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The Effect of Oxygen Pressure on the Oxidation of Iron at 350° and 400°C

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ABSTRACT

A kinetic study has been made of the effect of oxygen pressure (10^{-6} to 60 Torr) on the oxidation of Ferrovac E iron at 350° and 400°C. The initial rate of oxidation is found to increase with increasing oxygen pressure, while after 180 min the weight gain is independent of pressure (for pressures greater than 10^{-5} Torr). Initially Fe_3O_4 forms on the surface, and once this is covered by a continuous layer of $\alpha\text{Fe}_2\text{O}_3$ the oxidation rate is markedly reduced. The lower the oxygen pressure, the longer the time before $\alpha\text{Fe}_2\text{O}_3$ starts to nucleate, and no $\alpha\text{Fe}_2\text{O}_3$ is observed after oxidation at very low pressures (5×10^{-6} and 1×10^{-6} Torr). An induction period is observed for the oxidation at 5×10^{-6} Torr.

The literature contains a great number of papers on the oxidation of iron [e.g., (1)], but few studies have considered the effect of oxygen pressure on the oxidation kinetics. Recently Boggs and co-workers (2) have reported a study of the oxidation of zone-refined iron in the temperature range 220°-450°C, using pressures of 10^{-2} to 100 Torr. These authors find that for oxidation up to 350°C the oxide film thickness, after a given oxidation time, increases as the oxygen pressure is lowered. At 450°C, the oxidation appears to be independent of oxygen pressure. The present work examines more closely the low pressure oxidation of iron at 350° and 400°C, also extending the pressure range down to 10^{-6} Torr. The weight gains were measured using a vacuum microbalance (except for the very low pressure oxidation). The oxide phases present were identified by reflection electron diffraction and some oxide surfaces were replicated for examination by electron microscopy.

Experimental

Apparatus.—The oxidation apparatus is shown schematically in Fig. 1. A Cahn R. G. Electrobalance was mounted in a stainless steel chamber of an all metal U.H.V. system. After an overnight bake at 100°C (the maximum permissible temperature for the balance), pressures of less than 5×10^{-8} Torr were obtained, the outgassing rate of molecules from the walls, balance, etc. being $\sim 8 \times 10^{-8}$ Torr·l·sec⁻¹. The background gas as determined by a partial pressure analyzer (an A.E.I., M.S. 10 spectrometer) was mainly water vapor. To improve the vacuum capabilities of the system, all the original soldered connections in the balance were replaced by spot-welded platinum joints.

The electrobalance was used either on the 0.4 mg or 1.0 mg Recorder Range (weight change corresponding

to recorder full scale deflection), with a total noise level of about 3 μg .

Low oxygen pressures were measured using Varian ionization gauges; a U.H.V. gauge for pressures below 10^{-5} Torr and a milli-Torr gauge in the range 10^{-5} to 10^{-1} Torr. These pressures were controlled by a Granville-Phillips Automatic Pressure Controller, using the ion gauges as transducers. Higher oxygen pressures were measured using an Edwards capsule dial gauge, which was installed in the gas-handling section of the apparatus.

Materials purity.—Ferrovac E¹ iron, analyzed to contain the following impurity concentrations (in ppm): Mn, 24; Si, 10; Cr, 5; O₂, 200; Ni, 11; Al, 26; Cu, 10; Co, 5; and C, 70 was used. In some of the experiments 99.997% iron (zone-refined material from the Battelle Memorial Institute²) was also used.

¹ Ferrovac E is the trade name of a high purity iron produced by Vacuum Metals Corporation, Division of Crucible Steel Company of America.

² This material was supplied through the American Iron and Steel Institute.

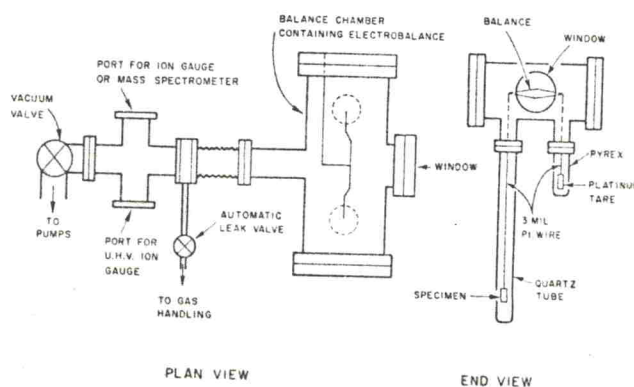


Fig. 1. Diagram of high vacuum microbalance apparatus

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