

for ionic diffusion in alumina:

$$\left. \begin{aligned} Q_a &= Q_s/5 + Q_{ma} \\ Q_c &= Q_s/5 + Q_{mc} \end{aligned} \right\} \text{Intrinsic}$$

$$\left. \begin{aligned} Q_{a1} &= Q_s/3 + Q_{ma} \\ Q_{c1} &= Q_{mc} \end{aligned} \right\} \text{Extrinsic, class 1} \\ \text{(excess cation vacancies)}$$

$$\left. \begin{aligned} Q_{a2} &= Q_{ma} \\ Q_{c2} &= Q_s/2 + Q_{mc} \end{aligned} \right\} \text{Extrinsic, class 2} \\ \text{(excess anion vacancies)}$$

6.2 Discussion

During the present work, the impurities added to alumina in various experiments were magnesia and tantalum pentoxide. The likely effect of adding each of these impurities will now be considered.

When magnesia enters the corundum lattice, either two Mg^{2+} ions will replace two Al^{3+} ions with the formation of an oxygen vacancy, or else three Mg^{2+} ions will replace two Al^{3+} ions with the third Mg^{2+} ion being accommodated in a spare octahedral lattice site. In the second instance the equilibrium vacancy concentration would not be expected to be different from that in an undoped crystal, and no difference in diffusion kinetics would be expected. The present work has shown that the introduction of magnesia into alumina markedly alters the activation energy observed in pressure-sintering, so that it would appear that the first of the above alternatives is correct and thus that a high fixed minimum concentration of anion vacancies will exist in magnesia-doped alumina. The concentration of cation vacancies must be simultaneously suppressed (to maintain the equilibrium of Equation (7)) so that the cations will be the less mobile species, and the observed activation energy ($\sim 130 \text{ kcal.mole}^{-1}$) must be the extrinsic (class 2) cation activation energy, Q_{c2} .

In alumina containing tantalum, the only likely mechanism is that three Ta^{5+} ions must replace five Al^{3+} ions, with the formation of two aluminium ion vacancies. Any other alternative would require the introduction of oxygen ions into interstitial positions, which is most unlikely because alumina consists basically of a close-packed oxygen lattice. Tantalum-doped alumina may thus be expected to contain a high fixed minimum concentration of cation vacancies and the sintering process will probably be controlled by the depressed concentration of anion vacancies. The observed activation energy for pressure-sintering in tantalum-doped alumina ($\sim 150 \text{ kcal.mole}^{-1}$) will thus be expected to be the extrinsic (class 1) anion activation energy, Q_{a1} .

Inspection of the set of equations representing the six possible diffusional activation energies in alumina indicates that

$$Q_{a1} > Q_a > Q_{a2}$$

and

$$Q_{c2} > Q_c > Q_{c1}$$

The activation energy for pressure-sintering in undoped alumina ($\sim 115 \text{ kcal.mole}^{-1}$) is lower than either of the other two observed energies (believed to be Q_{a1} and Q_{c2}), and so is likely to be one of the intrinsic activation energies Q_a or Q_c , depending on whether the anions or the cations are the less mobile.

The full set of six activation energies will now be

calculated from the values

$$Q_{c2} = 130 \pm 3$$

$$Q_{a1} = 150 \pm 5$$

$$Q_a \text{ or } Q_c = 115 \pm 4$$

The equations for the six activation energies can be arranged to give the following relationships:

$$Q_a = Q_{a1} - \frac{4}{9}(Q_{c2} - Q_c)$$

$$Q_c = Q_{c2} - \frac{9}{4}(Q_{a1} - Q_a)$$

$$Q_{ma} = \frac{5}{2}Q_a - \frac{3}{2}Q_{a1} = Q_{a1} - \frac{10}{9}(Q_{c2} - Q_c)$$

$$Q_{mc} = Q_{c2} - \frac{15}{4}(Q_{a1} - Q_a) = \frac{5}{2}Q_c - \frac{2}{3}Q_{c2}$$

$$Q_s = \frac{15}{2}(Q_{a1} - Q_a) = \frac{10}{3}(Q_{c2} - Q_c)$$

In the case where $Q_a = 115 \pm 4$, these equations give the following set of values:

$$Q_a = 115 \pm 4$$

$$Q_c = 51 \pm 23$$

$$Q_{a1} = 150 \pm 5$$

$$Q_{c1} = Q_{mc} < 36$$

$$Q_{a2} = Q_{ma} = 63 \pm 17$$

$$Q_{c2} = 130 \pm 3$$

$$Q_s = 262 \pm 68$$

Alternatively, if $Q_c = 115 \pm 4$, the following values are obtained:

$$Q_a = 143 \pm 8$$

$$Q_c = 115 \pm 4$$

$$Q_{a1} = 150 \pm 5$$

$$Q_{c1} = Q_{mc} = 105 \pm 9$$

$$Q_{a2} = Q_{ma} = 133 \pm 13$$

$$Q_{c2} = 130 \pm 3$$

$$Q_s = 50 \pm 23$$

The second of the above sets of values seems unlikely to be correct for two reasons. Firstly, it is predicted that no experimentally observable activation energy of less than about $100 \text{ kcal.mole}^{-1}$ is possible, whereas OISHI and KINGERY¹¹ observed an activation energy of roughly $60 \text{ kcal.mole}^{-1}$ for oxygen tracer diffusion at lower temperatures ($\geq 1450^\circ\text{C}$). Secondly, $Q_s \approx 50 \text{ kcal.mole}^{-1}$ seems very low for the formation energy of a Schottky defect containing five vacancies. It would mean that the formation energy per vacancy was only about half that determined for vacancies in sodium chloride.¹³

The first set of values, determined assuming that $Q_a = 115 \pm 4$, appears to be more satisfactory. $Q_s \approx 260 \text{ kcal.mole}^{-1}$, so that the formation energy per vacancy is about twice that determined for sodium chloride. In addition, the three anion activation energies (150 ± 5 , 115 ± 4 and $63 \pm 17 \text{ kcal.mole}^{-1}$) correspond closely to