



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°C for 3 hr ($\sim 70\text{\AA}$); (d) oxidized at 5×10^{-6} Torr, 400°C for 31 min ($\sim 50\text{\AA}$); (e) oxidized at 5×10^{-6} Torr, 350°C for 31 min ($\sim 60\text{\AA}$); (f) oxidized at 5×10^{-6} Torr, 400°C for 3 hr (900\AA); (g) oxidized at 10^{-5} Torr, 400°C for 3 hr (2200\AA); (h) and (i) oxidized at 10^{-3} Torr, 400°C for 3 hr (3100\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 Fe_3O_4 by diffusing iron and the oxidation of Fe_3O_4 to $\alpha\text{Fe}_2\text{O}_3$ by oxygen. Thus, at 10^{-5} Torr, the higher diffusion of iron through Fe_3O_4 at 400°C leads to continuous reduction of any $\alpha\text{Fe}_2\text{O}_3$ to Fe_3O_4 , while at 350°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 Fe_3O_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°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,