Fig. 9. Parabolic plot of data from the high pressure oxidation at 350° and 400°C.

Torr and 400°C; 60 Torr and 350°C, is shown in Fig. 9. In all cases, the initial oxidation conforms to a parabolic rate law, the duration of this period becoming shorter as the pressure is increased. The slower oxidation rate at 350°C makes the initial data for this temperature more reliable than the data at 400°C, and the time scale is expanded in Fig. 7 to show more clearly the first parabolic agreement. At the end of the first stage, the oxidation proceeds through an intermediate range before entering a second parabolic region of lower rate. It was found that the data did not fit a single logarithmic plot.

*Electron diffraction.*—The oxides present after oxidation, at various pressures and times at both 350° and 400°C, were identified by reflection electron diffraction and the results are summarized in Table II. "$Fe_3O_4$" in the table represents a cubic oxide, either $Fe_3O_4$ or $\gamma Fe_2O_3$, or both. Where $\alpha Fe_2O_3$ was detected (with the exception of the oxidation at $10^{-5}$ Torr and 350°C), this layer was too thick to permit reflections from the underlying $Fe_3O_4$ layer.

It can be seen from Table II that only a cubic oxide is formed at oxygen pressures below $10^{-5}$ Torr for both 350° and 400°C, while after 3 hr of oxidation at $10^{-4}$ and above, an outer layer of $\alpha Fe_2O_3$ is formed at both temperatures. For short time oxidations at $10^{-3}$ Torr and 350° and 400°C, only a cubic oxide is found to be present. An interesting finding is that $\alpha Fe_2O_3$ (in addition to cubic oxide), is detected after 3 hr of oxidation at 350°C and $10^{-5}$ Torr oxygen, while no $\alpha Fe_2O_3$ is found after the corresponding oxidation at 400°C.

*Electron microscopy.*—Electron photomicrographs of replicas of metal and different oxide surfaces are shown in Fig. 10 (a to i); the average thickness of the oxide is given in parenthesis.

Figures 10 (a) and (b) show the nature of the metal surface immediately prior to oxidation, *i.e.*, after the specimen had been hydrogen reduced at 600°C, and then held at 400°C for a few hours while the background pressure was reduced to ~3 × $10^{-8}$ Torr, it was quenched to room temperature. A smooth area of

Table II. Summary of electron diffraction analysis

| Pressure and time of oxidation | Phases observed | |
|---|---|---|
| | 350°C | 400°C |
| $10^{-6}$ Torr, 3 hr | "$Fe_3O_4$" | "$Fe_3O_4$" |
| 5 × $10^{-6}$ Torr, 31 min | "$Fe_3O_4$" | "$Fe_3O_4$" |
| 5 × $10^{-6}$ Torr, 3 hr | "$Fe_3O_4$" | "$Fe_3O_4$" |
| $10^{-5}$ Torr, 3 hr | $\alpha Fe_2O_3$ + "$Fe_3O_4$" | "$Fe_3O_4$" |
| $10^{-4}$ Torr, 3 hr | $\alpha Fe_2O_3$ | $\alpha Fe_2O_3$ |
| $10^{-3}$ Torr, 2¼ min | — | "$Fe_3O_4$" |
| $10^{-3}$ Torr, 5 min | "$Fe_3O_4$" | — |
| $10^{-2}$ Torr, 3 hr | $\alpha Fe_2O_3$ | $\alpha Fe_2O_3$ |
| 35 Torr, 3 hr | — | $\alpha Fe_2O_3$ |
| 60 Torr, 3 hr | $\alpha Fe_2O_3$ | — |

the surface is illustrated in Fig. 10 (a), compared with one of the roughest areas in Fig. 10 (b). The observed thermal facetting is similar to that found by Sewell *et al.* (8) on iron surfaces hydrogen annealed at 800°C.

Oxide nuclei present after the oxidation at $10^{-6}$ Torr for 3 hr at 400°C are observed in Fig. 10 (c), and the growth of these nuclei appears to be completely random. Replicas of specimens oxidized for 31 min at 5 × $10^{-6}$ Torr at both 400° and 350°C are shown in Fig. 10 (d) and (e); this was after the induction period when a noticeable weight increase could be observed with the Cahn microbalance (see Fig. 6). The influence of substrate structure on the oxidation is shown in Fig. 10 (e) where the outer texture of the oxide on the two grains is different. Large oxide nuclei are seen in Fig. 10 (d), and triangular shaped nuclei ~200Å in height are present near the grain boundary.

Surfaces of thicker oxides are shown in Fig. 10 (f to i). Figures 10 (f) and (g) show the variation of the degree of roughness of the oxide outer surface with the underlying crystal plane of the metal. The height of oxide facets on the upper left grain in Fig. 10 (f) range up to 300-400Å. The ridged structure of the $\alpha Fe_2O_3$ surface, found after oxidation for 3 hr at $10^{-3}$ Torr and 400°C [Fig. 10 (h) and (i)], is similar to that observed by Boggs *et al.* (2, 5) for oxidations under similar conditions.

## Discussion

The marked effect of oxygen pressure on the oxidation of iron at 350° and 400°C is clearly shown in Fig. 3, 4, and 5. As the pressure is increased from $10^{-6}$ to 60 Torr the initial rate of oxidation is increased. This period of high oxidation rate is, in general, followed by one of much lower oxidation rate.

The proposed mechanism to explain the different initial rates is as follows; initially $Fe_3O_4$ forms on the surface and the oxide layer grows as iron ions diffuse outward through cation vacancies in the oxide. The cation vacancies are formed at the outer surface of the oxide when oxygen is incorporated into the lattice. The concentration of vacancies and hence the concentration of iron ions diffusing to the $O_2/Fe_3O_4$ interface depends on the availability of oxygen at the outer surface. Thus, as the oxygen pressure is increased, the concentration of vacancies is increased and so the flux of iron ions is increased leading to an increased oxidation rate. This assumes that in the low pressure region the incorporation of oxygen into the lattice to form oxygen ions is pressure dependent.

The lowering of the oxidation rate may be due to either the formation of a continuous layer of $\alpha Fe_2O_3$, over the $Fe_3O_4$, or loss of contact between the oxide and the metal. Taper sections of these thin oxides did not yield conclusive evidence of oxide separation from the metal. Moreover, the electron diffraction data, summarized in Table II, supports the argument that the formation of a continuous hexagonal oxide layer reduces the oxidation rate. At pressures below $10^{-5}$ Torr, where no marked reduction in oxidation rate was observed, only cubic oxide was found to be present after 3 hr of oxidation (Table II). Also specimens which were removed before the decrease in rapid rate observed at higher pressures showed only "$Fe_3O_4$" by electron diffraction. In all cases where a marked decrease in oxidation rate had already occurred, electron diffraction showed only an outer layer of $\alpha Fe_2O_3$. These observations would indicate that in the rapid rate region, diffusion, probably of cations, through magnetite is the rate controlling process, while in the low rate region, diffusion, probably of oxygen ions, through $\alpha Fe_2O_3$ is the controlling process. This was partially confirmed by an experiment in which iron had been oxidized into the $\alpha Fe_2O_3$ region and then annealed, in vacuo, to convert all the oxide to $Fe_3O_4$ (9). On readmitting oxygen a rapid "magnetite-type" rate was initially observed, with again a later falling off in rate characteristic of control by $\alpha Fe_2O_3$.