148. *The Oxidation of Calcium in Dry Oxygen.*

By S. J. GREGG and W. B. JEPSON.

The oxidation of calcium in dry oxygen has been studied in the range 425—650° c. Below 475° the oxidation is negligibly slow, showing that the oxide film has protective properties, but at 500° and above, the rate is readily measurable. The oxide product is green and contains a relatively large concentration (0·4%) of free calcium. The curves of weight gain against time are characterised by an increasing rate up to a maximum followed by a decreasing rate; at 550° and above, a " breakaway " reaction occurs and a yellow oxide is formed. A linear rate of oxidation, hitherto assumed characteristic of the oxidation of calcium, was found only at one temperature, 500°.

The oxidation mechanism appears to be far more complicated than has hitherto been assumed.

IT is frequently stated [1] that the alkaline-earth metals, with the exception of beryllium, should oxidise at a constant or " linear " rate in oxygen; it is argued on the basis of

[1] T. B. Grimley in " Chemistry of the Solid State," Ed. Garner, Butterworths Scientific Publications, London, 1955; Kubaschewski and Hopkins, " Oxidation of Metals and Alloys," Butterworths Scientific Publications, London, 1953; Mantell and Hardy, " Calcium, Metallurgy, and Technology," Reinhold Publishing Corp., New York, 1945.

Pilling and Bedworth's rule [2] that, since the oxide occupies a smaller volume than that of the metal which is consumed in producing it, the former should be porous so that oxygen can diffuse up to the metal surface, which is continuously exposed. In particular, calcium has come to be regarded as a classical example of linear oxidation; yet the only relevant published work, apart from some runs of limited duration by Cubicciotti,[3] appears to be the original study in 1923 by Pilling and Bedworth.[2] These workers found that the metal oxidised at a constant rate at 300°, 400°, and 500°, and the porous nature of the calcium oxide was inferred from the relative volumes of oxide and of metal. Magnesium, the only other alkaline-earth metal to have been investigated,[4,5] is oxidised at a linear rate at temperatures above about 450°.

A comparison of the published results for the kinetics of oxidation of the two metals reveals two important differences: (*a*) the energy of activation for oxidation is very much less for calcium than for magnesium (10 as compared with 50 kcal. mole^{-1}) and (*b*) calcium oxidises at a constant rate from the start of the run, whereas with magnesium there is an induction period of many hours.

Accordingly, the kinetics of the oxidation of calcium in dry oxygen have been re-investigated, especially since the metal used in the original study was inevitably rather impure. The present work, which covers the range 425—650°, shows that the oxidation of calcium is much more complicated than has hitherto been assumed; and only at one temperature, *viz.* 500°, has a linear rate of oxidation been found, and even then it persisted for only 30 hr.

EXPERIMENTAL

The course of the oxidation was followed by the gravimetric determination of the weight gained by the sample on a thermal balance. The sample was suspended in the reaction
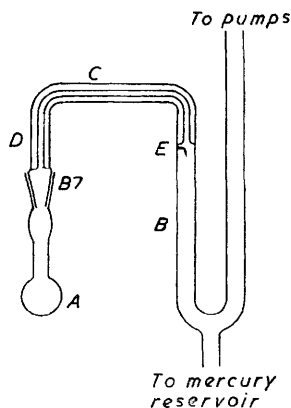

FIG. 1. *Apparatus for measuring the concentration of free calcium in calcium oxide.*

chamber by means of a wire of stainless steel passing through a hole (1/16 in. diam.) drilled in the specimen, and attached at its upper end to a platinum wire hooked to the underside of the balance pan. The arrangement was the same as that described earlier,[5] except that the oxygen was additionally dried by passing it over " Linde " molecular sieves.[6]

The calcium metal (Domal Magnesium Co.) was in the form of extruded stick (1 in. diam.) (Analysis, upper limits: Mg, 0·5; N, 0·025; Al, 0·010; Fe, 0·005; Mn, 0·004; Ni + Cu + Cr, 0·005; Cd, 0·00002; B, 0·00002; Li, 0·001; Na + K, 0·001%). For each oxidation run a slice

[2] Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529.
[3] Cubicciotti, *J. Amer. Chem. Soc.*, 1952, **74**, 557.
[4] Gulbransen, *Trans. Electrochem. Soc.*, 1945, **87**, 589; Leontis and Rhines, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, **166**, 265.
[5] Gregg and Jepson, *J. Inst. Metals*, 1958—1959, **87**, 187.
[6] Addison, Iberson, and Raynor, *Chem. and Ind.*, 1958, 96.

was sawn from the stick and filed to a thickness of about 5 mm. The choice of suitable surface preparation proved troublesome; abrasion with emery (grade 0) led to pick-up of abrasive, and the method finally adopted was filing on a " second-cut " file. After the final filing, the sample was rinsed with carbon tetrachloride (the metal could not be degreased in benzene vapour because of the ready reaction of the metal with water vapour in the air) and placed immediately in the reaction chamber through which a stream of dry oxygen was passing.

The oxide was found to contain some free calcium, which was determined by estimation of the hydrogen evolved on treatment with water. The solid was placed in the bulb A (Fig. 1) and outgassed. Bulb A was immersed in liquid oxygen and a known volume (0·5 ml.) of water distilled on to the solid. The mercury level was then raised into tube B, and the ice allowed to melt and react. When reaction was complete, the bulb A, together with the part of the capillary tube C up to D, was immersed in solid carbon dioxide–acetone to freeze out water, and the pressure read after raising the mercury to the standard mark E. From the calibrated volume of the apparatus it was possible to calculate the volume of hydrogen evolved and there-fore the free calcium content of the sample. Corrections for thermomolecular flow were negligible and the reproducibility was $\pm 1\%$.

<center>RESULTS</center>

At room temperature there is no apparent reaction between calcium and dry oxygen, and samples appeared to retain their lustre indefinitely; the oxide layer probably reaches a limiting thickness of several hundred Ångström units.

At 425° the mean weight gain of samples exposed for 70 hr. was only 1 mg., and at 475° was still quite small (3 mg. in 50 hr.); but at 500° and above, the oxidation became sufficiently fast to allow the plotting of detailed curves of weight gain against time.

The curve at 500° (Fig. 2) consists of three distinct branches, OA, AB, and BC, over which the rate of oxidation respectively increases, is constant, and decreases, with time. The mean of six runs gives the slope of AB, *i.e.* the rate of " linear oxidation," as $0·40 \pm 0·06$ mg. cm.$^{-2}$ hr.$^{-1}$. In the early stages the curves for 525° and 550° (Fig. 2) are similar to that for 500°, the rate increasing with rise in temperature in the usual way; but the linear branch AB is now absent, and at 550° there is an additional branch CD in which the rate once more increases with time.

At 575°, in three runs out of four, the curve was as shown in Fig. 3, in which the duration of branches OA and AB has become very short, and the predominant feature is branch BC where the rate continuously falls and eventually reaches a very low value (0·04 mg. cm.$^{-2}$ hr.$^{-1}$ during the last 24 hr.). In the fourth run at 575° (Fig. 2) the rate was much more rapid and showed a branch CD corresponding to that at 550°.

At 600° (Fig. 3) the graph on the whole conformed to the " lower " type of graph for 575° with an additional branch CD; and as far as the readings go, the 650° curve seems to conform broadly to the same pattern as at 600° and 575°.

When the sample was cooled at the end of the run, some cracks appeared in the oxide, and with thick oxide layers spalling occurred. The edges of the metal were usually rounded and if the oxide layer was removed by abrasion it could be seen that the metal had not been attacked evenly.

The most striking feature of the oxide layer was its colour, which varied from a dark green at 500° to a pale greenish-blue at 650°. The green oxide reacted rapidly with liquid water and more slowly with the moist air of the room to form a white product. The coloration is clearly caused by excess of calcium which, estimated by the method already described, amounted to 4·4 and 2·4 mg. g.$^{-1}$ of oxide formed at 525° and 550°, respectively.

The density of the scale formed at 525°, taken as typical, was measured by immersion in mercury,[7] and its value, 2·23 g. cm.$^{-3}$, is significantly less than that calculated from the X-ray lattice spacing,[8] *viz.* 3·37 g. cm.$^{-3}$; the calculated porosity is thus 34%. That an appreciable proportion of the pore volume is open to the exterior and thus accessible to ambient gas, is proved by the measurements of specific surface by krypton sorption,[9] which gave 6·0 and 5·4 m.^{2} g.$^{-1}$ for oxides prepared respectively at 525° and 575° (Fig. 3).

[7] Jepson, *J. Sci. Instr.*, 1959, **36**, 319.
[8] Wyckoff, " Crystal Structures," Interscience Publishers Inc., New York.
[9] Aylmore, Gregg, and Jepson, in the press.

Visual examination of samples oxidised at 500° to a weight gain corresponding to a point on AB (Fig. 2) showed a smooth surface consisting of a network of green and dark grey patches. Samples oxidised at 525° to a point along OA had the same appearance. Since the dark green oxide layer could be scratched away to reveal the bright metal below, it probably represents the tarnish layer only.

Some samples oxidised at 550° and above, when sectioned, revealed a bright yellow oxide sandwiched between the metal and green oxide; the formation of this yellow oxide was generally associated with the branch CD on the oxidation curve. Also, at 550° and upwards, particularly at 600°, some white oxide was seen in the form of isolated clusters standing out,
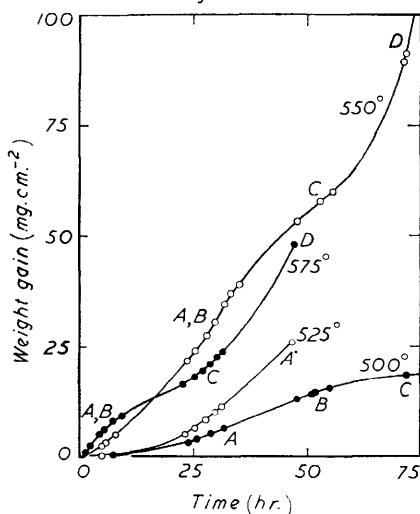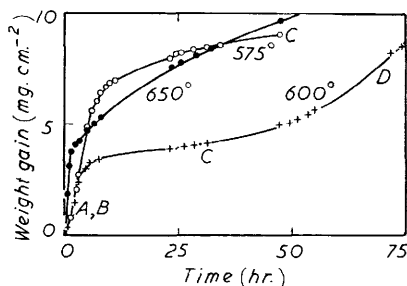
Fig. 2. *Oxidation of calcium at* 500—575°.

Fig. 3. *Oxidation of calcium at 575—650°.*

usually from the dark grey areas, to a height of about 0·5 mm. and with a base about the same size; their removal revealed a pit in the metal with rounded sides and containing partially detached metal, consistent in appearance with some evaporation having taken place.

DISCUSSION

These results cannot be fitted to any one of the simple rate curves used to describe the oxidation of other metals, and they are so complex as to preclude any calculations of the energy of activation of the reaction. An unusual feature is the presence of free metal in the oxide. The solubility of calcium in calcium oxide does not appear to have been measured but is almost certainly less than the concentration found in the present work; in any case the solubility of calcium in calcium oxide would be expected to increase with increasing temperature, whereas the concentration in the scale decreases.

The ready oxidation which occurs at 500° and above can only be due to a failure or cracking of the protective, or tarnish, layer which has thickened during the early stages of the run. Some evidence for this is provided by the kinetic measurements of Cubicciotti [3] for the early stages, where the rate first decreased corresponding to the formation of a tarnish layer and then increased in a manner typical of a breakaway reaction.[5,10] This breakaway occurred at a lower temperature, *viz.* 425°, as compared with 500° in the present study, perhaps because the metal was prepared by emery abrasion—a procedure which in the analogous case of magnesium is known to promote breakaway.[5]

From the patchy appearance of the oxidised sample, it is clear that the failure of the tarnish film occurs at a number of isolated points, and the branch OA corresponds to the

[10] Cathcart, Campbell, and Smith, *J. Electrochem. Soc.*, 1958, **105**, 442.

gradual extension of these areas laterally over the surface, and the formation of new patches.   Even along the linear branch AB of the 500° curve, the failure has not extended over the whole of the sample surface, for at the end of the branch (point B) some of the tarnish film can still be seen.   The branch AB thus probably represents merely a super-position of the accelerating branch OA and the decreasing branch BC, and therefore has no inherent physical significance; this is borne out by the curves for the higher temper-atures where the linear branch is absent.   With magnesium, on the other hand,[5] the rate continues to increase until the oxide scale has extended laterally to cover the whole of the metal surface; the metal then oxidises at a constant rate.

The specific surface data show that the oxide scale is porous to krypton, and therefore by implication to oxygen, so that the latter can pass freely through the scale.   The concept of a thin, continuous layer of oxide (barrier film) [11] which adheres to the metal and through which calcium ions must diffuse before reacting with oxygen (diffusion in calcium oxide is exclusively cationic [12]) is not completely satisfactory since it cannot account for what is perhaps the most striking feature of the present results, the relatively large content of free calcium in the oxide scale.   It might be thought that the calcium could enter the scale by vapour-phase diffusion through fine cracks in the barrier film; but preliminary experi-ments at 300° in moist oxygen (containing 0·31% by weight of water) gave a scale contain-ing 17 mg. of calcium per g., a value which is considerably greater than that of the present work, yet the extrapolated vapour pressure [13] of calcium at this temperature (10^{-8} mm.) is much too small to yield an appreciable rate of evaporation.

It is clear that much more experimental work, both on the kinetics of oxidation and on the structure and composition of the scale, is necessary before a satisfactory mechanism of oxidation can be formulated.

Finally it remains to comment on the increase in rate along the last branch, CD, at 550° and above; this could be explained by an actual detachment of the oxide layer from the metal whereby the surface of the metal is exposed over relatively large areas.   Reaction would then occur in the vapour phase (though still beneath a blanket of oxide) and the yellow colour of the oxide could result from a restricted supply of oxygen.   A simple calculation using the known saturated vapour pressure of calcium [13] gives the rate of evaporation as 93 mg. cm.$^{-2}$ hr.$^{-1}$, which is equivalent to an oxidation rate of 37 mg. cm.$^{-2}$ hr.$^{-1}$; this is in excess of that observed, so that the supply of calcium is not a rate-determining step.

Conclusion.—The oxidation of calcium in dry oxygen does not, as was earlier supposed, follow a linear rate law except for a limited period of time at 500°.   The effect of temper-ature on the shape and position of the oxidation curves is complicated and the rate of oxidation does not increase with increasing temperature in the normal way.   The oxide scale is shown to contain free calcium, the amount of which decreases with increasing temperature of oxidation.

WASHINGTON SINGER LABORATORIES,
          PRINCE OF WALES ROAD, EXETER, DEVON.   [*Received, July 6th*, 1959.]

[11] Dunn and Wilkins, Contribution to Review of Oxidation and Scaling, D.S.I.R., 1935; Tronstad and Hoverstad, *Trans. Faraday Soc.*, 1934, **30**, 1114; Evans, " Metallic Corrosion, Passivity and Pro-tection," Arnold, London, 1946, p. 134.
[12] Linder and Akerstrom, *Acta Chem. Scand.*, 1952, **6**, 468.
[13] Pilling, *Phys. Rev.*, 1921, **18**, 366; Douglas, *Proc. Phys. Soc.*, 1954, **67**, B, 783.