

Self-Diffusion in Simple Oxides (A Bibliography)

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The paper is directed towards the materials scientist who wishes to employ published values of diffusion coefficients in his investigations. A brief review of self-diffusion behaviour and the likely inaccuracies of the various techniques used in the measurement of diffusion is followed by a selected bibliography and tabulation of coefficients for oxides.

1. Introduction

The materials scientist frequently requires knowledge of the ease with which the ions that compose a substance move within that substance, i.e. rates of self-diffusion. For instance, creep, sintering, and the annealing of radiation damage can all depend on the ease of ionic motion. Corrosion rates of metals are often related to the diffusion of ions through the protective film that forms [1, 2]. Heat treatment of capacitors probably improves their resistivity by diffusional healing of flaws in the dielectric.

The study of diffusion has reached a high degree of sophistication and much is now known about the various processes, particularly in the simplest systems such as the single-crystal alkali-halides [3]. However, it is generally difficult for the materials scientist (i) to obtain estimates of diffusion rates in the materials that are of concern to him, and (ii) to appreciate in a general fashion the probable shortcomings in the data available. This review attempts to provide such a service for a practical class of materials—the simple oxides. A brief assessment of the behaviour expected, and of the techniques used to determine diffusion, is followed by a selected bibliography.

2. General Behaviour

The diffusion of an ion in a solid is characterised by a diffusion coefficient D cm²/sec. Since the diffusion is an activated process (the ion has to hop over an energy barrier in order to move), D is expressed by an equation of the form

$$D = D_0 \exp^{-Q/RT} \quad (1)$$

where D_0 cm²/sec is a constant, Q kcal/mole is

the activation energy for the process, R is the gas constant, and T is the absolute temperature. Values of D_0 may vary widely—in the following bibliography values between 10^{31} and 10^{-14} cm²/sec are reported, although values much above unity are suspect from a theoretical viewpoint. Q is occasionally quoted in electron volts, in which case R in equation 1 is replaced by k , Boltzmann's constant. As the temperature is increased, D usually follows a series of equations of the form of equation 1, where Q takes increasing discrete values as illustrated in fig. 1. In view of this it is desirable that D be determined over a wide range of temperatures before straight line relations are drawn. Clearly it is dangerous to attempt to extrapolate from known data.

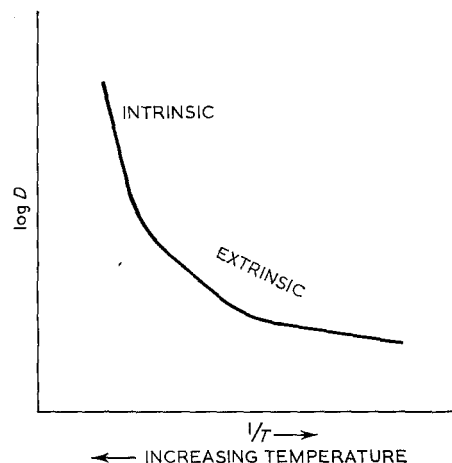


Figure 1 Relationship between the diffusion coefficient D of a given ion in a given solid, and the absolute temperature T , showing regions of different slope, i.e. activation energy.

2.1. Intrinsic Diffusion

In the high temperature region (say very roughly above three-quarters of the melting point) diffusion is generally intrinsic, i.e. the diffusing species are both formed and moved by the thermal energy available. Q is high (see fig. 1) being typically 150 ± 50 kcal/mole for oxides above 1000°C . Intrinsic D 's converge with increasing temperature, usually being within a few magnitudes of 10^{-10} cm²/sec at the melting point of the solid in question. They may vary by a magnitude or more with the orientation of the crystal considered. Intrinsic D 's for polycrystals lie between the extremes. In this context it must be noted that many chemical compounds have a variety of crystalline phases even at a given temperature, and that D will vary somewhat between phases as well. Further, intrinsic diffusion usually varies quite sharply with the ambient partial pressure of the species. For oxides, oxygen pressure is therefore important.

A rough rule is that the more insulating the oxide (this usually means the lighter the metal ion) the higher the value of Q for intrinsic diffusion of the metal. This has been particularly related to the ease with which the metal ion can be ionised to a higher valence state [4].

2.2. Extrinsic Diffusion

At lower temperatures, extrinsic factors such as impurities and inhomogeneities can retard or assist self-diffusion in a solid, altering D_0 and Q as in fig. 1.

At these temperatures D may vary widely between samples owing to these factors, and also to the earlier mentioned complications of phase and orientation, although here the situation is usually simplified with respect to pressure in that impurity controlled diffusion is usually independent of pressure [5]. One final consideration, that also applies to the intrinsic range, is that equation 1 may only apply for given stoichiometry and if, at a given pressure, the stoichiometry varies with temperature, equation 1 will not be obeyed. For oxides, values of Q for this extrinsic range (e.g. 300 to 1000°C) are typically 60 ± 40 kcal/mole.

At the lowest temperatures, near ambient and below, the easiest (i.e. lowest Q) processes dominate. These can include diffusion down dislocations [5] and across surfaces [6], and the situation can be further complicated by the substance being in a quenched state, since equilibration may take several days at these

temperatures [7]. The few relevant values of Q quoted below for oxides are in the range 20 ± 10 kcal/mole.

One can now see that diffusion coefficients measured at the highest temperatures can be fairly confidently used by other workers, provided that crystal orientations and oxygen pressures are compared. By contrast, data for the lower temperatures may vary by many magnitudes, regardless of the care taken in measurement simply because these values depend on extrinsic factors. Accordingly, if diffusion coefficients for below, say, three-quarters of the melting point in degrees Kelvin are to be taken from published work, every effort must be made to compare crystallinity and impurity content. Near ambient temperature and below thermodynamic equilibrium, surface paths, dislocation densities, etc, must be considered in addition.

2.3. General Trends

In simple inorganic compounds one generally finds that the anion (oxygen in oxides) diffuses more slowly than the cation. Exceptions for the oxides can apparently include UO_2 [8], TiO_2 [9], ThO_2 [9], Nb_2O_5 [9], ZrO_2 [9], HfO_2 [10], Fe_2O_3 [11], and WO_3 [25]. These compounds probably represent a group of materials that easily become oxygen-deficient, and the observation may only apply to lower temperatures. For instance, for Fe_2O_3 , crossover of D 's near 1000°C is suspected [12]. For UO_2 oxygen-diffusion may still be dominant at 1600°C [8], but this may owe something to the U^{4+} ion being exceptionally large.

Some oxides have metal and oxide diffusion coefficients that are within a few magnitudes of each other in the lower temperature region. These include Al_2O_3 [16] and, from more indirect evidence [17], Nb_2O_5 , Ta_2O_5 , and WO_3 .

Particularly at the lower temperatures, D can be increased by the presence of grain boundaries [13]. This is frequently true for anions [14-16], probably because they are usually the largest and therefore the most slowly diffusing ions in the solid, and it seems to occur by D_0 increasing with little change in Q .

2.4. Detailed Interpretation

A given ion may move in a solid by either thermally-created defects or impurity-created defects. It may diffuse by a variety of mechanisms, the simplest being as an interstitial (i.e. by passing from one interstitial lattice site to another) or

by jumping into vacant sites in the lattice. In principle, where the defect concentration and the energy of motion are understood on a microscopic scale for a given system, the macroscopic quantities D_0 and Q may be split into their constituent parts [24] and the correlation factor f of equation 2 below may be calculated [18, 20]. At present, such information is seldom available for the oxides and will not be further discussed in the present context.

3. Measurement Techniques

One can now turn to the techniques commonly used for the measurement of diffusion coefficients. Probably the most reliable are the various techniques based on the use of radioactive tracers, since these techniques are very sensitive, and usually enable the ion in question to be identified unambiguously. Recently, proton activation has been used to give radio-tracers for the study of oxygen-diffusion [26]. Previously, mass spectrometers monitoring the gaseous exchange of O^{18} gave the best values of O diffusion. This method identified the ion unambiguously but had other shortcomings [26].

With diffusion coefficients measured by other techniques the identity of the ion in question may only be implied. Into this category come measurement of kinetics of necking of spheres, shrinkage in sintering, creep, the growth of an oxide film on the metal, and measurement of ionic electrical conductivity. These latter methods are also subject to various quantitative interpretations, and therefore the magnitude of the coefficients implied can also be in great doubt. Considerations for necking, sintering and creep have been discussed elsewhere [5]. The theory of metallic oxidation usually calls for a uniform film [2], and this can be falsely taken to be the case in a given experiment [19]. With electrical conductivity, there is often only meagre evidence that ions are involved at all. However, since ionic conduction is rarely quoted in terms of values of D , and recourse to such data may be necessary, we now briefly consider the theory.

For ionic conduction entirely due to one type of ion the conductivity σ is related to D by the Nernst-Einstein equation [18]

$$\sigma f = D \left[\frac{Nz^2e^2}{kT} \right] \quad (2)$$

where z is the charge on the ion that is moving, e is the electronic charge, N is the number of ions per cm^3 , and k is Boltzmann's constant. f is the

"correlation factor", a crystallographic quantity that takes account of the fact that conductivity follows the motion of the defect (e.g. vacancy, interstitial) whereas tracer-diffusion follows the ion in question directly. f varies with the mechanism of diffusion and has been discussed elsewhere [20]. For magnitude estimates of D , f may be taken as 1, since its value usually lies between 0.5 and 1.5. Other pitfalls in the use of equation 2 are the fact that neutral species may contribute to D but not σ , particularly at low temperatures [21], and irrelevant relaxation processes may increase σ in some cases [22], leading to a spuriously high D as implied from equation 2. Further, equation 2 applies where only one ion and one diffusional mechanism contributes, and this is not always the case.

Two other types of measurement that have been interpreted in terms of diffusion rates in oxide specimens deserve mention. The first is the study of oxidation of reduced oxide (or reduction of stoichiometric oxide) using weight change or change in optical absorption. The second is the measurement of gaseous permeation when there is a difference of gas pressure across a material. Clearly these methods can be very insensitive and may be difficult to interpret.

4. Use of the Bibliography

The following bibliography is intended as a guide to the best available values of diffusion coefficients in simple solid oxides. It incorporates data from a few earlier and more restricted bibliographies that are available [9, 11, 23], and represents an attempt to cover the literature up to October 1967. A Table of Values summarises the data available, and detailed references are given in an Appendix that follows.

The bibliography should be seen in conjunction with the cautionary remarks above. The comments column is intended as some guide towards the reliability of the data by mention of the methods used. There is no indication of whether the diffusion is intrinsic or extrinsic, since even the workers themselves are seldom willing to speculate. For comparative purposes it is indicated whether single crystals or polycrystals were measured, the temperature ranges are quoted, as are the type of ion moving, and where possible the composition and stoichiometry of the material in which they move is indicated. Most of the work quoted refers to ambient oxygen pressures. The crystalline phase examined is not always indicated in the literature, but

where several phases are possible at the temperatures used (e.g. for ZrO_2 and iron oxides) the widest possible variety of data is presented. Where one phase only is usual, the least reliable data are omitted. Where data for a pure oxide is sparse, values for related mixed oxides are quoted. In the final section listing the references, the language is indicated where it is known not to be English. The references should, of course, be studied where further information is required and omission of figures for D_0 , Q , and D from the table must not be taken to imply that these quantities cannot be derived from a more thorough examination of the reference in question. Where values of D are required to high accuracy, a check should be made whether the values quoted refer to the true ("tracer") coefficient or the diffusion coefficient of the species which enables the ion to move (vacancy etc). These quantities are related by the correlation factor f as used in equation 2.

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N10
 Table of Values

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (°C)	Comments	Year
Aluminium oxide (Al ₂ O ₃)	1	Al	—	165	1100-1800	(S) from sintering shrinkage	1958
	2	Al	2.5×10^4	135	1700-1800	in wet H ₂ , He or O ₂ . (S) from sintering of spheres in dry H ₂	1958
	3	O	5.0×10^{18}	230	1700-1800	(S) (P) O ¹⁸ mass spec.	1960
			6.3×10^{-8}	57.6	1200-1620		
	4	Al	—	152 ± 25	1500-1700	(S) from creep	1961
	5	Al	28	130 ± 20	1600-1800	(P) Al ²⁶ radiotracer	1962
6	O	—	114 ± 15	1670-1905	(P) — $D = 4.0 \pm 3.0 \times 10^{-11}$ at 170	1963	
Barium oxide (BaO)	1	Ba	—	—	—	(S) Ba ¹⁴⁰ radiotracer	1951
	2	Ba	$10^{29 \pm 7}$ $10^{31 \pm 8}$ $10^{-9 \pm 1}$	253 306 14.5	1077-1247 1077-1247 277-1077	(S) bulk (S) surface (S) structure sensitive bulk	Ba ¹⁴⁰ radiotracer 1952
Beryllium oxide (BeO)	1	Be	5.56×10^8 6.14×10^{-2}	111.6 66.1	1570-1730 1730-1934	(P) Be ⁷ radiotracer	
	2	Be	—	114	—	(P) from creep 54 to 216 lb/in. ² *	1958
3	Be	1.37	91.9	1550-1725	(P) } Be ⁷ radiotracer	1961	
		1.10×10^{-6}	36.15	1725-2000			
4	O	5.2×10^{-7} 5.2×10^{-6}	42.9 42.9	1600-1900	(P) O ¹⁸ mass spec.; at least two processes operative	1961	
5	O	—	—	1600-1900	(P) O ¹⁸ mass spec.; "rapid" low-magnitude process only	1962	
6	O	2.95×10^{-5}	68.5	1560-1727	(S) O ¹⁸ mass spec.	1962	
7	Be	2.49×10^{-3}	62.5	1150-1800	(P) Be ⁷ radiotracer	1964	
		1.27×10^{-3}	64	1760-2000			
8	Be	1.23×10^{-6}	36	1490-1720	(S)		
		1.35	92	1550-1725			
9	Be	1.07×10^{-6}	36	1760-1825	(P) hot pressed	Be ⁷ radiotracer	
		5.56×10^3	111.6	1300-1730			
10	Be	6.14×10^{-2}	66.1	1730-1910	(P) slip cast sintered		
11	Be	3.2×10^{-3}	63.0	1100-1800	(P) Be ⁷ radiotracer and ionic conductivity	1966	
12	Be	—	52	1500-2000	(S) (P) Be ⁷ radiotracer	1966	
Bismuth oxide (Bi ₂ O ₃)	Bi	4.29×10^{-6}	62	500-1500	(P) Be ⁷ radiotracer, various points plotted	1967	
		4.5×10^{-1}	20.7	1330-1500			
Cadmium oxide (CdO)	O	8.0×10^6	93 ± 5	1500-2135	(P) Be ⁷ radiotracer—related to impurity	1963	
		1.3×10^6	93 ± 5	710 710 640-820			

*1.0 lb/in.² = 7×10^{-2} kg/cm²

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (°C)	Comments	Year
Cadmium oxide (CdO)	2	O	3.8×10^6 3.9×10^6	92 ± 4 92 ± 4	630-855	(S) } O ¹⁸ mass spec. (P) } (P) Ca ⁴⁵ radiotracer	1962
	1	Ca	0.4	81	900-1400	(P) Ca ⁴⁵ radiotracer	1952
Calcium oxide (CaO)	2	O	—	80	27-1127	(S) possible ionic conductivity giving D via the Nernst-Einstein equation	1966
	3	Ca	0.444	100.2 ± 2.8	1700-2150	(P) Ca ⁴⁵ radiotracer in CaO with 84% ZrO ₂	1966
Cerium oxide (CeO ₂)	4	{ Ca Ca	8.75 ± 1.32 1.95 ± 0.06	34.6 ± 0.95 34.02 ± 1.80	1000-1400 1000-1400	(S) Ca ⁴⁶ radiotracer near surface (S) Ca ⁴⁵ radiotracer near bulk	1967
	1	O	—	—	250-350	(P) CeO ₂ reduction	1951
Chromium oxide (Cr ₂ O ₃)	1	Cr	4.0×10^3	100	1000-1350	(P) Cr ⁵¹ radiotracer	1956
	2	Cr	4.29×10^{-8}	22	900-1100	(P) Cr ⁵¹ radiotracer	1958
	3	Cr	0.137	61.1	1045-1550	(P) Cr ⁵¹ radiotracer; independent of impurity	1961
	4	Cr	—	88.7	$D = 1.54$ at 1100 $D = 15.2$ at 1200 $D = 36.3$ at 1250	(P) film evaporation	1960
	5	Cr	—	—	$D = 5.0 \times 10^{-10}$ at 1300	(S) Cr ⁵¹ radiotracer	1963
	6	O	15.9	101	1100-1450	(P) O ¹⁸ mass spec.	1965
	7	Cr	—	—	$D = 1.54 \times 10^{-11}$ at 1100 $D = 4.55 \times 10^{-11}$ at 1150 $D = 1.52 \times 10^{-10}$ at 1200 $D = 3.63 \times 10^{-10}$ at 1250 $D = 5.0 \times 10^{-6}$ at 1300	(P) O ¹⁸ mass spec.	1960
Cobalt oxide (CoO)	8	Cr	—	—	1100-1450	(S) Cr ⁵¹ radiotracer	1965
	9	O	{ 440 3370	109.9 ± 7.3 123.0 ± 8.0	—	(P) sintering shrinkage-two interpretations	1966
	1	Co	2.15×10^{-9}	34.5 ± 0.4	800-1350	(P) Co ⁶⁰ radiotracer	1954
	2	O	some points plotted on graph	—	900-1400	(S) (P) O ¹⁸ reaction (P, n) F ¹⁸	1967
	3	O	some points plotted in [2]	—	1000	(S) (P) O ¹⁸ mass spec.	1962
	4	Co	—	—	$D = 1.39 \times 10^{-8}$ at 1100 4.07×10^{-9} at 1100 9.06×10^{-10} at 900 3.91×10^{-10} at 800	(S) deduced from changes in electronic conductivity at 1 atm/O ₂	1966
Copper oxide (Cu ₂ O)	1	Cu	3.58×10^{-2}	37	800-1000	(P) radiotracer during oxidation	1949
	2	Cu	4.36×10^{-2}	36.1 ± 2	800-1050	(P) radiotracer	1951
	3	O	6.5×10^{-3}	39.3 ± 4.4	1030-1120	(P) O ¹⁸ mass spec.	1958
	4	O	6.3×10^{-3}	39.3 ± 4.4	—	(P) O ¹⁸ mass spec. }	1959
		Cu	1.22×10^{-1}	36.1 ± 2.5	—	(P) O ¹⁸ mass spec. }	1962
	5	O	—	43.1 ± 4.4	1030-1100	(P) O ¹⁸ mass spec.	1962
	6	O	1.5×10^{-2}	39.3	1024-1120	(S) O ¹⁸ mass spec.	1963

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (°C)	Comments	Year
Erbium oxide (Er ₂ O ₃)	1	O	1.22	47.8	850-1250	(P) weight gain of reduced oxide on oxidation	1967
	1	O	—	—	(at 1200)	(vitreous) D 's given for 3-film thicknesses	1959
	2	O	10 ⁻³	27.6 ± 2.3	480-630	(vitreous) opt. absorption disappearance with temp. vapourisation relations found	1960 1964
Germanium oxide (GeO ₂)	3	Ge	—	—	—	(P) Ionic conductivity is postulated. Hence D can be calculated using the Nernst-Einstein relation. But see criticism in P. J. Harrop and J. N. Wanklyn. <i>J. Electrochem. Soc.</i> 110 (1963) 1285	1963
	1	O	—	—	—	(P) pressure drop across tube of Hf _{0.80} Ca _{0.14} O _{1.86}	1966
Hafnium oxide (HfO ₂)	2	O	22.0	55.7	1100-2050	(S) O ¹⁸ mass spec.	1967
	1	O	—	12.4-15.0	—	(P) D tracer and O ¹⁸ mass spec.	1958
Hydrogen oxide (ice)	2	H ₂ O	—	—	$D = 1 \pm 0.2 \times 10^{-10}$ at -2	(S) protons (tritons)	1963
	3	H	—	13.5	$\begin{cases} -35 & -0 \\ D = 2.0 \times 10^{-11} & \text{at } -7 \end{cases}$	(S) O ¹⁸ (p, n) F ¹⁸ reaction	1966
Iron oxides	4	H ₂ O	—	15.7	-29.5 to -5	(S) H ³ radiotracer	1964
	5	H ₂ O	—	15.7	-30 to -10	(S) H ³ radiotracer	1966
	6	H ₂ O	—	14.4 ± 0.7	-26.8 to -3.5	(S) H ³ radiotracer	1966
	7	H ₂ O	—	14.5 ± 1.0	-32 to -5	(S) H ³ radiotracer	1966
	1	Fe	4.0 × 10 ⁴	112	750-1300	(P) Fe ⁵⁹ radiotracer in Fe ₂ O ₃	1952
	2	Fe	0.118	29.7	700-1000	(P) Fe ⁵⁸ radiotracer in FeO	1953
		Fe	—	30.2	$D = 1.4 \times 10^{-2}$ at 1420	(P) oxidation FeO	1954
Iron oxides		Fe	5.2	55	750-1000	(P) oxidation Fe _{2.993} O ₄	1954
		Fe	4.0 × 10 ⁵	112	1000-1217	(S) oxidation Fe ₂ O ₃	1954
	3	Fe	0.014	30.2 ± 0.5	700-1000	(P) Fe ⁵⁸ tracer in Fe _{0.92} O in oxidation	1958
	4	Fe	0.25	53.9	770-1200	(P) Fe ⁵⁹ in Fe ₃ O ₄	1960
	5	O	10 ¹¹	146	1150-1250	(P) Fe ⁵⁹ in Fe ₂ O ₃	1960
	6	Fe	6.0 × 10 ⁵	$\begin{cases} 84.0 \pm 5.9 \\ 74.7 \pm 4.5 \end{cases}$	850-1075	(S) Fe ⁵⁸ tracer in Fe ₃ O ₄	1960
Lead oxide (PbO)	7	Fe	—	25 to 33	860-1260	(P) Fe ⁵⁹ tracer in FeO with 75.5 < Fe < 76.5%	1965
	8	O	2.04	77.9	900-1250	(P) O ¹⁸ mass spec. in α-Fe ₂ O ₃	1966
	9	Fe	1.3 × 10 ⁶	100.2	950-1050	(P) Fe ⁵⁹ tracer in Fe ₂ O ₃	1962
	10	Fe	—	24.8-37.4	900-1100	(P) by weight change FeO	1965
	1	Pb	—	—	$10^{-12} < D < 10^{-14}$ at 485-570	(P) contact method-decrease in surface activity	1949
	2	Pb	10 ⁵	66	400-590	(P) Pb ²¹² radiotracer	1952
Magnesium oxide (MgO)	3	O	5.39 × 10 ⁻⁵	22.4	500-650	(P) O ¹⁸ mass spec.	1963
	4	Pb	—	64	circa 640	(P) Pb ²¹⁰ radiotracer	1965
	1	Mg	2.3 × 10 ⁻¹	78.7	1400-1600	(S) radiotracer	1957
	2	O	2.5 × 10 ⁻⁶	62.4	1300-1750	(S) O ¹⁸ mass spec.	1960

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (°C)	Comments	Year
Magnesium oxide (MgO)	3	Mg	—	50	1000-1500	(S) ionic conductivity is found, permitting D to be calculated using the Nernst-Einstein equation	1962
	4	Mg	—	—	1061-1510	(S) ionic conductivity is found, permitting D to be calculated using the Nernst-Einstein equation	1962
Manganese oxide (MnO)	5	O	4.3×10^{-5} 4.8×10^{-14}	82.1 ± 3.0 30.2×3.0	1000 } 1000 }	(P) O ¹⁸ mass spec.	1966
	1	Mn	—	40.5-45.6	800-1200	(P) oxidation kinetics	1965
Neodymium (Nd ₂ O ₃)	1	O	—	—	—	(P) oxidation study D increased by excess O	1965
Nickel oxide (NiO)	1	Ni	4.1×10^{-2}	55	900-1000	(P) Ni ⁶³ radiotracer	1951
	2	Ni	2.8×10^6	119.5	1140-1400	(P) Ni ⁶³ radiotracer	1956
	3	Ni	5.0×10^{-4}	44.2 ± 3	1000-1400	(P) } Ni ⁶³ radiotracer	1957
		Ni	3.9×10^{-4}	44.2 ± 3	1000-1400	(S) }	1957
	4	Ni	1.7×10^{-2}	56 ± 1.3	700-1400	(S) (P) Ni ⁶³ radiotracer	1960
	5	O	—	—	$D = 3.9 \times 10^{-13}$ at 1300	(S) O ¹⁸ mass spec.	1960
		Ni	8.0×10^{-4}	53.5 ± 3	1300-1700	(S) Ni radiotracer	1962
	6	O	1.0×10^{-5}	54	1100-1500	(S) O ¹⁸ mass spec.	1962
	7	Ni	1.83×10^{-8}	45.6	1000-1400	(S) Ni ⁶³ radiotracer	1962
8	Ni	4.8×10^{-4}	48.4 ± 2	1190-1400	(S) Ni ⁶³ radiotracer during oxidation	1962	
9	Ni	—	—	$D = 3.59 \times 10^{-11}$ at 1100 1.12×10^{-11} at 1000 4.29×10^{-12} at 900 7.70×10^{-12} at 800	(S) deduced from change in electronic conductivity at 0.209 atm O ₂	1966	
Niobium oxides	10	Ni	1.26×10^{-5}	46.6	276-723	(P) electrical study of sintering shrinkage	1966
	1	Nb	—	—	800-1200	(P) Nb ⁹⁵ radiotracer in NbO _(3.4-2.8)	1961
	2	O	3.6×10^{-2}	28.2 ± 1.8	500-900	(P) Nb ₂ O _{4.978}	1962
	3	Nb	—	29.6	900-1100	(P) Nb ⁹⁵ in NbO	1963
	4	O	—	52-53	900-1100	(P) Nb ⁹⁵ in Nb ₂ O ₅ and Nb ₂ O ₄	1966
5	—	4.7×10^{-3}	27.6	600-1350	(S) ionic conductivity	1967	
6	O	—	—	700-950	(P) 2% ionic conductivity permitting D to be calculated from the Nernst-Einstein equation	1967	
Praseodymium oxide (PrO ₂)	6	O	—	—	$D = 7.9 \times 10^{-10}$ at 600 $D = 6.5 \times 10^{-9}$ at 815	(P) —	1965
	7	O	1.72×10^{-2}	49.4 ± 3.3	850-1200	(S) O ¹⁸ mass spec. Nb ₂ O ₅	1967
	1	O	—	42	700-990	(P) weight loss of PrO ₂ under vacuum	1958
Silicon oxide (SiO ₂)	1	O	—	27	$D = 1.2 \times 10^{-8}$ at 1078 $D = 4.2 \times 10^{-9}$ at 950	(vitreous) gaseous permeation	1961

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (°C)	Comments	Year
Silicon oxide (SiO ₂)	2	O	3.7×10^{-9}	55	1010-1220	(P) isotopic exchange	1962
			4.3×10^{-9}	56	900-1200	(S) Single crystal (P) Polycrystalline (vitreous) isotopic exchange	
	3	O	—	—	—	(vitreous) mass spec. for stripped film giving permeation constant	1962
	4	O	1.51×10^{-2}	71.2	925-1225	O ¹⁸ mass spec.	1963
	5	O	2.0×10^{-9}	29	850-1250	isotopic exchange	1965
	6	O	—	—	$D = 8.0 \times 10^{14}$ perpendicular to <i>c</i> axis and 4×10^{-12} parallel at 667	O ¹⁸ (p, α) N ¹⁵ reaction in quartz	1965
Strontium oxide (SrO)	7	O	—	—	—	O ¹⁸ (p, α) N ¹⁵ reaction in quartz	1965
	8	Na	1.88×10^{-2}	30	470-900	(P) Na ²² radiotracer in Na ₂ O.2CaO.3SiO ₂	1966
Tantalum oxide (Ta ₂ O ₅)		Na	3.67×10^{-2}	27.4	200-600	(Glass) ditto	
Terbium oxide (TbO ₂)	1	O	—	46	327-777	(S) possible ionic conductivity giving <i>D</i> via the Nernst-Einstein equation	1966
	1	Ta	—	14.7	-195-100	(S) ionic conductivity	1964
Titanium oxide (TiO ₂)	1	O	—	41.5	700-990	(P) weight loss of TbO ₂ under vacuum	1958
	1	Sn	10^6	118.7 ± 3.7	1000-1260	(P) radiotracer	1955
Titanium oxide (TiO ₂)	2	Sn	10^7	126	—	—	1955
	1	O	1.1	73	860-1030	(S) O ¹⁸ mass spec.	1960
Titanium oxide (TiO ₂)	2	O	2.3	75	710-950	(S) O ¹⁸ mass spec.	1962
			1.4×10^{-4}	53	950-1300	(S) O ¹⁸ mass spec.	
Titanium oxide (TiO ₂)	3	O	2.0×10^{-3}	60 ± 1.5	710-1300	(S) O ¹⁸ mass spec.	1965
	4	Ti	—	24	—	(S) implied from changes in optical absorption	1965
Tungsten oxide (WO ₃)	1	O	—	39	400-700	(P) from oxidation kinetics	1966
	1	O	5.5×10^{-8}	26.3 ± 1.5	160-350	(P) oxidation study in UO _(2.0-2.34)	1957
Uranium oxide (UO ₂)	2	U	—	90-125	1410-1750	(P) radiotracer in UO _(2.00-2.07)	1957
			2.6×10^{-5}	29.7 ± 2.3	450-600	(P) O ¹⁸ isotopic exchange in UO _(2.00-2.07)	
Uranium oxide (UO ₂)	3	O	1.2×10^3	65.3 ± 5	550-800	(P) in UO _{2.002}	1958
			2.1×10^{-3}	29.7 ± 2.5	320-500	(P) in UO _{2.063}	
Uranium oxide (UO ₂)	4	O	2.6×10^{-5}	29.7 ± 2.3	450-600	(P) in UO _{2.004}	1958
			4.0×10^{-4}	29.7	317-465	(P) in UO _{2.064}	
Uranium oxide (UO ₂)	5	U	—	90-125	1410-1750	(P) in UO _(2.0-2.91)	1960
			—	—	$D = 5.0$ to 45.0×10^{-18} at 1000	(P) sectioning and accounting in UO ₂ (U ²³⁵ radiotracer)	
Uranium oxide (UO ₂)	6	O	1.2×10^3	65.3	550-780	(P) surface activity increase in UO _{2.002} (U ²³⁵ radiotracer)	1960
			4.3×10^{-4}	88 ± 11	1450-1785	(P) surface activity method in UO ₂ (U ²³⁵ radiotracer)	1960

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (° C)	Comments	Year
Uranium oxide (UO ₂)	7	U	2.3×10^{-1}	104.6	1300-1600	(P) U ²³³ radiotracer in UO ₂	1961
	8	U	—	52	900-1200	(S) U ²³⁵ radiotracer	1964
					$D = 3.3 \times 10^{-16}$ at 1300 $D = 2.2 \times 10^{-16}$ at 1450		
	9	U	1.2 4.0×10^{-7}	108 70	1450-1700	(S) and (P) } surface activity method in UO ₂	1965
1450-1700					(S) and (P) }		
10	O	—	—	900-1000	(P) ionic conductivity in UO ₂	1967	
Uranium	11	U	—	—	D greater than for uranium	(P) U ²³⁵ radiotracer in UO _{2,00}	1965
					$D = 5 \times 10^{-16}$ at 1700	(S) U ²³⁵ radiotracer in UO _{2,00}	
					$D = 2.43 \times 10^{-14}$ at 1615	theoretical	
					500-1000		
Yttrium oxide (Y ₂ O ₃) Zinc oxide (ZnO)	14	U	—	—	O diffusion for UO _{2,000} is much lower than any of above values	(P) U ²³⁷ radiotracer bulk	1966
					1900-2150	U ²³⁷ radiotracer grain boundary	
					5.82×10^{-5}	(P) Y ⁹¹ radiotracer in Y ₂ O ₃	
					5.19×10^{-9}	(P) weight gain on oxidation of reduced oxide	
					2.41×10^{-4}	(P) ionic conductivity	
					7.24	(P) Zn ⁶⁵ radiotracer	
					—	(P) Zn ⁶⁵ surface activity	
					—	(S) Zn ⁶⁵ activity decrease	
					1.3	(S) ionic conductivity	
					3.0×10^{-9}	(S) Zn ⁶⁵ radiotracer	
					5.0	(S) and (P) Zn ⁶⁵ radiotracer	
					—	(S) and (P) Zn ⁶⁵ radiotracer	
					4.8	(P) Zn ⁶⁵ radiotracer (annealed in O ₂)	
					30	(P) Zn ⁶⁵ radiotracer (annealed in Ar)	
Zinc	10	Zn	—	—	$D = 6.0 \times 10^{-11}$ at 1290 $D = 2.2 \times 10^{-10}$ at 1290	(P) Zn ⁶⁵ radiotracer	1955
					800-1300	(S) Zn ⁶⁵ radiotracer	
					10^{-1}	(S) ionic conductivity	
					2.7×10^{-4}	(S) Zn ⁶⁵ radiotracer	
					170	(S) Zn ⁶⁵ radiotracer	
					—	(S) ionic conductivity	
					—	(S) Zn ⁶⁵ radiotracer	
					—	(S) (P) discussion on other work on ZnO	
					1.25×10^{-5}	(S) Zn ⁶⁵ radiotracer	
					6.52×10^{11}	(S) O ¹⁸ mass spec.	
					1.6×10^{-2}	(S) ionic conductivity	
					—	(P) Zn ⁶⁵ radiotracer	
					—		
					—		

Substance	Ref	Diffusing element	D_0 (cm ² /sec)	Q (kcal/mole)	Temperature range (°C)	Comments	Year
Zinc oxide (ZnO)	17	Zn	10^2	73	720-780	(P) Zn ⁶⁵ radiotracer	1960
	18	Zn	10	73	800-840	(S) Single crystal	1961
	19	Zn	3.0×10^{-7}	2.5	720-780	(S) Zn ⁶⁵ radiotracer	1955
Zirconium oxide (ZrO ₂)	1	O	1.0×10^4	28.1	$D = 10^{-16}$ at 400	(P) O ¹⁸ mass spec. in Zr _{0.88} Ca _{0.12} O _{1.88}	1959
	2	O	1.05×10^{-8}	29.3	700-1100	(P) from oxidation kinetics	1962
	3	O	5.5×10^{-2}	33.4 ± 3.1	400-850	(P) visual observation of oxidation of ZrO _{1.975}	1962
	4	O	—	—	700-1000	(P) estimated intrinsic diffusion in ZrO _{2.00}	1962
	5	O	—	—	700-1400	(P) ionic conductivity is postulated permitting D to be found from the Nernst-Einstein equation—see criticism in P. J. Harrop and J. N. Wanklyn, <i>J. Electrochem. Soc.</i> 110 (1963) 1285.	1965
	6	O	9.0×10^{-4}	28.7 ± 0.6	380-386	(P) from oxidation kinetics	1965
	7	O	—	—	500	(P) D estimated from diffusion in films from reaction O ¹⁷ (He, α)O ¹⁶	1965
	8	O	0.018	31.2 ± 4.3	800-1097	(S) (P) O ¹⁸ mass spec. in Zr _{0.888} Ca _{0.142} O _{1.888}	1966
	9	O	185	57.6	1100-2050	(P) Pressure drop across tube of Zr _{0.92} Ca _{0.08} O _{1.92}	1966
	10	Zr	0.035	92.5 ± 2.4	1700-2150	(P) Zr ⁹⁵ radiotracer in ZrO ₂ with 12 or 16 mole % CaO	1966
	11	O	—	—	$D > 0.22, D < 1.1 \times 10^{-8}$ at 1400	(P) ionic conductivity in tetragonal ZrO ₂	1966

Appendix

Detailed references are discussed in the Table of Values

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Letters

The Influence of Microporosity on the Ductility of Al/Al₂O₃ Alloys

Generally, the ductility of Al/Al₂O₃ (SAP) alloys decreases with increasing temperature and with decreasing deformation speed. Examples are given in figs. 1a and b. Electron micrographs [1] and density measurements [2] have indicated that this may be connected with the formation of microcracks.

This note presents first results of a systematic study on the influence of temperature on crack-formation in SAP alloys during tensile tests and creep.

Samples of 1.5 g were taken from the rupture zones of SAP specimens, of 10 mm diameter, broken in tensile and accelerated creep tests at temperatures between 20 and 620° C. The density of the samples was determined by the immersion technique; the precision was better than ± 0.002 g/cm³. SAP alloys with various fabrication histories and different oxide contents were investigated.

Typical results of density measurements of samples taken from tensile specimens of SAP with different Al₂O₃ contents (4, 7, 14 wt % Al₂O₃) are shown in fig. 1b. All alloys show the same behaviour. The density decreases slowly