



Fig. 10 (a) to (i). Electron photomicrographs of replicas of metal and different oxide surfaces; the oxide thicknesses are given in parenthesis. (a) and (b) metal immediately prior to oxidation; (c) oxidized at  $10^{-6}$  Torr,  $400^{\circ}\text{C}$  for 3 hr ( $\sim 70\text{\AA}$ ); (d) oxidized at  $5 \times 10^{-6}$  Torr,  $400^{\circ}\text{C}$  for 31 min ( $\sim 50\text{\AA}$ ); (e) oxidized at  $5 \times 10^{-6}$  Torr,  $350^{\circ}\text{C}$  for 31 min ( $\sim 60\text{\AA}$ ); (f) oxidized at  $5 \times 10^{-6}$  Torr,  $400^{\circ}\text{C}$  for 3 hr ( $900\text{\AA}$ ); (g) oxidized at  $10^{-5}$  Torr,  $400^{\circ}\text{C}$  for 3 hr ( $2200\text{\AA}$ ); (h) and (i) oxidized at  $10^{-3}$  Torr,  $400^{\circ}\text{C}$  for 3 hr ( $3100\text{\AA}$ ).

The time to formation of  $\alpha\text{Fe}_2\text{O}_3$  will depend on the temperature, oxygen pressure, and crystallographic orientation of the underlying metal. The kinetic stability of an  $\alpha\text{Fe}_2\text{O}_3$  film depends on a balance between its reduction to  $\text{Fe}_3\text{O}_4$  by diffusing iron and the oxidation of  $\text{Fe}_3\text{O}_4$  to  $\alpha\text{Fe}_2\text{O}_3$  by oxygen. Thus, at  $10^{-5}$  Torr, the higher diffusion of iron through  $\text{Fe}_3\text{O}_4$  at  $400^{\circ}\text{C}$  leads to continuous reduction of any  $\alpha\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , while at  $350^{\circ}\text{C}$  a presumably slower flux of iron allows, after some time, the formation of a continuous layer of  $\alpha\text{Fe}_2\text{O}_3$  (Fig. 6). At lower oxygen pressures only  $\text{Fe}_3\text{O}_4$  is observed. As the pressure is increased between

$10^{-5}$  and  $10^{-2}$  Torr the time to formation of  $\alpha\text{Fe}_2\text{O}_3$  is decreased. At above  $10^{-2}$  Torr the oxidation rates are essentially pressure independent, but, of course, temperature dependent. At these high pressures  $\alpha\text{Fe}_2\text{O}_3$  nucleates after a short time, accounting for the early turnover of the oxidation curves.

The similarity between the oxidation at  $10^{-2}$  Torr and 35 or 60 Torr is in disagreement with the results of Boggs *et al.* (2) who report that at  $350^{\circ}\text{C}$  the oxidation rate is strongly pressure dependent over this pressure range. Although Boggs finds the initial rate of oxidation to increase as the pressure is increased,