

improbable that oxygen ions take up interstitial positions, which means that the oxygen vacancies required for sintering or for oxygen tracer diffusion can exist only if Schottky defects are present. (A Schottky defect will be defined as an electrically neutral group of vacancies comprising two aluminium and three oxygen vacancies).

The thermodynamic theory of vacancy equilibrium, as discussed in textbooks on the subject,¹² predicts that, in the case of alumina:

$$(N_{va})^3 (N_{vc})^2 = \exp \{-Q_s/RT\} \quad (7)$$

where N_{va} is the equilibrium fraction of vacant anion sites, N_{vc} is the equilibrium fraction of vacant cation sites, and Q_s is the molar free energy of formation of a complete Schottky defect. The equation is valid provided that both types of vacancy are free to distribute themselves randomly within the lattice.

The diffusion coefficient appropriate to a given species of ion is proportional to the vacancy concentration for that species multiplied by a Boltzmann term containing the activation energy for movement, that is:

for anions,

$$D_a = k_1 N_{va} \exp \{-Q_{ma}/RT\} \quad (8)$$

and for cations,

$$D_c = k_2 N_{vc} \exp \{-Q_{mc}/RT\} \quad (9)$$

where k_1 and k_2 are constants, and Q_{ma} and Q_{mc} are the molar activation energies for the movement of anion vacancies and cation vacancies respectively.

6.1.1 Pure Crystal

In a crystal of alumina which contains no vacancies arising because of the presence of impurities, the equation

$$2N_{va} = 3N_{vc}$$

must be satisfied, to maintain overall charge neutrality within the crystal. Combining this equation with Equation (7), one obtains

$$N_{va} = 1.18 \exp \{-Q_s/5RT\}$$

and

$$N_{vc} = 0.784 \exp \{-Q_s/5RT\}$$

Substituting these values of N_{va} and N_{vc} into Equations (8) and (9), one obtains the two intrinsic diffusion coefficients

$$D_a = 1.18 k_1 \exp \{-(Q_s/5 + Q_{ma})/RT\} \quad (10)$$

and

$$D_c = 0.784 k_2 \exp \{-(Q_s/5 + Q_{mc})/RT\} \quad (11)$$

6.1.2 Crystal Containing a Fixed Minimum Concentration of Cation Vacancies

If an alumina crystal contains only either a concentration of a cationic impurity with a valency greater than that of aluminium or a concentration of an anionic impurity with a valency less than that of oxygen (e.g. halide ions), then (neglecting the possibility of interstitial anions) there will exist within the lattice a sufficient concentration of cation vacancies to neutralize the excess positive charge caused by the presence of the impurity. If the impurity concentration is low, and the

temperature is sufficiently high that the number of vacancies arising for thermodynamic reasons greatly exceeds the number required to neutralise the impurity ions, then the intrinsic diffusion coefficients derived in the last section will be appropriate. At lower temperatures, however, or in the presence of appreciable amounts of impurity, the concentration of cation vacancies may be considered constant, being of magnitude just sufficient to neutralize the impurity ions, and different diffusion coefficients will be observed.

Equation (7) is assumed to be valid under all conditions, and may now be written

$$(N_{va})^3 (C_c)^2 = \exp \{-Q_s/RT\}$$

where C_c is the constant cation vacancy concentration.

Hence

$$N_{va} = C_c$$

and

$$N_{va} = C_c^{-1/3} \exp \{-Q_s/3RT\}$$

Substituting these values into Equations (8) and (9) results in the two extrinsic diffusion coefficients:

$$D_{a1} = k_1 C_c^{-1/3} \exp \{-(Q_s/3 + Q_{ma})/RT\} \quad (12)$$

and

$$D_{c1} = k_2 C_c \exp \{-Q_{mc}/RT\} \quad (13)$$

which will be referred to as the "extrinsic, class 1" coefficients henceforward. It has been assumed that the presence of small amounts of impurity has negligible effect on Q_{ma} and Q_{mc} .

6.1.3 Crystal Containing a Fixed Minimum Concentration of Anion Vacancies

If an alumina crystal contains monovalent or divalent cation impurities, there will always exist sufficient anion vacancies to neutralize the excess negative charge caused by such impurities. At low temperatures, or in the presence of appreciable amounts of impurity, the concentration of anionic vacancies may be considered constant.

Hence

$$N_{va} = C_a$$

where C_a is the constant anion vacancy concentration.

Modifying Equation (7) accordingly gives:

$$(C_a)^3 (N_{vc})^2 = \exp \{-Q_s/RT\}$$

Hence

$$N_{vc} = C_a^{-3/2} \exp \{-Q_s/2RT\}$$

and substitution into Equations (8) and (9) results in two further extrinsic diffusion coefficients

$$D_{a2} = k_1 C_a \exp \{-Q_{ma}/RT\} \quad (14)$$

and

$$D_{c2} = k_2 C_a^{-3/2} \exp \{-(Q_s/2 + Q_{mc})/RT\} \quad (15)$$

which will be referred to as the "extrinsic, class 2" coefficients.

6.1.4 The Six Activation Energies

From Equations (10) to (15) it is seen that there are six possible activation energies which may be observed

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