valency of the aluminium atom, and for this ionic-covalent material, the balance between « acceptor » impurities such as Mg^{2+} , Ca^{2+} , K^+ and « donor » impurities, such as Si^{4+} will impose the electronic properties of the ceramic and therefore have an expected influence on defect nature and amount and thus on transport properties.

SINGLE CRYSTALS. — The determination of self- or heterodiffusion coefficients has to be done in single crystals, not only from a fundamental point of view to obtain the true diffusion coefficient in the bulk, but also to calculate the diffusion coefficients in grain boundaries and dislocations [19]. The penetration depths in ceramics being generally very low and therefore the bulk diffusion coefficients, their determination is more difficult than for metals. Moreover, dislocations are often present in the material (Fig. 1) and it is sometimes difficult to separate the contribution of the dislocation from the contribution of the pure bulk. Since there are

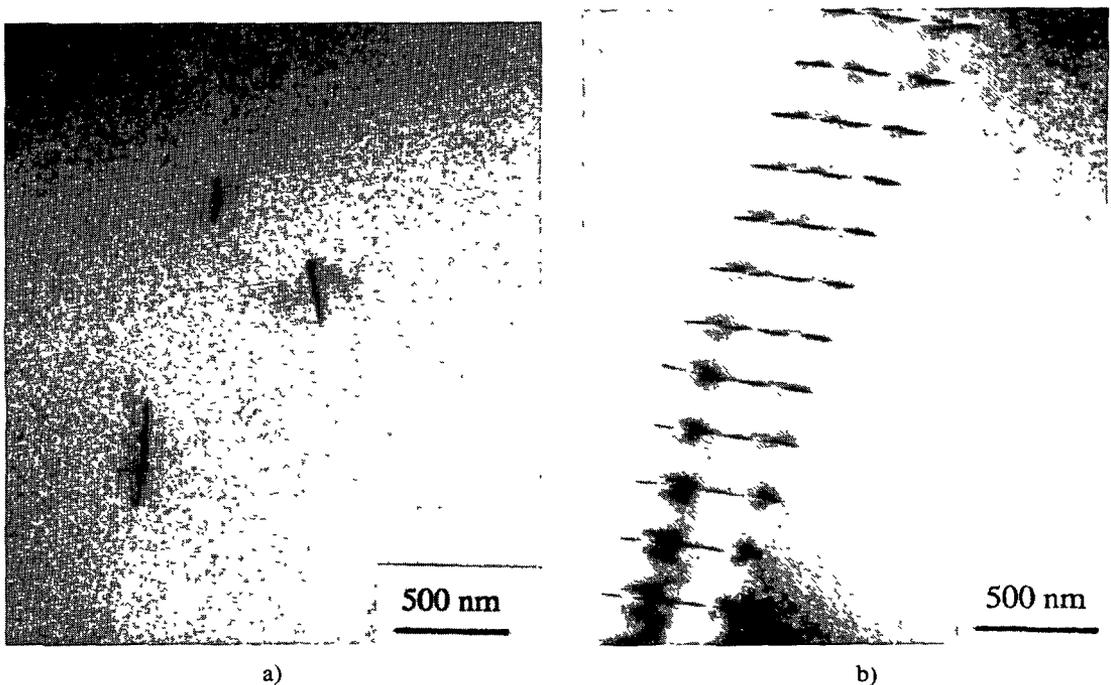


Fig. 1. — Type of dislocation arrangement observed in Verneuil-grown alpha-alumina single crystal [16]. a) Isolated dislocations. b) Dislocations arranged in sub-boundaries.

several elements in a ceramic, several bulk, dislocation and grain-boundaries diffusion coefficients have to be determined.

Elaborating ceramic single crystals, with the lowest amount of dislocations is not very easy. The main methods used are the Verneuil and the Czochralski methods which require high temperatures in order to obtain the crystallisation from a liquid phase on a well-oriented germ. Since the diffusion coefficients are higher in the liquid than in the solid phase, it can be well understood that segregation and/or precipitation of impurities or dopants will unavoidably occur, so as for metal solidification processes.

What are the specific problems due to the segregation of impurities or dopants during the elaboration of single crystals ?

In most cases, solubility of foreign atoms is very limited in ceramics at low temperatures. Equilibrium phase diagrams are consequently not well-established at these temperatures. The low solubility limits give rise to migration of the foreign atoms from inward to outward the bulk, that is to say, to the interfaces, sub-boundaries, grain boundaries or sample surfaces, where there is more place for foreign atoms.

Recent papers have been published about this topic : Cawley and Halloran [20] have characterized the dopant distribution in a yttrium-doped sapphire elaborated by the Verneuil method starting from a powder containing nominally 100 ppm weight yttria : they found a second phase decorating the surface of the crystal, phase suggested as yttrium garnet. Their results by emission spectroscopy indicated that the upper limit for the solubility of yttrium was lower than 10 ppm (detection limit of optical emission spectrometry), even at high temperature. This assumption was verified by Loudjani and co-workers [21].

Recent work on alumina was done by Petot-Ervas *et al.* [22, 23]. These authors investigated by SIMS and XPS the effect of cooling rate on the near surface distribution of Y, Ca and Si in alumina single crystals and found a higher solute concentration near the surface depending on the cooling rate : the segregation depth increasing with the cooling rate with more pronounced effects for calcium, as given in figure 2.

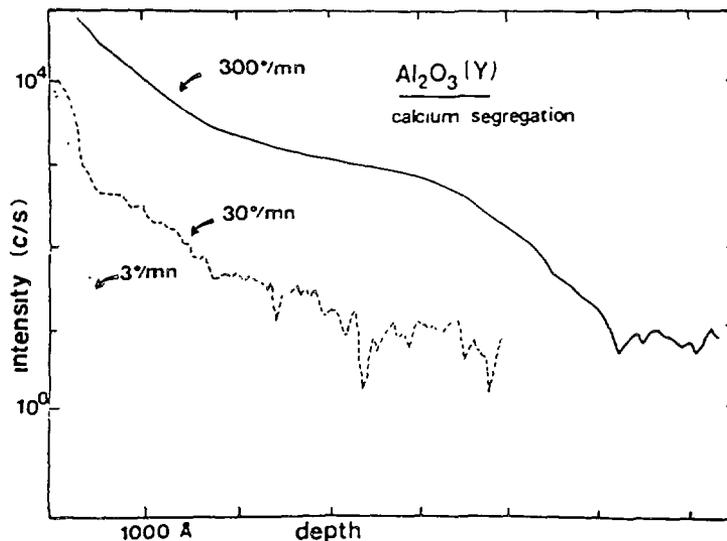


Fig. 2. — Near surface calcium segregation in an alumina single crystal as a function of the cooling rate [22]

This type of segregation is called « dynamic » segregation, in opposition with the « equilibrium » segregation and has been detailed by Monceau [24].

Impurity segregation phenomena near surfaces was also observed by Hirschwald and co-workers [25] for chromium in NiO and CoO and by Le Gall [16] for Y, Si, Ca and Mg in yttrium-doped alpha-alumina single crystals.

Thus, when impurities or dopants go to the sample surface, the bulk diffusion will occur near the surface in a material which is enriched with impurities or dopants. In these conditions the bulk diffusion coefficient values could be erroneous and not representative of the diffusion in the ceramic material.

This remark is also true for diffusion in dislocations : in this case, since the repartition of impurities or dopants is not the same near the surface and in the dislocations, and since the value of the bulk diffusion coefficient is needed to calculate the diffusion coefficient in dislocations, the interpretation of diffusion coefficients in dislocations may be sometimes doubtful.

One important problem related to segregation phenomena is the question of the chemical analysis of the sample : what is the significance of a global analysis of the specimen when all the impurities or dopants are segregated or precipitated at the interfaces ? Only a ponctual analysis, for instance by STEM in the region of diffusion will give the true ponctual impurity content and is suitable for further interpretations.

POLYCRYSTALS. — Many ways are used to elaborate polycrystals.

The first one is called « natural sintering », where the cold compaction of the powder is followed by an annealing at a given temperature during a given time. Success of this natural sintering of ceramics, that is obtention of a specific mass quite equal to the theoretical volumic mass, requires an annealing at high temperature and during a long time. In order to enhance the sintering and also to avoid an heterogeneous grain size, additives are sometime used, as MgO for Al_2O_3 .

One other way is to prepare a cold compacted powder and to operate a hot uniaxial pressing or a hot isostatic pressing (« H.I.P. »). We tried the two processes for alumina and chromia. Figure 3 gives the evolution of the density as a function of isostatic pressure and sintering time for « hipping » of chromia. Although this result was very satisfying, it appeared that this

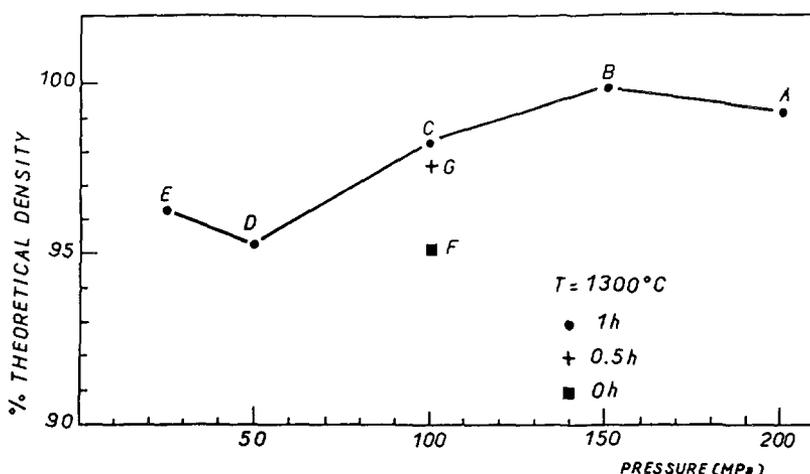


Fig. 3. — Evolution of the density as a function of isostatic pressure and sintering time for « hipping » of chromia [11].

process led to high stressed materials unsuitable for further surface preparation. The hot uniaxial pressure sintering was preferred in this case.

Kingery and co-workers [26, 27] observed segregation phenomena in magnesium oxide : elements such as scandium, chromium, iron, aluminium, silicon, calcium and titanium segregate well in the grain boundaries of MgO, the intensity of the segregation depending on the nature of the element (Fig. 4).

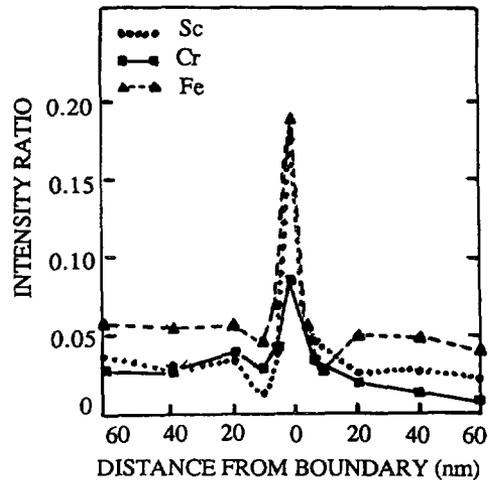


Fig. 4. — Segregation of dopants or impurities in magnesium oxide [28].

The same authors find similar results for aluminium oxide : substantial segregation occurs for Y^{3+} , Si^{4+} , Ti^{4+} , Zr^{4+} , but not for Mg^{2+} , Ti^{3+} or Cr^{3+} . Kingery's results on MgO suggest that the cooling rate could have an influence on the amount of segregated foreign atoms. The same type of problem was encountered by Kingery in segregation of aluminium in silicon carbide [28] and by McCune *et al.* [29] and Loudjani [18] for precipitation of yttrium garnet in polycrystalline yttrium-doped alumina as shown in figure 5.



Fig. 5. — Precipitation of yttrium garnet in yttrium doped alpha alumina polycrystals [18].

Preparation of the specimen for diffusion tests.

In all cases, the rough material has to be annealed in order to avoid stresses produced during the elaboration. But remember that each annealing could have a bad influence because of segregation under cooling...

Pieces of single crystals and polycrystals have to be cut, generally with a diamond saw, with well-defined dimensions suitable for diffusion tests. If possible, single crystals have to be oriented and this is sometimes difficult, due to the small size of the specimen and due also to the non conventionnal crystalline structure of the ceramics.

Ceramic material being chemically resistant, the microstructures of the ceramic polycrystals are revealed by a short annealing at high temperature (thermal grooving) and observed through an optical microscope or a scanning electron microscope. One example is given in figure 6 for dense polycrystalline chromia elaborated by hot uniaxial pressing. It is of the most importance, as for metals, to know this microstructure to define the condition of the diffusion annealing for measuring the grain-boundary diffusion coefficient.

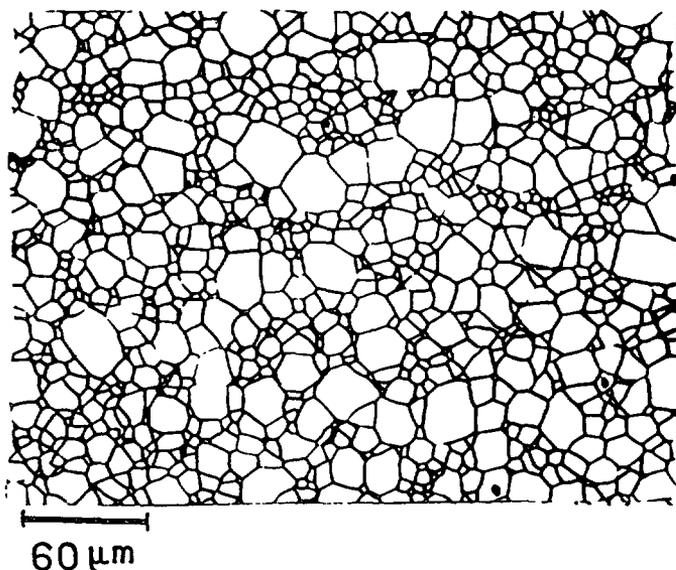


Fig. 6. — Microstructure of chromia dense polycrystalline specimen after a hot uniaxial pressing [11].

The following phase of preparation is polishing of the sample surface. Taking into account the very low penetration depths in ceramics, it is necessary that polishing is undertaken with the most care, using fine diamond pastes, in order to avoid a degradation of the region near the surface and to prepare a very flat surface needed for a precise determination of the penetration depth.

Some works showed that the microstructure of the near surface region was particularly affected by polishing [30]. An annealing at high temperature is then mandatory to obtain a good reference surface.

Deposition of the tracer.

For metallic tracers, the electrolytic way cannot be used, since ceramics are mainly insulators. Several methods can be used to deposit the tracer.

The deposition of a drop of a solution containing the tracer, radioactive or not, is easy but leads to an inhomogeneous deposit of the tracer. This is verified by autoradiography when using a radioactive tracer. It is not very important when the microstructure of the specimen is homogeneous.

Sputtering of tracer leads to a more homogeneous deposit and the depth of the deposit can be well controlled. In case of a radioactive tracer, the installation may be contaminated.

Implantation is also a good method because the quantity of atoms introduced is well-known, but this method needs to know the implantation profile and to make a stabilisation annealing after implantation and before the diffusion annealing itself.

For diffusion of oxygen, the isotopic exchange between ^{18}O and ^{16}O is used [11, 15, 16]. In this case the major difficulty lies in the knowledge of the tracer concentration at the initial surface.

For self-diffusion in carbides radioactive ^{14}C or neutral ^{13}C can be used. In all cases, by using an inactive isotope for self-diffusion, it is preferable to choose the isotope with the lowest natural isotopic concentration. An example of implantation profile is given in the figure 7.

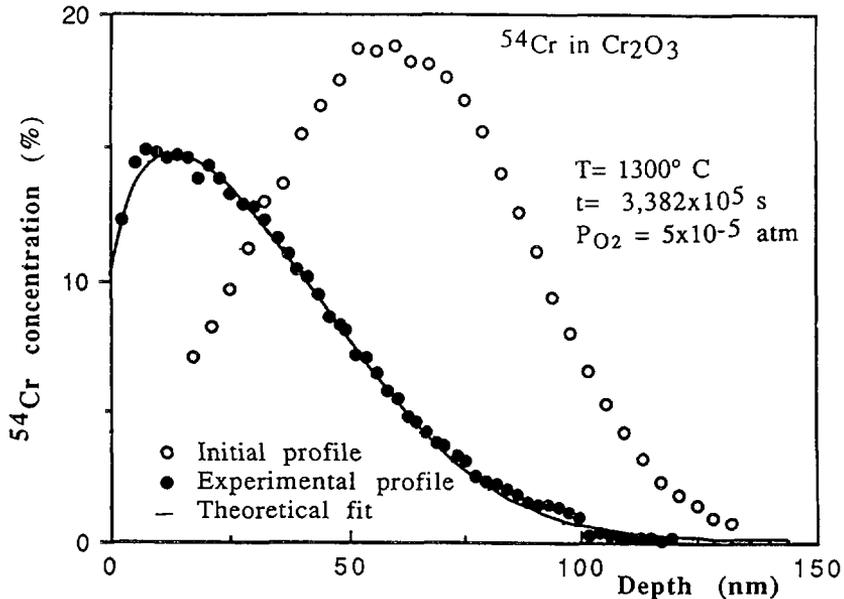


Fig. 7. — Implantation profile of chromium on the surface of chromia [11, 12].

Diffusion annealing.

The annealing time must be chosen accurately in order to obtain the best profiles allowing the best precise determination of bulk or grain-boundary diffusion coefficients. In case of diffusion in alumina, if the annealing time is too long, cationic diffusion in dislocations can mask the bulk diffusion even at high temperature, due to the fact that dislocations are mostly often present in the material at high temperatures. This phenomenon can lead to anomalously high cationic diffusivities.

Penetration profiles.

Two ways are employed to obtain penetration profiles, depending on the nature of the tracer.

For radioactive tracers, the profiles are obtained by plotting the residual activity of the tracer *versus* the penetration depth. The residual activity is the measured activity of the whole specimen after a mechanical grinding of the specimen to a given depth. The lost depth can be calculated by the measure of the weight loss after grinding. Of course, for single crystals, the steps must be as low as possible, because of the generally low penetration depths. Figure 8 gives an example of penetration profile for diffusion of ^{26}Al in $\alpha\text{-Al}_2\text{O}_3$ single crystals [16, 31].

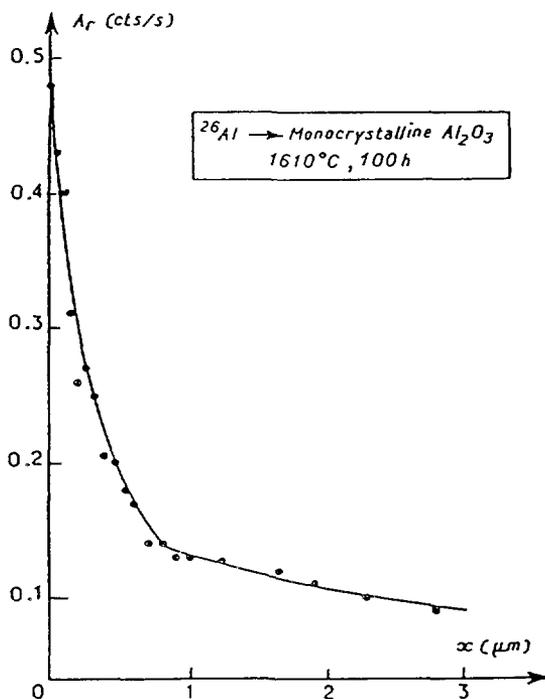


Fig. 8. — Penetration profile for diffusion of ^{26}Al in alpha alumina single crystals [16, 31].

For a non radioactive tracer, SIMS is used for obtaining the penetration profiles. Figure 9 shows a penetration profile of ^{54}Cr in Cr_2O_3 and the associated crater.

The advantage of this method is that profiles of dopant or impurity concentration can also be obtained. Moreover, for diffusion in ceramics, with several types of atoms, SIMS allows to give together the penetration profiles of cation and anion, in order to determine which is the more rapid species. Figure 10 shows the simultaneous penetration profiles of chromium and oxygen in the same specimen of chromium sesquioxide [11-14]. One can observe that oxygen goes undeniably faster than chromium in single crystals of chromia. This result is essential for understanding of oxidation, sintering and creep results, since it was mainly assumed that cations move faster than anions.

Penetration profiles can also be obtained on polycrystals. Figure 11 shows a comparison between penetration profiles in a Cr_2O_3 single crystal and in a Cr_2O_3 polycrystal after a

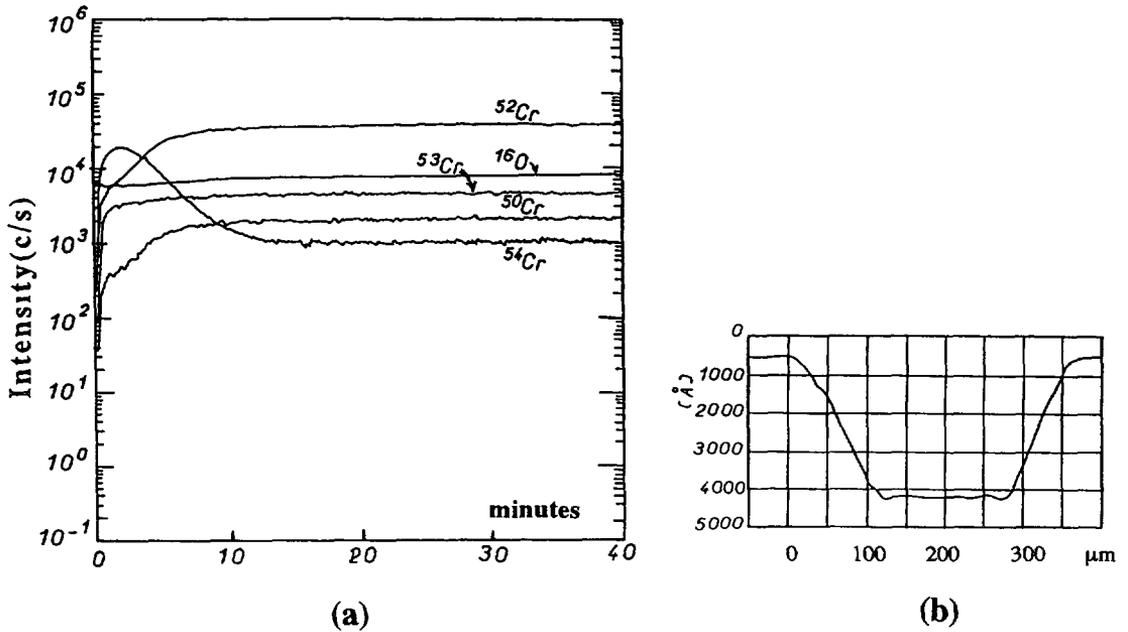


Fig. 9. — SIMS spectrum (a) for diffusion of chromium in chromium sesquioxide and crater (b) used to calculate the penetration depth [11, 12].

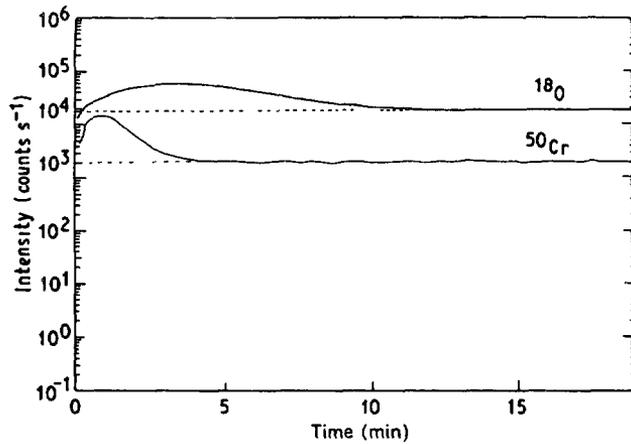


Fig. 10. — Simultaneous penetration profiles of chromium and oxygen in the same specimen of Cr_2O_3 [11, 13].

diffusion treatment during quite the same time : bulk diffusion occurs to 50 nm, since diffusion in grain boundaries goes as far as 250 nm. Only the penetration profile relative to the bulk allows an accurate determination of the bulk diffusion coefficient.

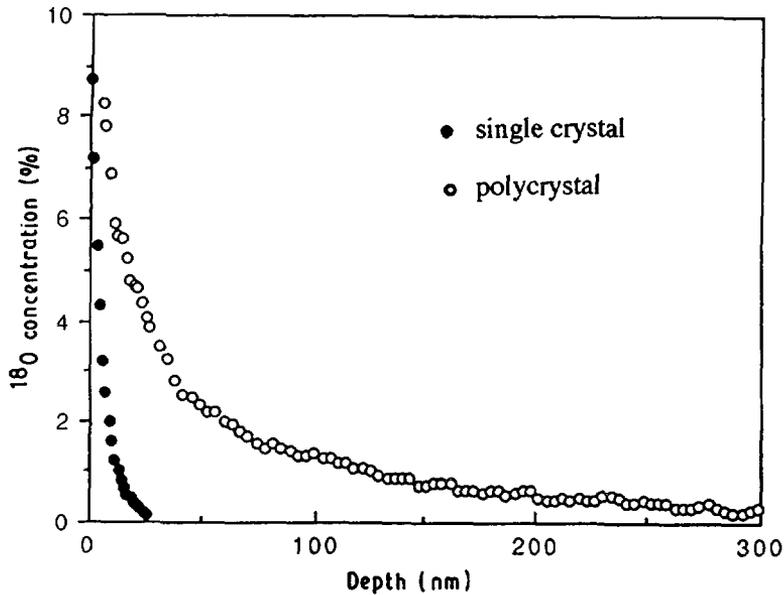


Fig. 11. — Comparison between penetration profiles in a Cr_2O_3 single crystal and in a Cr_2O_3 polycrystal [11, 14].

Calculation of diffusion coefficient values.

Appropriate solution of Fick's equations depending on the initial experimental conditions allows to determine the diffusion coefficient value. Solutions corresponding either to a thin deposit or to a constant surface concentration (or a thick deposit) are used [20]. Figure 12 gives an example for a diffusion profile of oxygen in an alumina undoped single crystal and the corresponding curve $\text{Argerf}\left(\frac{y}{2\sqrt{Dt}}\right)$ allowing to calculate the diffusion coefficient. The tail of the curve corresponds to diffusion in short-circuits, such as dislocations in the present case [16]. In this case, it was shown by a microstructural observation that dislocations were arranged in sub-boundaries (cf. Fig. 1).

For diffusion in chromia, due to evaporation of the ceramic at high temperature during diffusion annealing, a more completed and complex equation had to be used, as mentioned by Tarento [32].

Diffusion coefficients in grain boundaries are determined by using the solution given by Le Claire [33], which takes the grain size, the width of the grain boundary, and the diffusion coefficient in the bulk into account. Figure 13 gives a plot of the logarithm of the concentration *versus* the penetration depth at the power 6/5, which allows to calculate the product $D_{\text{gb}} \delta$ of the diffusion coefficient in grain-boundaries, D_{gb} , by the width δ of the grain-boundary.

The classical value of the grain-boundary width δ is given to be equal to 1 nm. Many questions can be asked, which are not yet solved :

- What is the true value of the grain-boundary width in ceramics ?
- Is this width always the same for all ceramic materials ?
- What is the dependence of the segregated species on the grain-boundary width ?

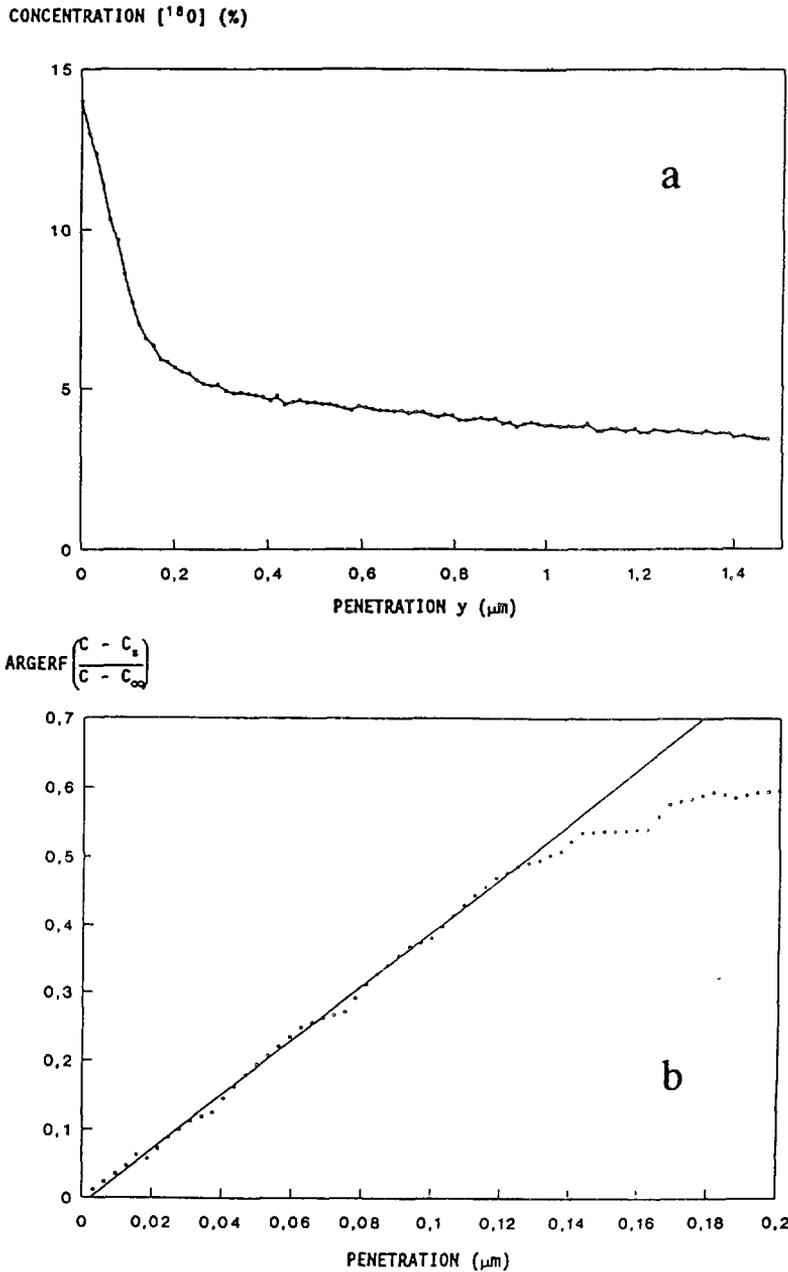


Fig. 12. — Diffusion in alpha-alumina (a)-Plot of ^{18}O concentration vs. penetration depth y . (b) Plot of $\text{Argerf}\left(\frac{C - C_s}{C - C_\infty}\right)$ [15].

- Is it possible to have self-segregation, that is segregation either of cations or of anions in grain boundaries ?
- What about the space charge ?

Moreover, since each ceramic specimen can be considered as a new material, it would be essential to know the fine structure of each material..

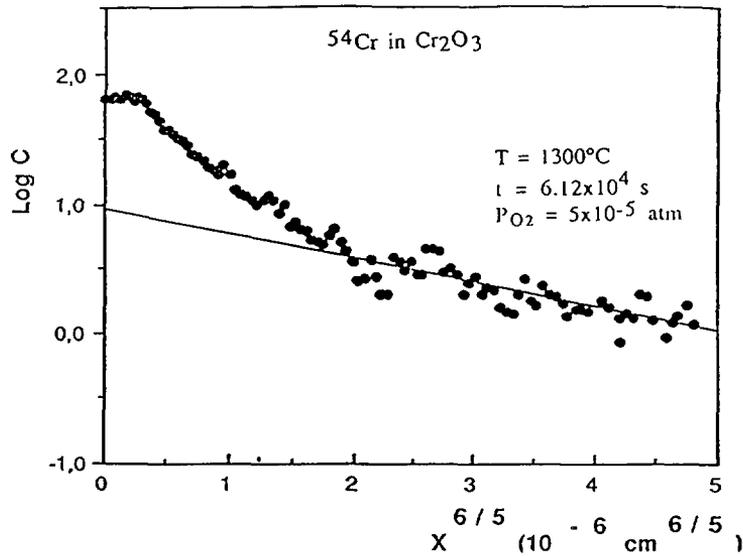


Fig. 13. — Plot of the logarithm of the concentration *versus* the penetration depth at the power 6/5 for diffusion of chromium in chromia [11, 14].

Some results and interpretations.

BULK DIFFUSION. — In figure 14 are plotted Arrhenius graphs about anionic and cationic diffusion in Al_2O_3 [15], Cr_2O_3 [11-13] and Fe_2O_3 [34, 35]. The diffusion coefficients for chromia and alumina are of the same order of magnitude and much lower than the results found by Atkinson *et al.* [34] and Hoshino *et al.* [35] for diffusion in hematite. For chromia, Sabioni *et al.* [11-13] find that oxygen diffuses undeniably faster than chromium whereas Le Gall *et al.* observe that aluminium diffusion in alumina is very slightly higher than oxygen diffusion. For diffusion in hematite cationic and anionic diffusion coefficients are quite the same.

A plot of $\log D$ vs. T_m/T (Fig. 15), where T_m is the melting point, lets show the diffusion coefficient value at the melting point. This graph includes results obtained by Lesage *et al.* for diffusion of chromium, nickel and iron in alumina [36], by Moya *et al.* for diffusion of silver [37]. For alumina and chromia, $D(T_m)$ is found to be equal to about 10^{-12} - $10^{-13} \text{ cm}^2 \text{ s}^{-1}$, both for cationic and oxygen diffusion. As shown in figure 15, other results obtained by Reed *et al.* [38] and by Reddy *et al.* [39] for diffusion of oxygen in alpha-alumina give also the same value at the melting point.

Remember that for solid metals $D(T_m)$ values are equal to 10^{-7} - $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [19].

Diffusion in carbides as mentioned by Matzke leads to $D(T_m)$ equal to 10^{-7} - $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for diffusion of the metallic species, whereas diffusion of carbon is equal to about 10^{-5} - $10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The values of experimental activation enthalpy measured for the same type of diffusion may be different depending on the authors. These values are equal to the sum of the enthalpies of defect formation, migration and segregation. The amount of impurities may be high enough to produce a high concentration of extrinsic point defects. In these conditions, the enthalpy of formation of the natural defects is equal to zero and the experimental activation enthalpy is equal to the migration enthalpy of the point defect, affected or not by an enthalpy of segregation.

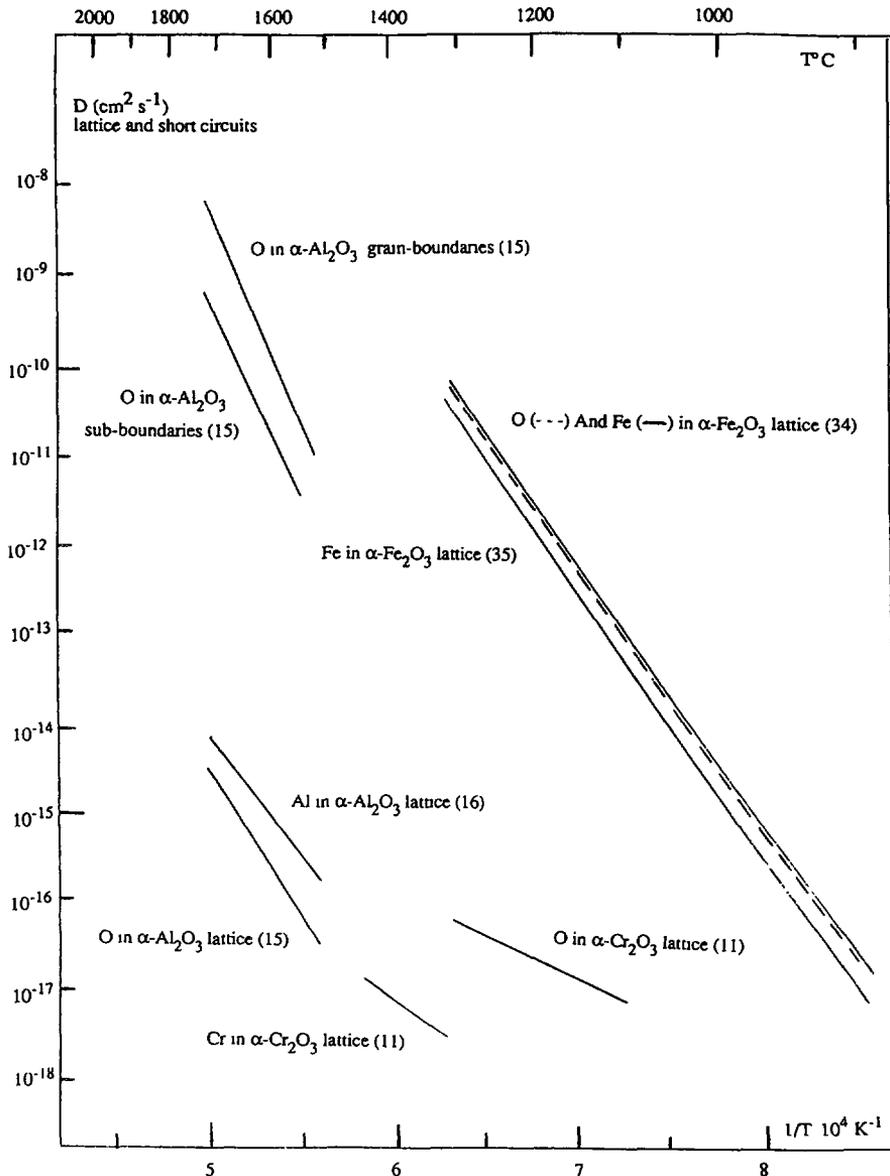


Fig. 14. — Arrhenius plots for diffusion in corundum structure oxides.

Results for diffusion of oxygen in alpha-alumina single crystals give values of activation enthalpies between $582 \text{ kJ}\cdot\text{mol}^{-1}$ [40] and $787 \text{ kJ}\cdot\text{mol}^{-1}$ [37]. The scattering of these values is due to the fact that the nature and amount of defects are different from one sample to one other.

After determination of diffusion coefficients and activation enthalpies, it seems to be necessary to interpret these values, that is to know the nature of the diffusing defect. Such informations can be obtained by carrying out diffusion experiments under different partial pressure of the anionic species X, the concentration of a defect [Def] depending generally on

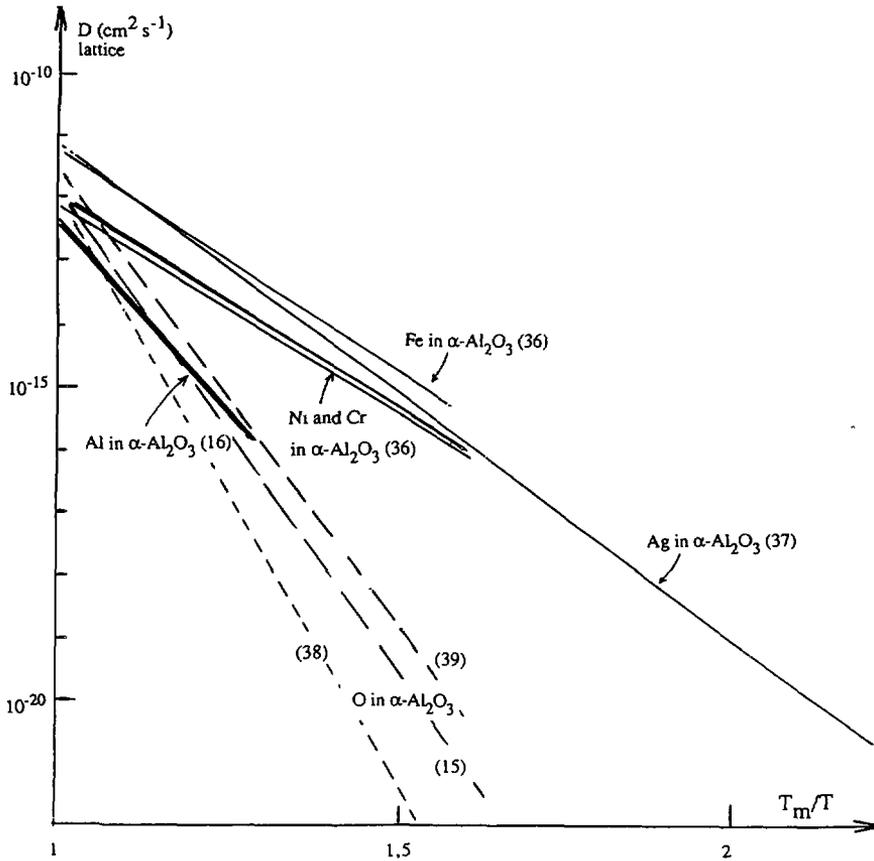


Fig. 15. — Plots of $\log D$ vs. T_m/T for diffusion in alpha-alumina.

this partial pressure p_X .

$$[\text{Def}] = K \cdot p_X^{1/n}$$

For the oxides, low oxygen partial pressures can be obtained by mixing CO and CO₂ and measured by the way of a zirconia gauge.

Since several point defects are present in the material, such as electrons and electronic holes, cationic and anionic vacancies, cationic and anionic interstitials, impurities, a lot of equilibria can be written. Table I gives an example for defects in Cr₂O₃ [12] showing the complexity of the problem. More of one defect are often present together in the material, so it is difficult to give a good interpretation of the exponent found. Moreover, many times the impurity amount is so high that no influence of the partial pressure of the anionic species is observed, giving rise, as mentioned above, to an « extrinsic » behaviour.

Theoretical investigations about activation enthalpy of formation, motion and segregation can help us to understand the values deduced from the experiment, but it is sometimes not easy to compare these last values, obtained for impure materials, with values calculated for an ideally pure material.

Some of these works can be used as a basis for comparison : Jacobs *et al.* for α -alumina [41, 42], Catlow *et al.* for α -alumina and rutile [43] and for hematite and chromia [44, 45].

Table I. — *The different possible point defects expected in chromia and the associated exponents for the oxygen partial pressure dependence [12].*

Electrical neutrality	Point defects in Cr sublattice		Point defects in Oxygen sublattice				Electronic defects		Expected electrical behaviour
	$[V_{Cr}^{\bullet}]$	$[Cr_i^{\bullet}]$	$[O_i]$	$[O_i']$	$[V_o]$	$[V_o']$	$[e']$	$[h]$	
(1) $[V_{Cr}^{\bullet}] = [Cr_i^{\bullet}]$	0	0	1/4	0	-1/4	0	-1/4	1/4	intrinsic ionic
(2) $3[V_{Cr}^{\bullet}] = 2[V_o]$	0	0	1/4	0	-1/4	0	-1/4	1/4	intrinsic ionic
(2') $3[V_{Cr}^{\bullet}] = [V_o]$	-3/16	3/16	3/16	-1/8	-3/16	1/8	-5/16	5/16	intrinsic ionic
(3) $[O_i'] = [V_o]$	0	0	1/4	0	-1/4	0	-1/4	1/4	intrinsic ionic
(3') $[O_i] = [V_o]$	-3/4	3/4	0	-1/2	0	1/2	-1/2	1/2	intrinsic ionic
(3'') $2[O_i'] = [V_o]$	-1/4	1/4	1/6	-1/6	-1/6	1/6	-1/3	1/3	intrinsic ionic
(3''') $[O_i] = 2[V_o]$	-1/4	1/4	1/6	-1/6	-1/6	1/6	-1/3	1/3	intrinsic ionic
(4) $[e'] = [h]$	3/4	-3/4	1/2	1/2	-1/2	-1/2	0	0	intrinsic semiconductor
(5) $[h] = 3[V_{Cr}^{\bullet}]$	3/16	-3/16	5/16	1/8	-5/16	-1/8	-3/16	3/16	p type semiconductor
(6) $[e'] = 3[Cr_i^{\bullet}]$	3/16	-3/16	5/16	1/8	-5/16	-1/8	-3/16	3/16	n type semiconductor
(7) $[e'] = [V_o]$	0	0	1/4	0	-1/4	0	-1/4	1/4	n type semiconductor
(7') $[e'] = 2[V_o]$	1/4	-1/4	1/3	1/6	-1/3	-1/6	-1/6	1/6	n type semiconductor
(8) $[h] = [O_i]$	0	0	1/4	0	-1/4	0	-1/4	1/4	p type semiconductor
(8') $[h] = 2[O_i']$	1/4	-1/4	1/3	1/6	-1/3	-1/6	-1/6	1/6	p type semiconductor
(9) $\alpha[F_{Cr}^{\bullet}] = [e']$	3/4	-3/4	1/2	1/2	-1/2	-1/2	0	0	extrinsic semiconductor
(10) $\beta[F_{Cr}^{\bullet}] = [h]$	3/4	-3/4	1/2	1/2	-1/2	-1/2	0	0	extrinsic semiconductor
(11) $\alpha[F_{Cr}^{\bullet}] = 3[V_{Cr}^{\bullet}]$	0	0	1/4	0	-1/4	0	-1/4	1/4	extrinsic ionic
(12) $\beta[F_{Cr}^{\bullet}] = 3[Cr_i^{\bullet}]$	0	0	1/4	0	-1/4	0	-1/4	1/4	extrinsic ionic
(13) $\alpha[F_{Cr}^{\bullet}] = 2[O_i']$	0	0	1/4	0	-1/4	0	-1/4	1/4	extrinsic ionic
(13') $\alpha[F_{Cr}^{\bullet}] = [O_i]$	-3/4	3/4	0	-1/2	0	1/2	-1/2	1/2	extrinsic ionic
(14) $\beta[F_{Cr}^{\bullet}] = 2[V_o]$	0	0	1/4	0	-1/4	0	-1/4	1/4	extrinsic ionic
(14') $\beta[F_{Cr}^{\bullet}] = [V_o]$	-3/4	3/4	0	-1/2	0	1/2	-1/2	1/2	extrinsic ionic

Lawrence *et al.* for chromia [46]. Since the experimental values of activation energies have been obtained with materials whose defect amount and nature are not known with the best precision, the comparison with theoretical values must be done very carefully.

DIFFUSION IN SHORT CIRCUITS. — As mentioned by Moya *et al.* [47], in a review of diffusion data, diffusion coefficients along dislocations and grain boundaries appear to be more than 4 orders of magnitude higher than the lattice diffusion coefficients. Sabioni [11] found such results for diffusion of chromium in chromia. Recent works by Prot [15] and Le Gall [16] (see Fig. 14) for alumina verify this fact and allows to announce some interesting remarks :

- for oxygen diffusion in undoped alpha-alumina, diffusion in grain boundaries is faster than diffusion in sub-boundaries whereas for oxygen diffusion in yttrium-doped alpha-alumina, diffusion in grain boundaries is lower than diffusion in sub-boundaries ;
- the presence of yttrium as a dopant enhances the lattice diffusion of oxygen and lowers the diffusion in short-circuits ;
- the activation energy of diffusion in short circuits is much higher than the activation energy for lattice diffusion, due probably to interactions between oxygen and impurities segregated or precipitated in the short-circuits.

Conclusion.

The purpose of this paper was not to give a review of all data of diffusion in ceramics, but to point out some problems encountered in determinations of diffusion coefficients in ceramics. Influence of impurities and short circuits on diffusional behaviour seems to be a very important problem giving rise to caution in interpretation of results. A systematic local analysis of the specimen in the place where diffusion is occurring will be very useful and will allow suitable comparisons between theoretical and experimental data for activation energies.

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