Discussion

E. N. Skinner,[4] Jr., and J. T. Eash.[4] Through their extensive study of the corrosion of metals and alloys by high-temperature steam, the authors have obtained data undoubtedly of considerable practical worth to those concerned with power-plant design, as well as valuable information with respect to the little understood question of high-temperature corrosion.

With regard to their results on the three samples of malleable nickel, it may be useful to state here that experience has made it apparent that nickel which is used at temperatures between 750 and 1400 F should be low in carbon. In this temperature range, it has been found that, regardless of the atmosphere, nickel containing carbon may become embrittled with time due to an intergranular precipitation of graphite. In any application involving the use of wrought nickel at these temperatures, the commercial carbon-free nickel which contains a maximum of 0.02 per cent carbon should be specified.

The results of some laboratory tests that we have conducted on the oxidation of nickel in tap-water steam suggest that the presence of minor quantities of residual elements associated with the production of malleable nickel for widely diverse fields of application has a marked effect on its oxidation resistance in steam. Carbon is particularly harmful in promoting rapid intergranular corrosion such as found by the authors.

Our tests indicate, in addition, that a nickel which does not contain small amounts of residual elements has a low rate of oxidation in steam. Such a product is found in electroplated nickel. Specimens of this type of nickel exposed at 1100 F for 600 hr oxidized at approximately one seventh the rate of a wrought nickel containing about 0.08 per cent carbon; furthermore, this electroplated nickel was completely free from the intergranular attack noted by the authors.

The practical value of electro-nickel in steam applications is a matter which designers of equipment may wish to consider.

H. L. Solberg,[5] G. A. Hawkins,[6] and J. T. Agnew.[7] Through the courtesy of The Detroit Edison Company and the authors the Engineering Experiment Station of Purdue University has been provided with copies of progress reports covering the extensive high-temperature corrosion studies which have been carried on by the company over the past several years. The writers have greatly appreciated the fine spirit of co-operation which has made this information available to us, and wish to congratulate the authors on the excellent job they have done in condensing the contents of these numerous and extensive reports into this paper.

The writers reported[8] in an earlier paper upon certain tests which were carried on with steam at 1200 F, and with the specimens subjected to sharp fluctuations in temperature, in order to determine the resistance of the scales formed on the various alloy steels to spalling under fluctuating-temperature conditions. It was found that, in general, as the chromium content was increased to 4–6 per cent, the scale which was formed became more dense and brittle. The addition of either silicon or aluminum in more than normal amounts tended to aggravate the tendency of the scales to spall under temperature fluctuations. These results are confirmed by The Detroit Edison Company tests. Steels containing more than 7 per cent of chromium formed a tightly adherent thin scale which showed no tendency to spall under the test conditions.

Tests with specimens of various shapes indicated that the spalling action of low-chrome steels was severe on the outside of bars and on flat surfaces but was negligible on the inside surfaces of a tube section of 1-in-ID tubing. It is probable that the scale which is formed on a concave surface is in compression and, consequently, resists spalling caused by temperature fluctuation and furnishes better protection than does the scale which is formed on the outside of bar stock. It is, therefore, possible that the long-time corrosion rates determined in The Detroit Edison tests on $^1/_2$-in. round bars are higher than those which would be encountered in superheater tubing in which the shape of the tube might tend to hold the scale in place.

The Detroit Edison tests show a marked reduction in the corrosion rate of carbon-moly steel, as compared with that of low-carbon steel. The results obtained at Purdue University with a fairly large number of specimens of each type of steel do not indicate a very significant difference in the corrosion rates of these steels. Both cast and rolled specimens were tested at temperatures of 1100 F and higher, under conditions of steady as well as fluctuating temperatures for periods of time which were shorter than those employed by The Detroit Edison Company. Table 5 of this discussion has been compiled from previously published data[8] and summarizes some of these results. All specimens were given the heat-treatment recommended by the producers of the steels used in these tests.

TABLE 4 COMPARISON OF CORROSION OF LOW-CARBON AND CARBON-MOLY STEELS

Length of test, hr	Reference	Temperature, deg F	Low carbon: No. of spedimens	Low carbon: Average penetration, in.	Carbon-moly: No. of specimens	Carbon-moly: Average penetration, in.	Ratio of penetration, carbon-moly to low carbon
500	Table 9[a]	1100	16	0.001317	16	0.00122	0.926
570	Table 10[a]	1200	2	0.0118	2	0.01252	1.06
570	Table 10[a]	1200	2	0.01139	2	0.01049	0.92
1300[b]	Table 12[a]	1200	4	0.0156	4	0.0152	0.975

[a] From reference (8) of this discussion.
[b] Constant temperature for 500 hr followed by intermittent operation for 800 hr.

F. N. Speller.[9] The experimental data from the 5-year period of testing by The Detroit Edison Company is a welcome addition to our limited knowledge of the corrosion of metals in steam at 925 and 1100 F. It would be useful to know whether the corrosion found is uniform or localized in the form of pitting. Considering the relative cost, the favorable corrosion rate of 0.50 molybdenum plus 1 per cent chromium steels is encouraging. In 1933, we published data showing the favorable physical and corrosion-resistant properties of 3 per cent Cr compared with 5 per cent Cr steels. For oil-cracking tubes at 1100 F, the 2-$^1/_4$ per cent Cr, 1 per cent molybdenum steel has since then shown

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[8] "Corrosion of Unstressed Steel Specimens and Various Alloys by High-Temperature Steam," by H. L. Solberg, G. A. Hawkins, and A. A. Potter, Trans. A.S.M.E., vol. 64, 1942, pp. 303–316.
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very promising results in practice. In fact, experience in high-temperature oil-cracking around 1100 F affords experience on the relative strength of these steels over long periods at elevated temperatures that should be quite useful in the design of high-pressure steam boilers.

Authors' Closure

Respecting the comments of Messrs. Skinner and Eash, we are glad to have an explanation of the intergranular deterioration that was observed in the three samples of malleable nickel. The explanation that this was due to intergranular precipitation of graphite agrees with the results of our tests in that the lesser amount of intergranular deterioration was found in the sample which had the lowest carbon content.

It is interesting also to learn that the corrosion rate of electroplated nickel exposed to 1100 F steam for 600 hr was approximately one seventh that of wrought nickel containing 0.08 per cent carbon. The weight loss for electroplated nickel, as calculated from the factor given by Skinner and Eash in their 600-hr test, i.e., one seventh the value for wrought nickel, would indicate that, although the corrosion rate appeared to compare favorably with that found for the chromium and chromium-nickel stainless steels, on the basis of a 7461-hr test, the corrosion rate of electroplated nickel might not be found to compare so favorably with that for these stainless steels.

The comment of Messrs. Solberg, Hawkins, and Agnew that scale on a concave surface is more protective than on a convex surface and, consequently, the results given in the paper may be somewhat high, as compared with corrosion rates that would be encountered in the inner surface of tubes in service, is probably true. With respect to the relative rates of corrosion instead of the actual rates under service conditions of the 46 different materials, it is felt that, since each material was tested by the same type of specimen, i.e., $^1/_2$-in-diam bar specimens, the comparative tendency of these materials to corrode and scale has been established. To interpret such data in terms of corrodibility of tube forms in service, will require more such studies as those carried on at Purdue University. There are many applications in power plants, such as turbine buckets, various sections of turbine shells, valve-trim materials, and other uses in which the service conditions would be similar to those under which our tests were made.

In contrast to the Purdue test results, our tests have shown a marked reduction in the corrosion rate of carbon-molybdenum steel as compared with that of carbon steel. Our finding is based upon consistent test results obtained over a period of approximately 16,000 hr of exposure to 1100 F steam, during which time four different specimens of each sample were examined. Our shortest exposure period was approximately 4000 hr, whereas the Purdue results are based upon exposure periods of only 500 hr in 1100 F steam. To compare the test results of the two separate investigations, the shape of the "rate-loss" curve would have to be determined between 0 and 4000 hr of exposure in steam at 1100 F. This point is significant. Furthermore, the metallographic examination made of our test specimens at the conclusion of each 4000-hr exposure period showed a marked difference in the thickness of the scale on carbon steel, as contrasted with carbon-molybdenum steel. The carbon-steel specimens consistently had a much thicker and less adherent scale than the carbon-molybdenum steels. Two different carbon steels and two different carbon-molybdenum steels were each tested at 1100 F. At 1200 F there may be very littly difference in the scaling resistance of carbon steel and carbon-molybdenum steel as shown in Table 4, given in the Purdue comments. At 925 F we found practically no difference between the scaling rate of carbon and carbon-molybdenum steels.

Our test results indicate that carbon content is a significant factor in the corrosion rate of carbon steels exposed to steam at 1100 F. Consistently higher weight losses and thicker scale were found for low-carbon steel than for medium-carbon steel. We did not study the effect of carbon content as related to the corrosion resistance of carbon-molybdenum steel in steam at 1100 F.

Mr. Speller's question concerning whether the corrosion found is uniform or localized in the form of pitting is answered as follows: In general the corrosion found on the carbon steels and the low-and medium-alloy steels was quite uniform. Whenever the surface of the specimens was completely covered with a scale of measurable thickness, which could be seen easily at a magnification of 100 diam in a cross-sectional specimen, we prefer to think of the corrosion as being of a uniform type provided that no intergranular attack has occurred. In the case of the cast materials, considerable surface roughness was observed beneath the scale which is believed to be due to segregation in the cast alloy. Similar materials when tested in the wrought condition did not show such roughening of the surface beneath the scale.

Pitting of the surface as a result of exposure to 1100 F steam was found in the stainless materials, particularly in the 18 Cr-8 Ni without columbium, and in the 12-Cr steels with the exception of Sample 19 which was a Type 416, 12-Cr steel and which had shown very little surface attack after 16,526 hr of exposure. Pitting of the surface was also found in Inconel and "K" monel after 7461 hr of exposure. Intergranular attack at the surface was found in the nickel samples and, as mentioned by Messrs. Skinner and Eash, this was caused by intergranular precipitation of graphite at the test temperature.

No tests were made of 1 per cent chromium, 0.50 per cent molybdenum steels in 1100 F steam. Two steels of that general type were tested but contained a high silicon content and are, therefore, not comparable to such steels with normal silicon. A 1 per cent chromium, 0.50 per cent molybdenum steel was tested in 925 F steam for 13,165 hr. At that temperature its corrosion rate appeared to be about the same as that of 0.50 per cent molybdenum steel and plain-carbon steel, all of which had scaled approximately the same amount. In steam at 1100 F, however, the beneficial effect of 1 per cent of chromium would probably enhance the corrosion resistance of 0.50 per cent molybdenum steels. No tests were made of steel containing $2^1/_4$ per cent chromium, 1 per cent molybdenum, but from its favorable showing in oil-cracking applications at 1100 F, as reported by Mr. Speller, it probably would be suitable for many steam-power-plant applications.