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Discussion

R. C. COREY.⁵ Since its inception, the work at Purdue University on the corrosion of metals and alloys by high-temperature steam has been followed with considerable interest. No other laboratory studies of this important subject, either here or abroad, have been as comprehensive as the present series, and the authors are to be commended for the excellent data that they have obtained.

It is gratifying to note that the authors conducted their tests for 500 hr. All too frequently one finds data in the literature on the rate of corrosion, intended for general use, but which are based upon extremely short test periods. In a recent article,⁶ it was shown that with everything else essentially equal, the corrosion rate varies markedly with the duration of test. It may be argued that regardless of the test period, the relative rate of corrosion of different metals and alloys studied simultaneously under the same conditions will remain the same. Considering, however, that the rate of corrosion of most metals and alloys is greatest initially (except in the unusual case where corrosion increases linearly with time), it is possible that an otherwise satisfactory metal will appear to be unfavorable if the test period is too short.

It is not clear why the authors changed the unit for expressing corrosion from that of penetration, as used in previous reports, to percentage loss of original weight. In order that data of this kind may be compared with those of other investigators, the rate of corrosion is expressed more rationally in terms of the amount of metal lost per unit area in unit time, or as the depth of penetra-

⁵ Research and Development Department, Combustion Engineering Company, New York, N. Y.

⁶ "Corrosion by Hot Gases," by R. C. Corey, *Combustion*, vol. 15, 1943, pp. 34-39.

tion in unit time. The literature on high-temperature corrosion studies is confusing and difficult to correlate as the result of the use of units which cannot be reduced to a common basis.

If the authors have the data available, it might be of interest to plot the loss of metal against time and thereby determine the specific type of scaling that occurs. Such information would be valuable for interpreting the corrosion mechanism of the various alloys that were studied. Recent papers^{7,8} on this subject indicate that scaling may occur linearly, parabolically, or logarithmically with time, depending upon the temperature, conditions, and the metal under study. Thus, the sharp break at a certain temperature noted by the authors for certain of the alloys studied may be the result of recrystallization⁹ of the oxide above a certain temperature, which may lead to logarithmic scaling, a factor determined only by the type of plot just mentioned.

The chemical analyses of the scales are of great interest as such data are the first step toward developing a mechanism for corrosion. It is not apparent why the Si increased and the Mo and Cr decreased in amount in the middle oxide layer with increasing chromium content of the alloy at both 1500 F and 1700 F. It is suggested that if possible the authors should have an X-ray diffraction study made of these scales to determine how these elements are distributed, that is, as solid solutions, stoichiometric compounds, or spinels. Such information would afford them valuable supplementary data.

The data of Table 1 of the paper show that Cb-stabilized 18-8 steel loses about 12 per cent of its weight between 1728 F and 1765 F. It might be of interest to study plain 18-8 steel at the same temperature for 500 hr in order to determine if the Cb decreases the corrosion resistance of this alloy.

With reference to the remarks of the authors concerning diffusion of oxygen through the oxide, the following is offered as an alternate explanation: Assuming for the moment that the gas phase diffuses through the oxide to meet and react with metal ions, it is probable that steam and not oxygen, as the authors state, would be involved as it is not until oxidation takes place that oxygen is released, and then it probably combines immediately as an oxide. On the other hand, it is doubtful that a steam molecule could diffuse interstitially through a compact oxide lattice because of the large size of the gas molecule with respect to the interatomic spacing of the lattice. However, if the oxide was porous or fissured the gas could reach the metal ions readily. Also there are cases where a gas like oxygen may be taken into solid solution in an oxide which is deficient in oxygen atoms, i.e., an oxide that is not of stoichiometric composition. The oxide FeO and certain of the spinel type of oxides like FeO-Fe₂O₃, FeO-Al₂O₃, and FeO-Cr₂O₃ are capable of taking a small amount of oxygen into solid solution, but the quantities involved are too small to be significant, thus the rate of scaling probably depends primarily upon the rate at which the iron ions reach the oxide-gas interface.

W. TRINKS.¹⁰ On account of being a furnace engineer, the writer's interest in high temperature begins where the power engineer quits. In furnace work we have learned that water vapor scales iron and steel more rapidly than air does. The writer attributes this phenomenon to dissociation. The professors of thermodynamics tell us that dissociation at the temperature

⁷ "The Transition State Theory of the Formation of Thin Oxide Films on Metals," by E. A. Gulbransen, preprint 83-4, 1943, The Electrochemical Society.

⁸ "Laws Governing the Growth of Films on Metals," by U. R. Evans, preprint 83-10, 1943, The Electrochemical Society.

⁹ "Oxidation of Metals and the Formation of Protective Films," by N. F. Mott, *Nature*, vol. 145, 1940, pp. 996-1000.

¹⁰ Professor of Mechanical Engineering (Emeritus), Carnegie Institute of Technology, Pittsburgh, Pa.

in question is negligible. They are right, if we limit ourselves to permanent dissociation. They are wrong if we consider instantaneous dissociation. Collision of the molecules causes some dissociation at all temperatures. Ordinarily, the atoms reassociate immediately without leaving any trace of their dissociation; but if a material is present for which oxygen has a greater affinity than it has for hydrogen, it goes after that material, because the oxygen is atomic (in the nascent state) and leaves the unwanted hydrogen to look out for itself.

Water vapor is triatomic and, for that reason is dissociated or cracked more easily than the diatomic oxygen molecule.

The variations in the composition of the scale are what we should expect. Iron oxide has a vapor pressure. Every steel-furnace engineer knows that fact. In a superheater tube the heat comes from the outside. The scale next to the tube is hotter than the scale next to the steam. For that reason the iron oxide gets away from the tube toward the cooler steam. It is a migration which some people call diffusion.

As regards cracking of the scale, we know from the sheet industry that a thin scale adheres and that a thick scale cracks. If we could chromium-plate the inside of the tubes and have the plating stick, then we should have a thin retentive greenish chromium scale which would not crack.

AUTHORS' CLOSURE

The authors are indebted to Messrs. Corey and Trinks for

their written discussions and for their excellent comments concerning the mechanism of scale formation.

Mr. Corey has suggested that the data on corrosion be presented in terms of penetration rather than per cent loss in weight. In their earlier reports (1, 2, 3),¹¹ the authors presented the data in terms of inches of penetration. However, the high-temperature tests reported in this paper produced very thick layers of scale on some of the specimens which were originally 6 in. long and 1/2 in. in diam. This resulted not only in a significant reduction in the diameter of the parent metal during the course of the tests but also produced a shortening of the specimens and a tapering of the parent metal at the ends of the specimens.

Mr. Corey has made some pertinent comments on the effect of time upon the usefulness of corrosion data. The tests which are reported in Table 1 are for 500 hr, and data for shorter periods of time are not available. However, the authors have published data showing the effect of time upon the corrosion of various steels for periods up to 2000 hr at a steam temperature of 1100 F (2).

In conclusion, the authors wish to thank all of those who presented discussions for their interest, comments, and constructive suggestions.

¹¹ Numbers in parentheses refer to Bibliography at end of original paper.