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THE ACTION OF OXYGEN AND HYDROGEN SULPHIDE UPON IRON-CHROMIUM ALLOYS AT HIGH TEMPERATURES

R. L. RICKETT AND W. P. WOOD

Abstract

The action of oxygen and hydrogen sulphide upon iron-chromium alloys at high temperatures was investigated with the determination of the mechanism of reaction as the principal object.

The alloys that were studied contained up to 28 per cent chromium. The temperature range covered in the investigation was from 760 to 1095 degrees Cent. (1400 to 2000 degrees Fahr.), and exposure times up to 150 hours were used. The gain in weight of the specimens was measured, and the chemical composition, microstructure, and crystal structure of typical specimens of scale were investigated.

Hydrogen sulphide was found to cause much greater scaling than oxygen under similar conditions. Increasing amounts of chromium greatly increased the resistance to oxidation but only slightly increased the resistance to attack by hydrogen sulphide under the conditions of this work.

The effect of alloy composition and type of atmosphere is explained on the basis of the type of scale produced and the consequent variation in rates of diffusion through the scale. The compositions of the various types of scale are also explained on the basis of diffusion. The effects of temperature and of time were found to be consistent with a diffusion hypothesis.

ALLOYS suitable for use at high temperatures have become increasingly important during the last few years. The properties of these alloys that are of interest in connection with such use are their physical properties at high temperatures and their resistance to continued attack by the atmospheres in which they are used. A

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The authors are members of the society. R. L. Rickett is associate investigator, Department of Engineering Research and W. P. Wood is professor of metallurgical engineering, University of Michigan, Ann Arbor, Mich. Manuscript received April 28, 1933.

very large number of papers dealing with the physical properties of metals and alloys at elevated temperatures has appeared and much work along this line is now being done. The subject of resistance to deterioration at high temperatures through the action of the atmospheres encountered in service has, on the other hand, received very little attention in the technical literature in spite of the importance of such action in many applications.

The resistance of metals and alloys to attack by gases at high temperatures may be investigated with the object of obtaining quantitative data as to the amount of attack under definite conditions or with the aim of determining the mechanism of reaction. A knowledge of the mechanism of attack is essential to an understanding of the behavior of the so-called heat resistant alloys that are in use and would be of great value in developing new alloys. The present paper gives the results of an investigation to determine the nature of the action of corrosive gases upon heat resistant alloys so far as is possible from a study of the action of oxygen and hydrogen sulphide upon iron-chromium alloys. Chromium in sufficient quantities is known to confer marked resistance to oxidation, and the iron-chromium alloys possess most of the heat resistant characteristics of the more complex alloys. Oxygen and hydrogen sulphide were selected for this investigation because they are two fairly typical and quite different corrosive agents.

Although the mechanism of attack was the principal object of this investigation, it was first necessary to obtain definite data as to the effect of various factors upon the amount of attack. This paper is, therefore, divided into two parts. In Part I are considered the effects of time, temperature, type of atmosphere, and alloy composition upon the amount of attack, and in Part II there is developed a possible mechanism of reaction from a consideration of the data given in Part I, and the results of an examination of the products of reaction.

PART I

DATA ON THE ACTION OF OXYGEN AND HYDROGEN SULPHIDE UPON IRON-CHROMIUM ALLOYS AT HIGH TEMPERATURES

The technical literature and the work of the authors concerning the action of oxygen and hydrogen sulphide upon iron-chromium alloys at high temperatures will now be considered.

Discussion of Literature

Only a few of the articles that deal with the oxidation of iron-chromium alloys give the actual results of experimental work. One such article is that of Hatfield¹ who determined the amount of scaling in oxygen of alloys that contained 13 and 18 per cent chromium. This work covered the temperature range from 700 to 1000 degrees Cent. (1290 to 1830 degrees Fahr.). Hatfield found that at 700 degrees Cent. there was little difference in the amount of oxidation of the two alloys, but as the temperature increased the rate of oxidation of the lower chromium alloy increased much more rapidly than that of the higher chromium alloy. Mathews² has reported the results of oxidation tests of iron-chromium alloys that contained from 13 to 26 per cent chromium. From his data no direct comparisons of different alloys are possible, but the temperature at which a considerable amount of scale was produced increased as the chromium content of the alloys increased. Schmidt and Jungwirth³ found that alloys containing 28 to 30 per cent chromium scaled less at 1000 degrees Cent. (1830 degrees Fahr.) than did those containing 20 to 24 per cent chromium, and very much less than the latter at 1100 degrees Cent. (2010 degrees Fahr.). MacQuigg⁴ does not give any actual experimental results, but he states that the iron-chromium alloys show a marked increase in resistance to oxidation up to 9 per cent chromium, that from 9 to 20 per cent chromium, the resistance continues to increase but at a slower rate, while above 20 per cent chromium there is another sharp increase in the resistance to oxidation.

Most of the published work on the action of hydrogen sulphide upon iron-chromium alloys is concerned with temperatures of 500 degrees Cent. (930 degrees Fahr.) or below. Some results determined by Scholl and published by French⁵ indicate that at 480 degrees Cent. (895 degrees Fahr.) the amount of attack in hydrogen sulphide decreases continuously as the chromium content increases up to about 18 per cent, and that beyond this chromium content there is little

¹Hatfield, *Journal*, Iron and Steel Institute, Vol. 115, 1927, p. 483-522.

²Mathews, *Industrial and Engineering Chemistry*, Vol. 21, 1929, p. 1158-64.

³Schmidt and Jungwirth, *Archiv für d. Eisenhüttenwesen*, Vol. 5, 1932, p. 419-26.

⁴MacQuigg, *Transaction*, American Institute of Mining and Metallurgical Engineers, Vol. 69, 1923, p. 831, *Proceedings*, American Society for Testing Materials, Vol. 24 II, 1924, p. 373-82. A.S.T.M. High Temperature Symposium, 1931, p. 432-49.

⁵French, *Transactions*, American Electrochemical Society, Vol. 50, 1926, p. 47.

further change. White and Marek,⁶ and also Sayles,⁷ found that increasing amounts of chromium up to 20 per cent slightly decreased the amount of attack by hydrogen sulphide at 500 degrees Cent. (930 degrees Fahr.). White and Marek also found that the rate of reaction increased as the time increased. Wellmann⁸ found that at 550 degrees Cent. (1020 degrees Fahr.) an alloy containing 23 per cent chromium scaled considerably less in hydrogen sulphide than did one that contained 14 per cent chromium. A 25 per cent chromium alloy was found by Gruber⁹ to be attacked nearly as much as was pure iron when exposed in hydrogen sulphide at temperatures of 800 and 1000 degrees Cent. (1470 and 1830 degrees Fahr.). The action of sulphur-containing gases at relatively low temperatures has also been investigated in connection with studies of corrosion of oil refinery equipment.^{10, 11, 12} In this work some increase in resistance to attack with increasing chromium additions has been found.

SCOPE OF INVESTIGATION

It may be well to point out here that this investigation was not carried out with the idea that the experimental values obtained could be used directly to predict the amount of attack in service under a given set of conditions. In practical applications of the alloys a large number of factors are involved, and reliable data regarding the behavior of iron-chromium alloys under such conditions can only be obtained in the laboratory when all these factors are known and taken into account. The aim of the present work was rather to determine the specific effects of such factors as might be used to determine the nature of the reactions that take place at high temperatures between iron-chromium alloys and the gases under consideration.

With this in mind, the principal factors selected for study were time, temperature, and alloy composition. Periods of time up to 150 hours were used in the oxidation tests, and up to 50 hours in the work on hydrogen sulphide. The temperature range covered was from 760 to 1095 degrees Cent. (1400 to 2000 degrees Fahr.). Alloys that contained up to 28 per cent chromium were exposed for differ-

⁶White and Marek, *Industrial and Engineering Chemistry*, Vol. 24, 1932, p. 859-61.

⁷Sayles, *Fuels and Furnaces*, Vol. 8, 1930, p. 835.

⁸Wellmann, *Zeit. für Elektrochemie*, Vol. 37, 1931, p. 142-56.

⁹Gruber, *Zeit. für Metallkunde*, Vol. 23, 1931, p. 151-7.

¹⁰Duff, *Proceedings*, American Petroleum Institute, Vol. 11, 1930, p. 155-7.

¹¹Whitman and Roberts, *Ibid*, Vol. 11, 1930, p. 150-4.

¹²Kendall and Speller, *Metal Progress*, Vol 19, February, 1931, p. 40.

ent periods of time at a temperature of 980 degrees Cent. (1800 degrees Fahr.), and at different temperatures for a 25-hour period. The compositions of the alloys used are given in Table I.

Table I
Compositions of Alloys

| Alloy | Composition — Per Cent — | | | | | | |
|-------|--------------------------|--------|-----------|---------|------------|---------|--------|
| | Chromium | Carbon | Manganese | Silicon | Phosphorus | Sulphur | Nickel |
| R | 0 | 0.22 | 1.48 | 0.02 | | 0.033 | |
| AA | 10.93 | | 0.39 | | | | |
| HL | 12.33 | 0.12 | 0.57 | | | | |
| HN | 10.93 | | 0.39 | | | | |
| AC | 16.91 | | 0.49 | | | | |
| CL | 20.32 | 0.20 | 0.42 | | | | 0.26 |
| CN | 19.50 | | 0.37 | | | | |
| AB | 26.82 | | 0.83 | | | | |
| FL* | 28.53 | 0.16 | 0.45 | 0.40 | 0.027 | 0.020 | 0.22 |

*Analysis by courtesy of The Midvale Company.

PROCEDURE

The action of oxygen and hydrogen sulphide upon iron-chromium alloys was determined by exposing specimens of the alloys to the action of these gases under definite conditions and measuring the gain in weight. The furnaces that were used consisted of fused silica tubes wound with chromel wire and packed in silocel. The tubes were 1½ inches in internal diameter and 30 inches long, and were wound with the wire for about 15 inches along the central portion. The ends were closed with rubber stoppers through which were inserted a glass inlet tube and a porcelain thermocouple protection tube at one end, and a glass outlet tube at the other end. This outlet tube dipped into mercury to form a seal.

Oxygen from commercial tanks was used. This gas was dried by being passed through tubes filled with anhydrous calcium chloride, but not otherwise purified. The amount of oxygen supplied to each furnace was measured by means of a flow gage that indicated the pressure drop through a constricted tube, a U-tube containing glycerine being used to measure this drop in pressure. The flow gages were calibrated by determining the time necessary to displace a measured volume of water at different rates of flow of gas. A pressure regulator was found convenient in maintaining a steady flow of gas to the furnaces. This pressure regulator consisted of a glass tee in the gas line, one arm of which dipped into mercury for an adjustable distance. The flow of gas could be set at a value slightly greater than that required for the furnace and the excess then bubbled out through the mercury with the result that a slight drop in pressure

at the tank did not reduce the flow of gas to the furnace. The depth of immersion of the end of the outlet tube from each furnace was also adjustable, and was regulated so that a positive pressure of about $\frac{1}{2}$ -inch of water was maintained within the furnaces. The amount of oxygen supplied to each furnace was 30 cubic centimeters per minute (at room temperature).

In the work with hydrogen sulphide the gas was diluted with nitrogen so that the mixture contained about 20 per cent by volume of hydrogen sulphide. This was done in order to obtain a more rapid flow of gas through the furnace without using too large quantities of hydrogen sulphide. This gas is readily decomposed at high temperatures, and, unless the rate of flow is fairly rapid, a large proportion of the sulphur vapor that results from the decomposition diffuses back to the inlet end of the furnace where it condenses. The hydrogen sulphide that was used was obtained from tanks of the compressed gas. It was not purified in any way except for the removal of water vapor by anhydrous calcium chloride. Nitrogen of the best grade obtainable commercially was used, and contained less than 0.3 per cent of oxygen. This amount of oxygen was sufficient to form a considerable amount of oxide in the scale and had to be removed as completely as possible before the gas was used. The removal of oxygen was accomplished by passing the gas through alkaline pyrogallate solution and then over phosphorus. The gas was then thoroughly dried with calcium chloride, ascarite, and phosphorus pentoxide in series. Any remaining oxygen was removed by passing the gas over fine iron turnings at 700 degrees Cent. and metallic calcium at 400 degrees Fahr. The rates of flow of the two gases were adjusted and measured separately by means of pressure regulators and flow gages of the same type as were used for oxygen. The gases were mixed just before they reached the furnaces and the rate of flow of the mixed gas was 60 cubic centimeters per minute (at room temperature). Analyses were made at intervals of the gas entering and leaving the furnace. The gas was collected and analyzed over mercury, sodium hydroxide solution being used as an absorbent for hydrogen sulphide. Mercury is slowly attacked by hydrogen sulphide but if the mercury is dry the rate of attack is not rapid enough to materially affect the results.

Temperature measurements were made with chromel-alumel thermocouples and a portable potentiometer. Porcelain tubes were used to protect the thermocouples from the furnace atmosphere. The

thermocouples were calibrated periodically by comparison with a noble metal couple that was used as a laboratory standard and was, in turn, checked at intervals with a similar couple calibrated by the Bureau of Standards. The temperature variation during a run was kept within ± 7 degrees Cent.

The specimens were cut from round bars either $\frac{1}{2}$ -inch or $\frac{3}{8}$ -inch in diameter and were about $1\frac{1}{2}$ inches long. They were first filed to removed scale and surface irregularities and then finished with various grades of emery cloth and emery paper, the final polish being with No. 00 emery paper. They were then stamped on one end, washed in alcohol and ether successively, and weighed to the nearest 0.5 milligram.

The specimens were placed in the center of the heated portion of the furnaces so that they nearly touched the ends of the thermocouple protection tubes. They were mounted on supports made by wiring together two small unglazed porcelain tubes with platinum wire. For the tests in oxygen the furnaces were brought to the desired temperature before the specimens were inserted. At the end of a run the specimens were removed without cooling the furnace and were placed in metal boxes to cool so that any scale that might fall off during cooling could be collected. In the case of the tests in hydrogen sulphide it was necessary to avoid any possibility of oxidation of the specimens. They were therefore placed in the cool furnace which was then flushed with purified nitrogen and brought up to the desired temperature after which the hydrogen sulphide was turned on. This procedure was reversed at the end of a run.

The amount of attack during a run was determined by measuring the gain in weight. This was necessary because no satisfactory method could be found for removing the scale that was formed. The specimens heated in oxygen could be easily removed from the supports before weighing. When hydrogen sulphide was used it was difficult to remove the specimens from the supports and therefore the supports and specimens were weighed together before and after the runs. The areas of the specimens were measured before the tests, and the amount of scaling was expressed as the gain in weight per unit area of the original specimens.

RESULTS

Effect of Time—The effect of time upon the reaction of oxygen and of hydrogen sulphide upon iron-chromium alloys at 980 degrees

Cent. (1800 degrees Fahr.) is shown in Figs. 1 and 2, respectively.

The curves given in Fig. 1 show that the rate of oxidation of the alloys containing 0, 12, 17, and 28 per cent chromium decreased continuously as the time increased. The results obtained with the

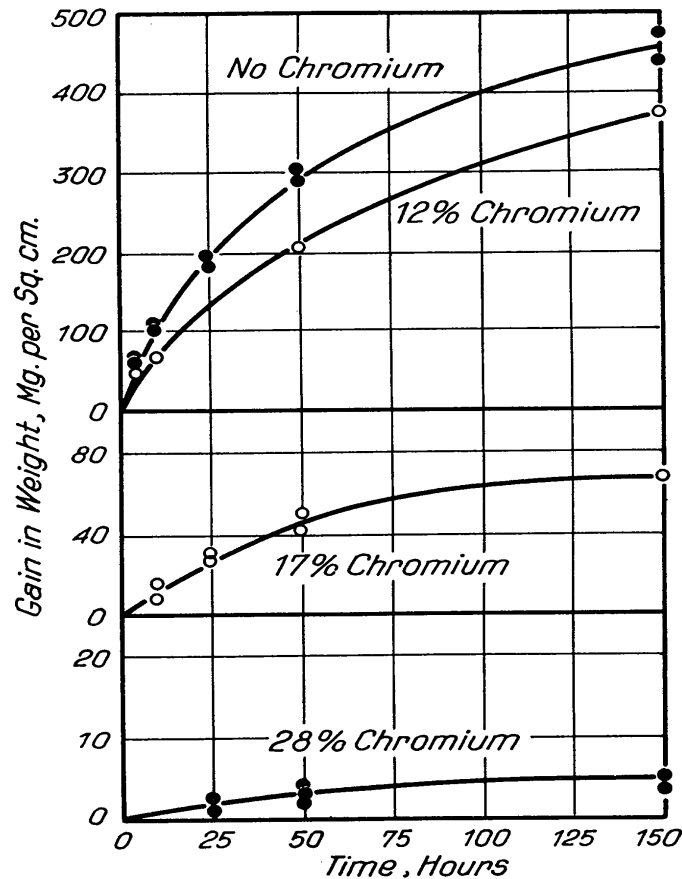


Fig. 1—Effect of Time on Amount of Oxidation at 980 Degrees Cent.

20 per cent chromium alloy varied so much that the form of the time-oxidation curve for this alloy could not be determined.

In order to determine the forms of the curves shown in Fig. 1, the same results were plotted using logarithmic scales for the time and the gain in weight. The points as thus plotted showed slight but definite deviations from straight lines over certain portions of the range. However, it was possible to represent the course of oxidation of each alloy on this type of graph by a straight line from which none of the points deviated by more than 10 per cent. From these straight lines the following equations were derived to represent the course of oxidation of the various alloys:

$$\begin{aligned}
 &0 \text{ chromium alloy, } W^2 = 1440t \\
 &12 \text{ per cent chromium alloy, } W^{1.6} = 108t \\
 &17 \text{ per cent chromium alloy, } W^{1.5} = 6t \\
 &27 \text{ per cent chromium alloy, } W^{1.35} = 0.05t,
 \end{aligned}$$

where W is the gain in weight in milligrams per square centimeter after a period of exposure of t hours. These equations show that as the chromium content of the alloys increases the exponent becomes more nearly unity, or in other words the amount of oxidation is more

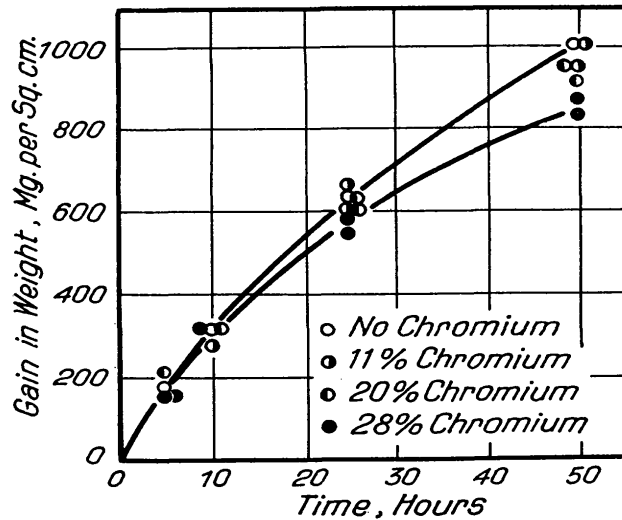


Fig. 2—Effect of Time on Amount of Reaction with Hydrogen Sulphide at 980 Degrees Cent.

nearly proportional to the time. The value of the proportionality factor in the equations is seen to decrease very markedly as the chromium content increases.

The effect of time upon the amount of sulphur that reacted with the alloys when exposed in hydrogen sulphide at 980 degrees Cent. (1800 degrees Fahr.) is shown in Fig. 2. The results are similar to those obtained with oxygen in that the amount of sulphur in combination with the metal increased as the time of exposure increased but at a decreasing rate. When these results were plotted using logarithmic coordinates the points were found to follow straight lines within the limits of the experimental error. The equations for these lines were found in the same way as were those for oxygen and the results are as follows:

$$\begin{aligned}
 &0 \text{ chromium alloy, } W^{1.2} = 100t \\
 &11 \text{ per cent chromium alloy, } W^{1.2} = 93t \\
 &20 \text{ per cent chromium alloy, } W^{1.3} = 199t \\
 &28 \text{ per cent chromium alloy, } W^{1.3} = 170t
 \end{aligned}$$

In these equations W is the gain in weight in milligrams per square centimeter and t is the time in hours, as before. These equations show that the amount of attack in hydrogen sulphide was more

nearly proportional to the time of exposure than in the case of oxygen. The amount of attack after a given time of exposure was also much greater in an atmosphere of hydrogen sulphide than in oxygen as may be seen by comparing Figs. 1 and 2.

Effect of Temperature—The effect of temperature upon the amount of oxidation in 25 hours is shown in Fig. 3. The rate of oxidation of the alloys that contained 12 and 20 per cent of chro-

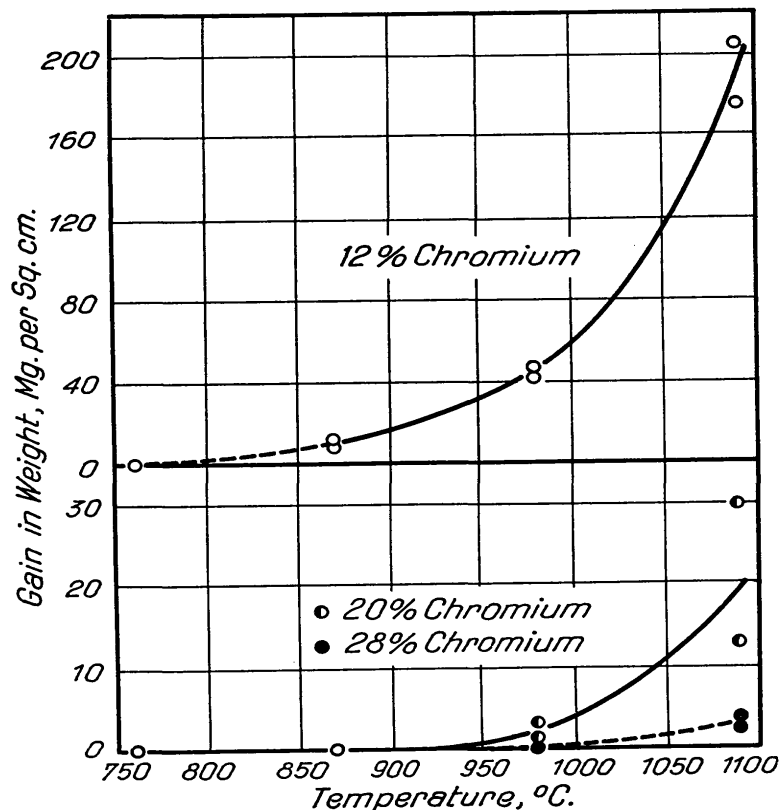


Fig. 3—Effect of Temperature on Amount of Oxidation in 25 Hours.

mium increased slowly at first and then much more rapidly as the temperature increased. The 28 per cent chromium alloy did not show any such great increase in rate of oxidation as the temperature was increased up to 1100 degrees Cent. It was found that the solid portions of the curves in Fig. 3 could be represented by equations of the form:

$$\log W = kT, \text{ or } W = a^{bT}$$

In these equations W is the gain in weight per unit area, T is the temperature in degrees centigrade, and k , a , and b are constants. The portions of the curves shown as dotted lines did not follow these equations or at least did not have the same constants as the rest of the curve for the same alloy.

Fig. 4 shows the effect of temperature upon the amount of reaction in 25 hours in hydrogen sulphide. Only two alloys were selected for this work since the difference between the different alloys was found to be so slight. It was found that the following equations fitted the curves shown in Fig. 4 very well:

$$\begin{aligned} & \text{11 per cent chromium alloy,} \\ & W = -1.555T + 0.002225T^2 \end{aligned}$$

$$\begin{aligned} & \text{28 per cent chromium alloy,} \\ & W = -1.440T + 0.00198T^2 \end{aligned}$$

In these equations W is the gain in weight in milligrams per square centimeter in 25 hours and T is the temperature in degrees centi-

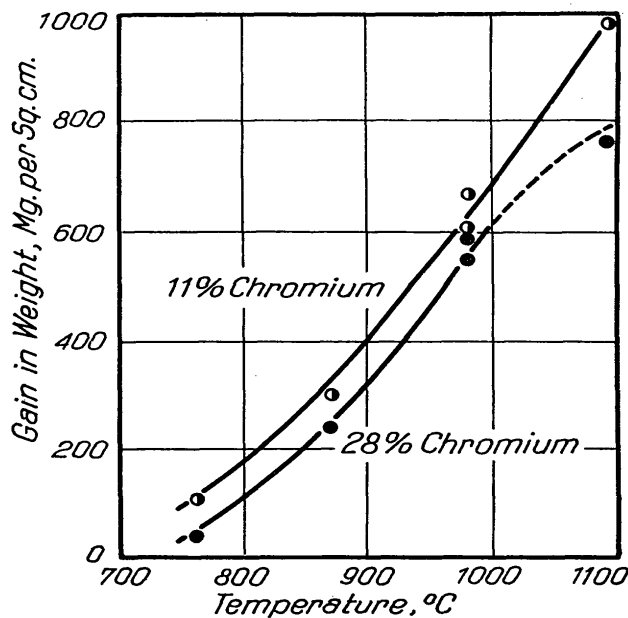


Fig. 4—Effect of Temperature on Amount of Reaction with Hydrogen Sulphide in 25 Hours.

grade. It is seen from a comparison of Figs. 3 and 4 that over the temperature range investigated the increase in rate of attack was more nearly proportional to the increase in temperature in the case of hydrogen sulphide than in the case of oxygen.

Effect of Composition—The effect of increasing amounts of chromium on the amount of oxidation is shown in Figs. 5 and 6. Fig. 5 shows that at a temperature of 980 degrees Cent. the most rapid increase in resistance to oxidation occurred between about 10 and 20 per cent chromium. The resistance increased slowly as the chromium content increased above 20 per cent, but there was probably

not much further change above 25 per cent chromium at this temperature. As the temperature increased the chromium content at which the curves began to flatten out also increased as is shown in Fig. 6. A similar variation in resistance to oxidation has been shown by Hauttmann¹³ in the case of iron-aluminum alloys.

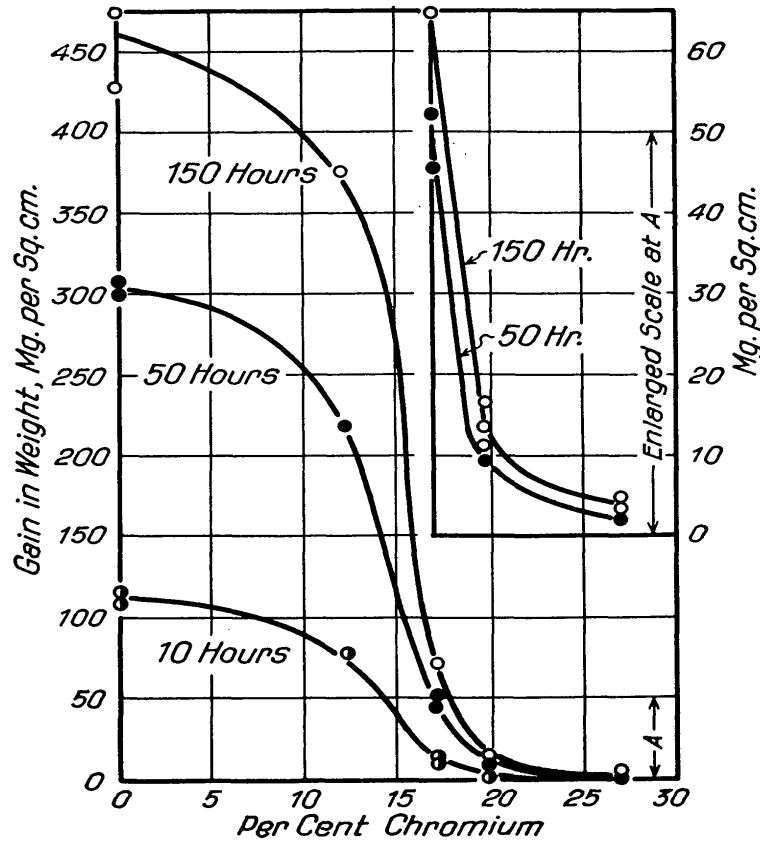


Fig. 5—Effect of Chromium Content on Amount of Oxidation at 980 Degrees Cent.

The effect of alloy composition upon the amount of attack when the various alloys were heated in hydrogen sulphide at 980 degrees Cent. (1800 degrees Fahr.) is shown in Fig. 7. On exposing the alloys for comparatively short periods of time there was no consistent variation in amount of attack with variations in chromium content. However, when the period of exposure was longer and the thickness of the scale correspondingly greater there was found a slight decrease in the amount of attack as the chromium content of the alloy increased. This decrease was very much less marked than in the tests made in oxygen.

Effect of Gas Velocity—In order to determine the effect of gas velocity on the amount of oxidation the 11 and 28 per cent chromium

¹³Hauttmann, *Stahl und Eisen*, Vol. 51, 1931, p. 65-7.

alloys were heated for 25 hours at 980 degrees Cent. in a stream of oxygen supplied at a rate of 90 cubic centimeters per minute (at room temperature) instead of the 30 cubic centimeters per minute used in the rest of the work. No significant variations in amount of

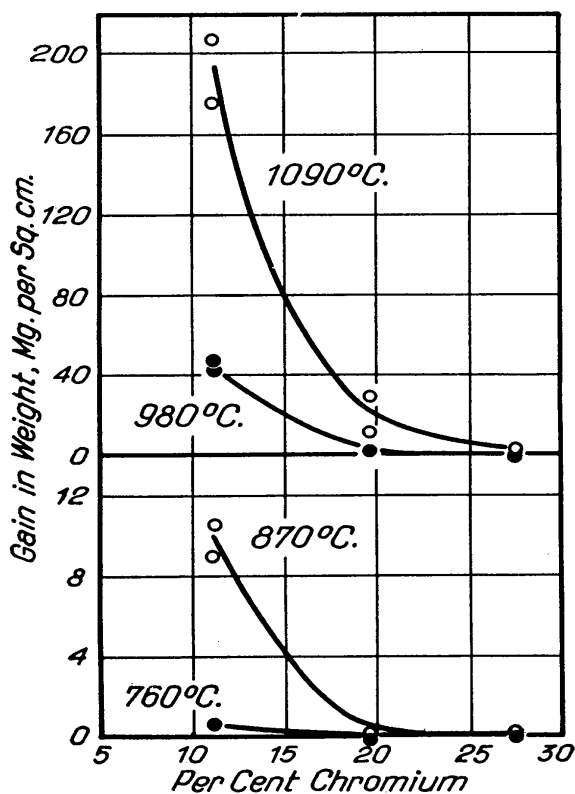


Fig. 6—Effect of Chromium Content on Amount of Oxidation in 25 Hours.

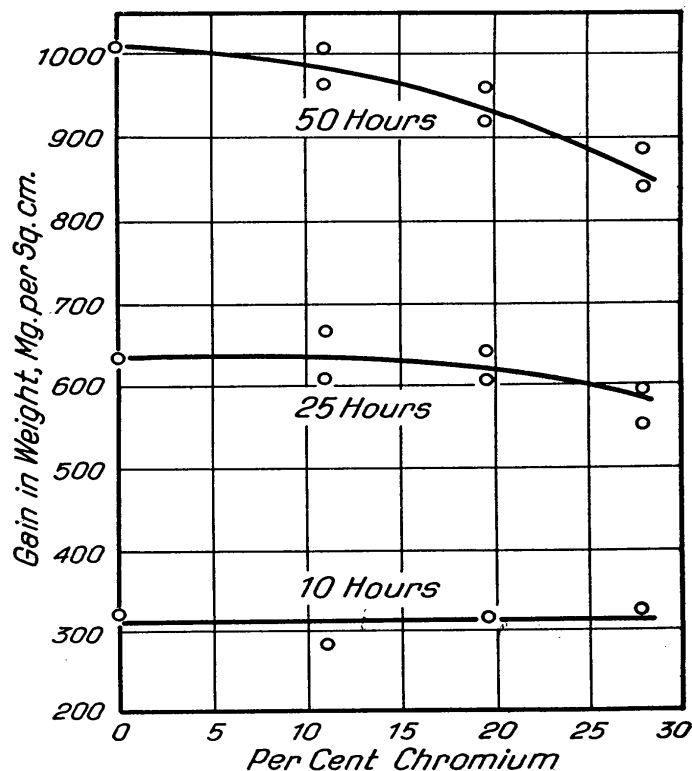


Fig. 7—Effect of Chromium Content on Amount of Reaction with Hydrogen Sulphide at 980 Degrees Cent.

oxidation were found. Similar tests in hydrogen sulphide using 1/2 and 1 1/2 times the usual flow of gas likewise showed no evidence of any effect on the rate of attack.

PART II

THE MECHANISM OF REACTION OF OXYGEN AND HYDROGEN SULPHIDE WITH IRON-CHROMIUM ALLOYS

In the remainder of this paper the literature dealing with the mechanism of reaction of gases with metals and alloys in the solid state will be considered, and a mechanism of reaction of oxygen and hydrogen sulphide with iron-chromium alloys will be developed from a consideration of the results given in Part I, and the data secured by investigating the products of reaction.

Review of Literature

An important contribution to the subject of the mechanism of oxidation of metals at high temperatures was made by Pilling and Bedworth.¹⁴ These authors classify metals as noble and base according to whether their oxides have relatively high or low dissociation pressures. They postulate that the oxidation of base metals takes place at the metal oxide interface and that two types of oxides may be formed. If the oxide layer is cellular then it offers little resistance to further oxidation and the rate of oxidation at a given temperature is constant. When a compact oxide is formed, further oxidation must take place by the diffusion of oxygen through the layer of oxide already formed, and at a given temperature the rate of oxidation is inversely proportional to the thickness of this oxide layer. The theory of Pilling and Bedworth has been criticized because it postulates that all oxidation takes place at the oxide-metal interface so that the scale must be plastic if oxidation is to continue without cracking the scale already formed. Pfeil¹⁵ has made a contribution to the theory of oxidation that eliminates this difficulty. He observed that the scale formed by the oxidation of iron consisted, in general, of three layers, and that the boundary between the inner and middle layers corresponded in position and appearance to the original surface of the specimen. He also found that particles of foreign materials placed on the surface of the specimen were enveloped by the scale without change of position. From these observations Pfeil concluded that there must be a diffusion of iron outward as well as a diffusion of oxygen inward. In some work by Murphy¹⁶ and his associates it has been shown that, in addition to the diffusion of the oxidizing gas inward and the metal outward, it may be necessary, in some instances, to take into consideration the rate of diffusion of gaseous products of reaction outward through the scale.

Several investigations of the oxidation of alloys have shown that different layers of the scale produced may contain vastly different proportions of the alloying elements. Thus, Dunn¹⁷ found in a study of the oxidation of copper-zinc alloys that alloys containing from

¹⁴Pilling and Bedworth, *Chemical and Metallurgical Engineering*, Vol. 27, 1922, p. 72-4.

¹⁵Pfeil, *Journal*, Iron and Steel Institute, Vol. 119, 1929, p. 501-547.

¹⁶Murphy, Wood, and Jominy, *TRANSACTIONS*, American Society for Steel Treating, Vol. 19, 1932, p. 193-246.

¹⁷Dunn, *Journal*, Institute of Metals, Vol. 46, 1931, p. 25-52.

60 to 75 per cent copper formed a scale that consisted largely of zinc oxide, that the scale on alloys of from 78 to 86 per cent copper consisted of an outer layer of cupric oxide, a middle layer of zinc oxide, and an inner layer of cuprous oxide, while alloys higher in copper formed a scale that consisted largely of copper oxides. Dunn explains the absence of appreciable amounts of copper oxide in the scale formed on the alloys lower in copper on the hypothesis that the rate of diffusion of zinc in these alloys is sufficient to reduce copper oxide as fast as it is formed, or in other words that there is, in effect, a preferential oxidation of the zinc. He does not explain the results obtained in the case of the alloys that contain from 78 to 86 per cent copper. Hauttmann¹³ has also proposed a theory of selective oxidation to account for the fact that the scale formed on iron-aluminum alloys that contained 9 per cent or more of aluminum consisted principally of aluminum oxide while on alloys that contained less than 4 per cent aluminum the scale appeared to mostly consist of iron oxides.

Pfeil¹⁵ has published results that do not accord with the hypothesis of preferential oxidation. He has shown that the oxidation of a large number of alloys of iron with other elements results in the formation of three layers of scale, of which the outer layer contains a higher proportion of iron, and the inner layer a lower proportion of iron than the original alloy. This was found to be true both in the case of alloys of iron with elements that have a greater affinity for oxygen and those that have a lower affinity for oxygen than has iron. Dunn¹⁷ found that the scale formed on a copper-silicon alloy containing up to 5 per cent silicon was practically free from silica, which is not in accord with his theory of preferential oxidation since silicon forms a much more stable oxide than does copper. It thus appears that no adequate explanation has been given to account for the varying proportions of the alloying elements found in the scale formed by the oxidation of alloys.

A MECHANISM OF SCALING

It remains now to develop a mechanism of scaling that will account for the effects of time, temperature, alloy composition, and

¹³Loc. cit.

¹⁵Loc. cit.

¹⁷Loc. cit.

nature of the atmosphere on the action of oxygen and hydrogen sulphide on iron-chromium alloys.

Reaction of Gases at High Temperatures with Alloys in the Solid State—It may be well at this point to consider what happens when an alloy is exposed to a gas with which it reacts. If the component metals of the alloy are all capable of reacting with the gas under the conditions of the test, then the first step is a chemical reaction between the gas and the surface layer of the alloy with the formation of a mixture or solid solution of those reaction products that are in equilibrium with the partial pressure of the reacting gas in the furnace atmosphere, and in which the component metals are in the same ratio as in the original alloy. If this layer of reaction products is physically continuous, then further reaction must involve diffusion into or through this layer and may also involve chemical reactions within the layer itself. There is the possibility that diffusion may take place in two directions through the layer of reaction products, inward and outward. It is obvious that there must be diffusion inward if scaling is to proceed, otherwise the metal-oxide interface would not be maintained and further scaling could only proceed by the evaporation of metal from the surface of the alloy and the transfer of this metal outward through the scale. It is highly improbable that there is any appreciable evaporation of either iron or chromium at the temperatures with which we are concerned here. The probability that metal or a product of reaction diffuses outward was first demonstrated by Pfeil who showed that in the case of the oxidation of iron the original surface of the metal was retained in position and form, even after scaling had proceeded to a considerable depth into the specimen. The present authors observed this same phenomenon in their work on the action of hydrogen sulphide on the iron-chromium alloys. Fig. 10 shows the clear outlines of the original surfaces of two specimens from which portions of the outer layers of scale had been removed. It also shows how marks stamped on the end of one of the specimens were reproduced in reverse on the inner face of the second layer of scale.

Rate of Scaling—The problem of scaling is essentially one of reaction in a heterogeneous system. Two factors are involved in determining the velocity of such reactions; one is the actual velocity of chemical reaction at the interface between the reacting phases, and the second is the rate at which the products of reaction are removed from the interface, or in some cases the rate at which one or

more of the reactants reaches the interface. This second factor obviously involves diffusion processes, and if the rate of diffusion is less than the rate of chemical reaction at the interface then the diffusion rates will determine the actual velocity of scaling.

It is of interest to determine whether the rate of chemical reaction or the rate of diffusion is the controlling factor in the reactions that were investigated in the present work. Taylor¹⁸ cites figures compiled by Öholm which show that for diffusion processes the temperature coefficient per 10-degree rise is from 1.2 to 1.5, while if the rate of reaction is the controlling factor the temperature coefficients are greater and frequently range from 2 to 4 per 10-degree rise in temperature. In Table II are given values of the temperature coefficient per 10-degree rise for scaling in both oxygen and hydrogen sulphide as computed from the results of the present work. These coefficients are of the order of magnitude of those that were reported

Table II
Temperature Coefficient per 10 Degrees Cent. Rise in Temperature
25-Hour Tests at Temperatures Given

| Alloy | Temperature Coefficient per 10 Degrees Cent. | | | |
|--------------|--|---------------------------------|--|---|
| | Oxygen 900 Degrees Cent. | Oxygen 1050 Degrees Cent. | Hydrogen Sulphide 900 Degrees Cent. | Hydrogen Sulphide 1050 Degrees Cent. |
| 12% chromium | 1.25 | 1.15 | 1.14 | 1.10 |
| 20% chromium | 1.0+ | 1.44 | ∴∴ | ∴∴ |
| 28% chromium | 1.0+ | 1.72 | 1.14 | 1.09 |

by Öholm for diffusion and are much less than those for chemical reactions. Therefore, it may be concluded that the rate of diffusion determined the rate of scaling in this work.

Proposed Mechanism of Scaling—On the basis of the foregoing considerations it is possible to offer the following hypothesis to explain the results of the present work:

1. The alloy first reacts with oxygen or hydrogen sulphide with the formation of a surface layer of those oxides or sulphides of iron and chromium that are in equilibrium with the partial pressure of oxygen or hydrogen sulphide in the furnace atmosphere, and in which the two metals are in the same ratio as in the original alloy.

2. After the formation of this initial layer of scale the rate of scaling is determined by the rate of diffusion of certain substances through the scale.

3. There is a diffusion of the reacting gas or of higher prod-

¹⁸Taylor, Treatise on Physical Chemistry, Vol. II, 1931, p. 1025.

ucts of reaction inward and of the component metals of the alloy or of lower products of reaction outward through the scale. These diffusion processes may be accompanied by chemical reactions within the scale as well as the chemical reaction that takes place at the scale-metal interface.

Since diffusion is such an important factor it is worth while to consider the diffusion equation :

$$\frac{dW}{dt} = - D \frac{dc}{dx}$$

In this equation $\frac{dW}{dt}$ is the rate of diffusion, D is the diffusion constant per unit of cross-sectional area, and $\frac{dc}{dx}$ is the concentration

gradient. The diffusion constant depends upon the nature of the substance which is diffusing and the chemical composition and physical structure of the medium through which diffusion takes place. The concentration gradient depends upon the distance through which diffusion takes place and is limited by the maximum solubility of the substance that diffuses. From this equation it is evident that, where the rate of diffusion is the controlling factor, a high rate of scaling requires a high diffusion coefficient, high solubility of the reactant in the scale, or the occurrence of reactions within the scale that will increase the effective concentration gradients of the reactants. The authors wish to particularly emphasize the following three of the possible conditions.

1. Only one phase can be formed as the result of the reaction with each of the components of the alloy and the solubilities of the reactants in this phase are low. In this case the rate of scaling would be expected to be comparatively slow.

2. Only one phase can be formed as the result of the reaction with each of the components of the alloy but the solubilities of the reactants in this phase are high. The rate of scaling would be much greater than in the first case.

3. Two or more phases may be formed as the result of the reaction and these phases may interact. In this case the rate of scaling may be comparatively rapid.

A determination of the chemical composition, crystal structure, and microstructure of the scale formed in oxygen and in hydrogen

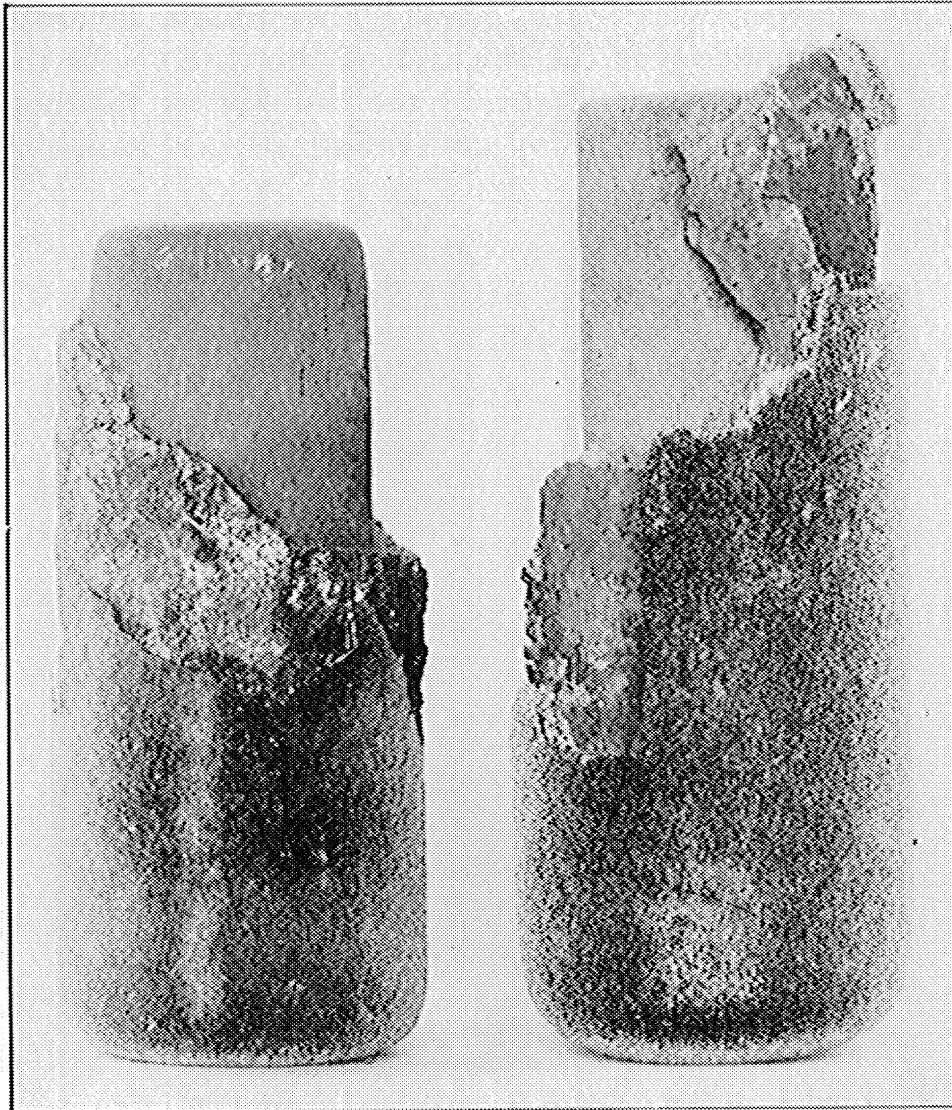


Fig. 8—Oxide Scale on Alloy Containing 12 Per Cent Chromium. Specimen at Left Heated 50 Hours and One at Right Heated 150 Hours at 980 Degrees Cent. (1800 Degrees Fahr.). Magnification 2.

sulphide gave interesting information as to possible reasons for the behavior of the various alloys in the two gases. The results of this investigation of the scale will now be considered and will be followed by a discussion of various factors that affect scaling in view of these results and the proposed mechanism of scaling.

CHARACTERISTICS OF OXIDE AND SULPHIDE SCALE

General Characteristics of Scale—The appearance of the scale formed in oxygen on two of the iron-chromium alloys is shown in Figs. 8 and 9. Three distinct layers of scale were formed on the lower-chromium alloy. The outer layer was blue-gray in color while

the other two layers were dark gray. The middle layer was the thinnest and the inner layer the thickest of the three. As the chromium content of the alloys increased the number of distinct layers of scale decreased. On the alloy containing 28 per cent chromium

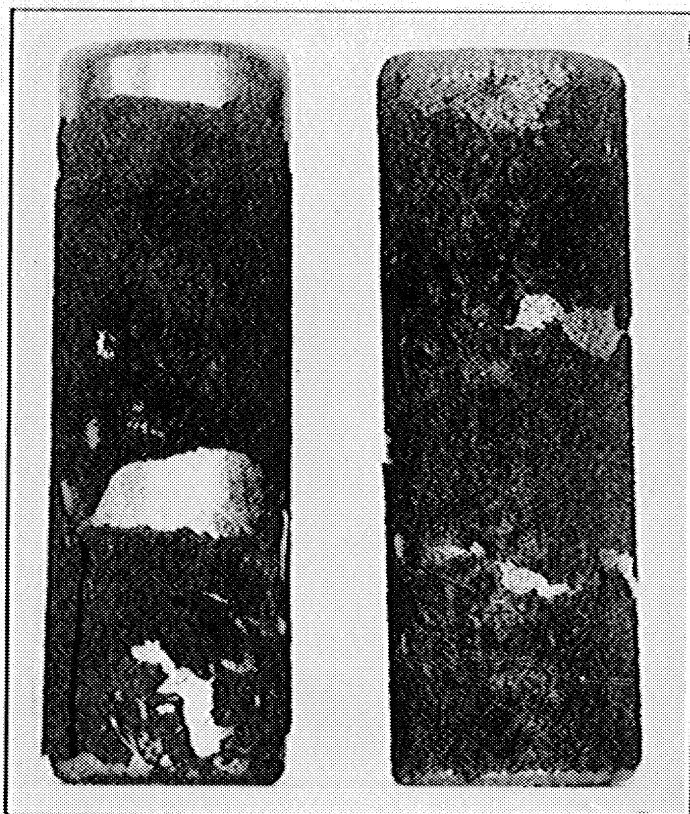


Fig. 9. Oxide Scale on Alloy Containing 28 Per Cent Chromium. Specimen at Left Exposed for 50 Hours and One at Right for 150 Hours at 980 Degrees Cent. (1800 Degrees Fahr.). Magnification 2.

there was formed an extremely thin single layer of scale that fell off readily after the specimens were cooled.

Fig. 10 shows the appearance of specimens heated in hydrogen sulphide. The alloy composition did not have much effect on the type of scale produced in this gas. The fact that the original outlines of the specimens were preserved during scaling in hydrogen sulphide has already been mentioned. Two layers of scale occurred outside this original surface and consisted of very coarse crystals of a brassy-yellow color. Three layers of scale could be distinguished inside the original surface but they could not be readily separated. These layers were gray in color and had a dull luster.

Chemical Composition of Scale—The composition of the scale

formed on various alloys in oxygen is given in Table III, and the composition of that formed in hydrogen sulphide is given in Table IV.

The principal features shown by the oxide scale are the rapid increase in the proportion of chromium in the scale as the chromium content of the alloys increases and the higher proportion of chromium

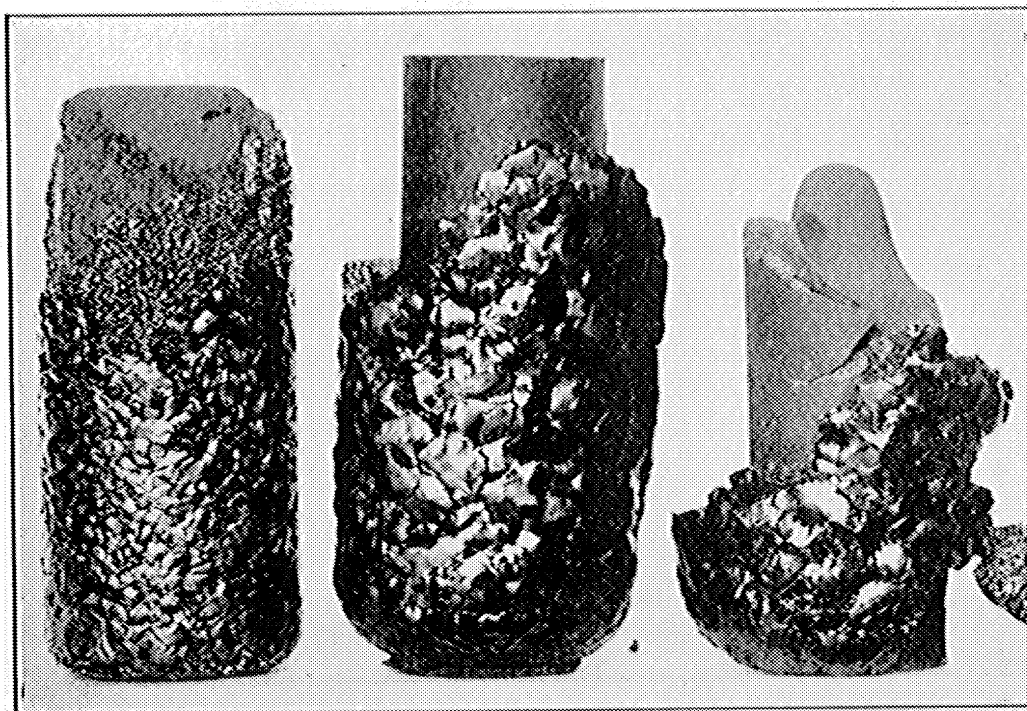


Fig. 10.—Sulphide Scale on Alloy Containing 11 Per Cent Chromium. Specimens Exposed for 10, 25, and 50 Hours, Respectively, from Left to Right. Magnification 1.7.

in the inner layer of scale as compared to the outer layer in cases where more than one layer was formed. This latter phenomenon was also observed by Pfeil¹⁵ in the case of a number of alloys of iron, as has been mentioned. It is significant that the alloy that contained 28 per cent of chromium was by far the most resistant to oxidation of those investigated and formed a scale that consisted largely of chromium oxide.

The sulphide scale did not show as wide a variation in chromium content as the composition of the alloys varied from 11 to 28 per cent chromium. There was, however, a marked decrease in the proportion of chromium in the scale as the distance from the metal increased.

Crystal Structure of Scale—The constituents present in various layers of scale formed on the different alloys and the lattice dimen-

¹⁵Pfeil, Loc. cit.

Table III
Chemical Composition of Oxide Scale

| Per Cent Chromium in Alloy | Temp. Degrees Cent. | Time Hours | Layer of Scale | Per Cent Iron | Per Cent Chromium | Per Cent Manganese | Ratio: |
|----------------------------|---------------------|------------|----------------|---------------|-------------------|--------------------|-------------------|
| | | | | | | | Cr |
| | | | | | | | Cr+Fe+Mn × 100 |
| 12.33 | 980 | 50 | Outer | 70.0 | None | * | 0 |
| 12.33 | 980 | 150 | Inner | 57.02 | 18.58 | * | 24.55 |
| 20.32 | 980 | 50 | Single | 57.60 | 11.20 | * | 16.25 |
| 20.32 | 1090 | 50 | Outer | 64.60 | 4.45 | * | 6.44 |
| 20.32 | 1090 | 50 | Inner | 48.10 | 14.66 | * | 23.35 |
| 28.53 | 980 | 50 | Single | 6.20 | 55.78 | 5.32 | 81.40 |

*Manganese a few tenths of 1 per cent or less.

Table IV
Chemical Composition of Sulphide Scale

| Per Cent Chromium in Alloy | Degrees Cent. | Time Hours | Layer of Scale | Per Cent Iron | Per Cent Chromium | Per Cent Sulphur | Ratio: |
|----------------------------|---------------|------------|----------------|---------------|-------------------|------------------|--------|
| | | | | | | | Cr |
| | | | | | | | Cr+Fe |
| 10.93 | 980 | 50 | Outer | 60.50 | 0.49 | 37.35 | 0.8 |
| | | | Second | 48.55 | 11.05 | 38.83 | 18.5 |
| | | | Remainder | 43.75 | 15.70 | 36.20 | 26.4 |
| 28 | 980 | 50 | Outer | 59.95 | 0.98 | 37.30 | 1.6 |
| | | | Second | 39.05 | 19.37 | 39.75 | 33.2 |
| | | | Remainder | 26.80 | 32.55 | 38.53 | 54.5 |

FeS = 36.5% S.
CrS = 38.2% S.

sions of these constituents were determined by means of X-ray powder diagrams using sodium chloride as a reference substance. The space available here is too limited to present more than a small portion of the results of this work. Table V gives the constituents found in some of the oxide scales. It will be noticed that no evidence of the presence of ferrous oxide was found.

Table V
Constituents in Oxide Scale

| Alloy Per Cent Chromium | Temp. Degrees Cent. | Time Hours | Layer | Constituents |
|-------------------------|---------------------|------------|--------|---|
| 12 | 980 | 150 | Outer | Fe ₂ O ₃ and Fe ₃ O ₄ |
| | | | Middle | (Fe, Cr) ₂ O ₃ and (Fe, Cr) ₃ O ₄ |
| | | | Inner | (Fe, Cr) ₃ O ₄ |
| 20 | 1090 | 50 | Outer | (Fe, Cr) ₂ O ₃ |
| | | | Inner | (Fe, Cr) ₃ O ₄ |
| 28 | 980 | 50 | Single | (Cr, Fe) ₂ O ₃ and (Fe, Cr) ₃ O ₄ |

In the various layers of sulphide scale formed on alloys that contained 11 and 28 per cent chromium the principal constituent had the structure of FeS and from the results of the chemical analyses was evidently a FeS-CrS solid solution. A few lines due to a second, unidentified, constituent were found in the powder diagrams of the three inner layers of scale.

Microstructure of Scale—It has already been mentioned that the number of distinct layers of the scale formed in oxygen decreased as the chromium content of the alloys increased. The appearance of the constituents of the scale also varied considerably with changes in chromium content of the alloys as shown in Figs. 11 to 16, inclusive. The method of mounting the specimens for polishing was essentially that described by Pfeil.¹⁹ Severe pitting of the brittle scale occurred during polishing and could not be avoided even by using great care. In spite of the numerous pits the photomicrographs yield some definite information and so will be discussed briefly here.

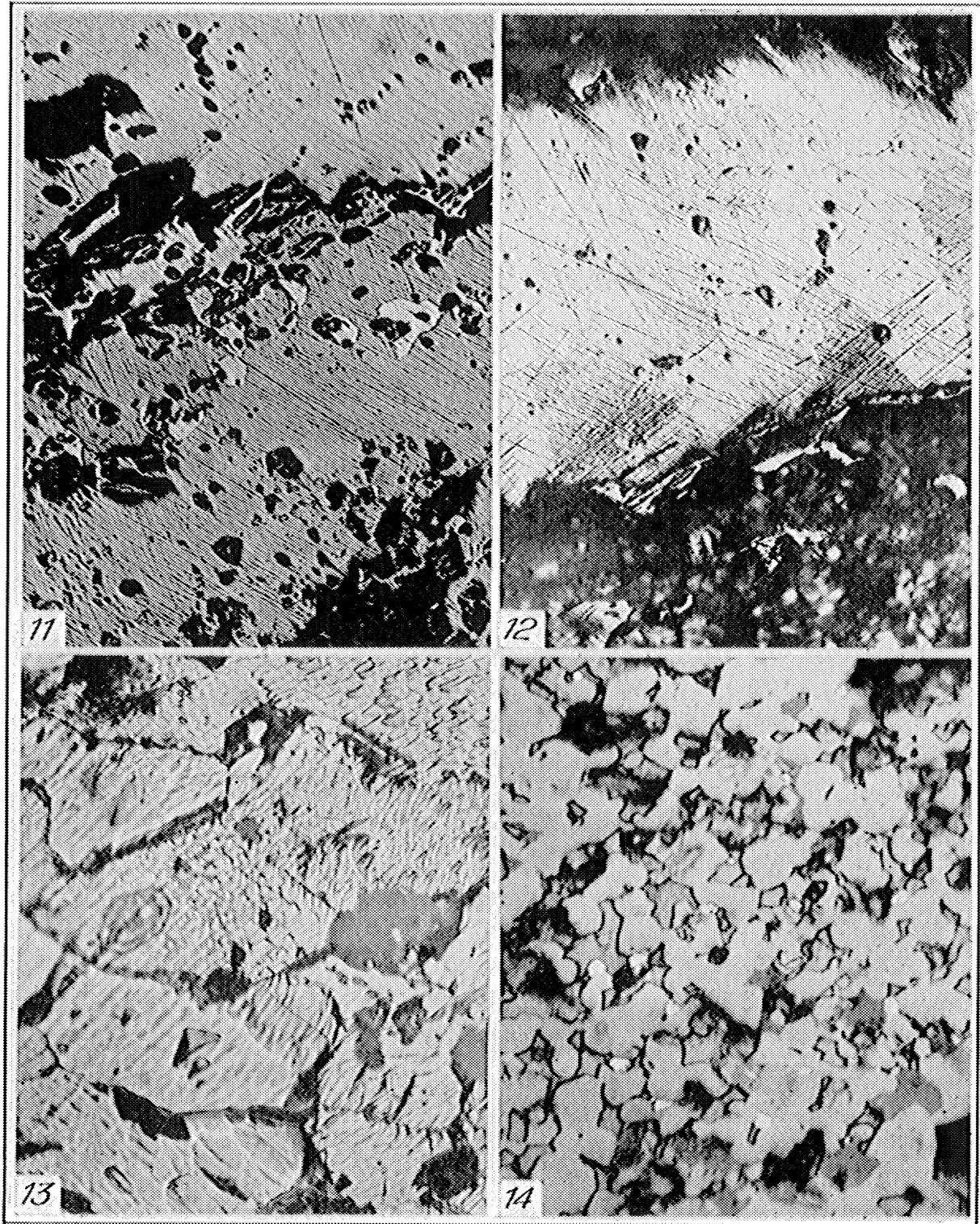
The outer layer of scale formed on the 12 per cent chromium alloy in oxygen was found by chemical analysis to consist largely of iron oxide and from Fig. 11 is seen to consist of two constituents. X-ray analysis showed that Fe_2O_3 and Fe_3O_4 were present in this layer of scale. The outer portion then, is probably Fe_2O_3 and was found to be only slowly etched by concentrated hydrochloric acid, while the inner portion which is darker in color and was readily attacked by even dilute hydrochloric acid is evidently Fe_3O_4 . The structure of the inner layer of scale on the same specimen is shown in Fig. 14, and is seen to contain at least four constituents. The identity of these constituents is uncertain but the white particles are probably unoxidized metal while the unetched matrix is quite possibly chromite, FeCr_2O_4 . This constituent was completely unattacked by concentrated hydrochloric acid, which is characteristic of chromite as described by Schneiderhölml and Ramdor.²⁰ The crystal structure of chromite is almost identical with that of Fe_3O_4 and was the only one found by X-ray analysis of this layer of scale.

On the alloy with 17 per cent chromium only one layer of scale was formed and the structure of this is shown in Fig. 15. The outer portion resembles that on the lower-chromium alloy, was very slightly etched after long treatment with concentrated HCl, and is probably Fe_2O_3 with possibly some Cr_2O_3 in solid solution. The inner portion is lighter in color than the inner portion of the outer layer of scale on the 12 per cent chromium alloy and was unattacked by concentrated hydrochloric acid. It resembles the matrix of the inner layer of scale on the lower-chromium alloy and is very probably chromite.

The structure of the single layer of scale formed on the 28 per

¹⁹Pfeil, *Journal*, Iron and Steel Institute, Vol. 123, 1931, p. 237-58.

²⁰Schneiderhölml and Ramdor, *Lehrbuch der Erzmikroskopie* (Berlin) 1931.



12 Per Cent Chromium Alloy

Fig. 11—Outer Layer of Oxide Scale Formed at 980 Degrees Cent. and Cooled in Air. Unetched. $\times 100$.

Fig. 12—Outer Layer of Scale from Same Specimen as Fig. 11. Heavily Etched in HCl. $\times 100$.

Fig. 13—Dark Zone of Outer Layer of Oxide Scale More Lightly Etched than in Fig. 12. $\times 500$.

Fig. 14—Third, or Inner, Layer of Oxide Scale Formed at 980 Degrees Cent. and Cooled in Air. Etched with Dilute HCl. $\times 1000$.

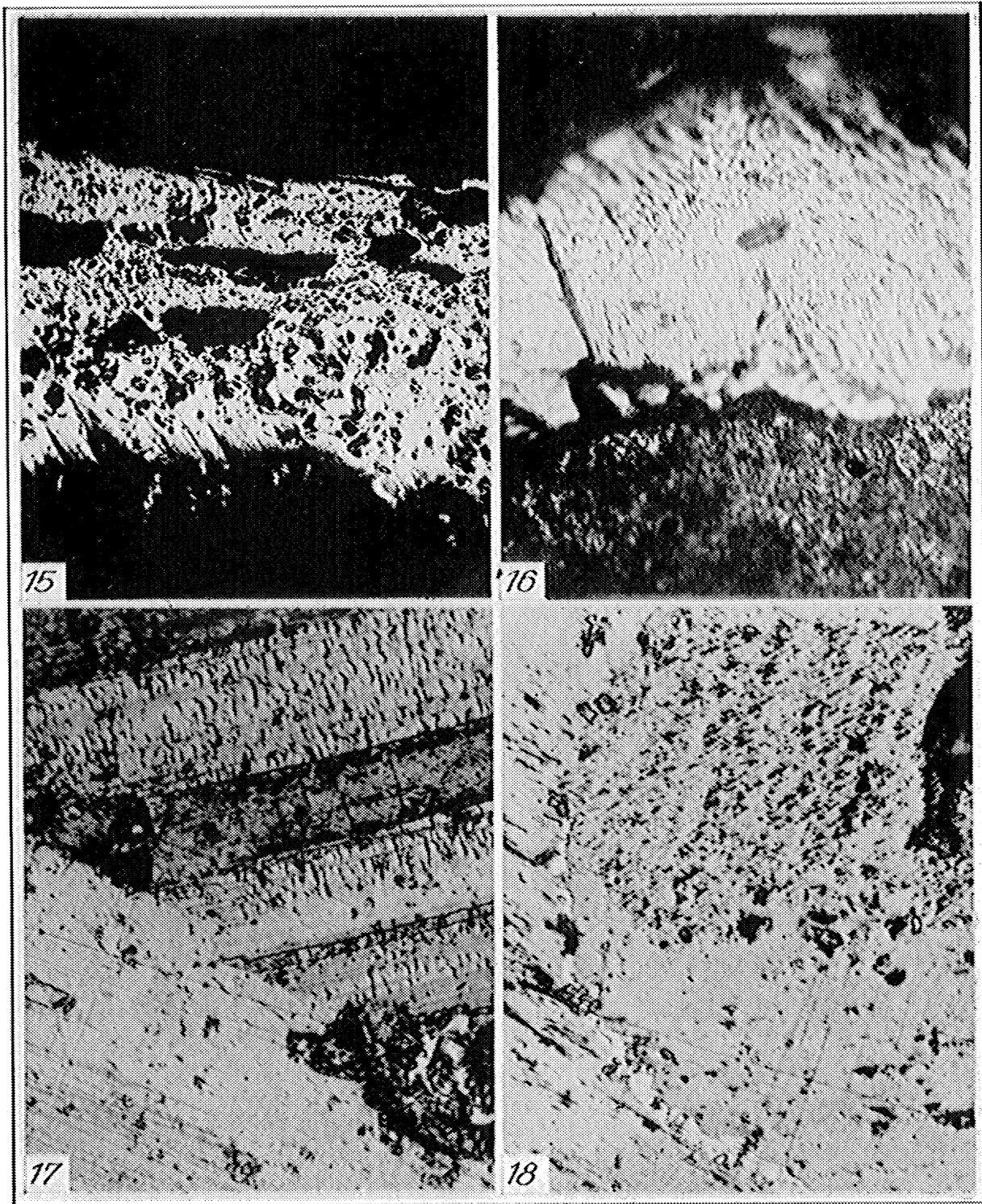


Fig. 15—Oxide Scale Formed on 17 Per Cent Chromium Alloy at 980 Degrees Cent. Unetched. When Etched Outer Portion (at Top) was Slowly Attacked by Concentrated HCl and Remainder was Entirely Unattacked. $\times 100$.

Fig. 16—Oxide Scale on 28 Per Cent Chromium Alloy Heated at 980 Degrees Cent. This Specimen was Polished at an Angle. Etched with Concentrated HCl. $\times 500$.

Fig. 17—Outer Layer of Sulphide Scale on 28 Per Cent Chromium Alloy Heated at 980 Degrees Cent. Etched in Dilute HCl. $\times 1000$.

Fig. 18—Second Layer of Scale on Same Specimen as Fig. 17. Etched in Dilute HCl. $\times 1000$.

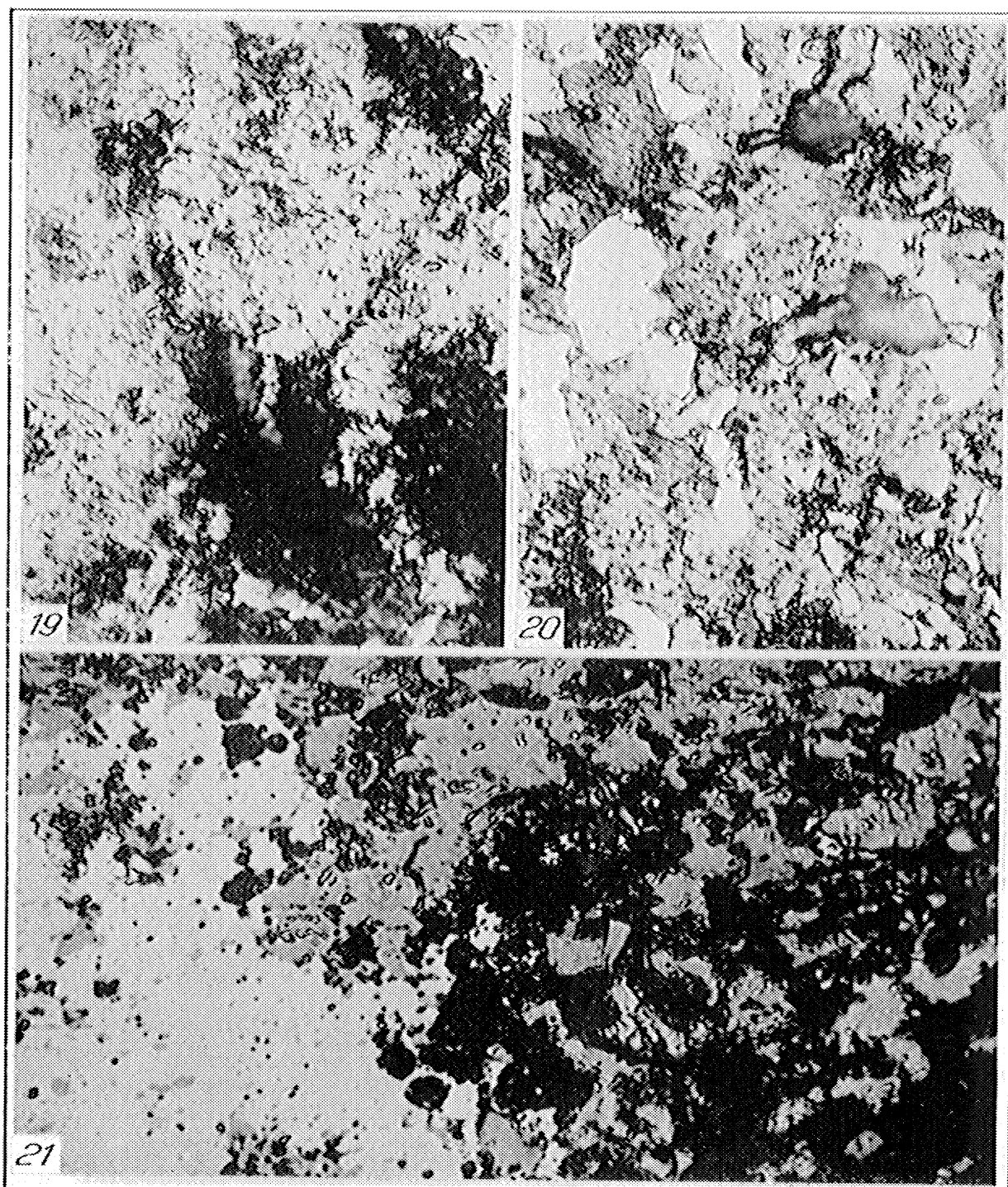


Fig. 19—Third Layer of Scale on Same Specimen as in Figs. 17 and 18. Etched in Dilute HCl. $\times 1000$.

Fig. 20—Fifth, or Inner, Layer of Scale on Same Specimen as at Left. Etched in Dilute HCl. $\times 1000$.

Fig. 21—Boundary Between Scale and Metal on Same Specimen as Fig. 17. Unetched. $\times 1000$.

cent chromium alloy in oxygen is shown in Fig. 16. Only one constituent is seen, although the X-ray results indicated two. The specimen shown was polished at an angle and may not represent a complete cross section of the scale. The results of chemical analysis showed a high proportion of chromium in this scale while most of the lines on the X-ray diagram corresponded to the structure of Cr_2O_3 which is probably the principal constituent of this scale.

The microstructure of the scale formed in hydrogen sulphide did not vary much with changes in chromium content, and therefore photomicrographs of the scale from only one alloy are shown. Figs. 17 to 21, inclusive, show the structure of typical portions of the scale found on a specimen of the 28 per cent chromium alloy. In the outer layer only one constituent was found as is shown in Fig. 17. Very pronounced twinning was observed in the outer layer of scale in this particular alloy, while in the scale formed on some of the other alloys the twinning occurred in other layers but in the same constituent. From the X-ray and chemical data this constituent appears to be a solid solution of FeS and CrS with probably some excess sulphur in solution. A second, lighter colored, constituent is seen in the second and remaining layers of scale and is most pronounced in the inner layer. This constituent has not been identified but a very few lines that do not correspond to the FeS-CrS type of structure were found in the X-ray diagrams of the inner layers of scale. The color of the FeS-CrS constituent changes from a distinct brassy-yellow in the outer layer to a light gray in the inner layer, due perhaps, to the higher proportion of chromium in the inner layers. The amount of pitting was much more pronounced in the inner layers and may be responsible for the dull appearance of these layers when examined visually. Fig. 21 shows that inclusions of the FeS-CrS constituent extended into the metal.

DISCUSSION OF ACTION OF OXYGEN AND HYDROGEN SULPHIDE ON IRON-CHROMIUM ALLOYS

The action of oxygen and of hydrogen sulphide upon iron-chromium alloys may now be considered in connection with the mechanism of scaling that has been developed.

Oxidation of Iron-Chromium Alloys—The characteristics of the various types of scale produced offer an explanation for the increase in the resistance of the iron-chromium alloys to oxidation as the chromium content of the alloys increases. The oxidation of the 12

per cent chromium alloy at temperatures of 1100 degrees Cent. and below resembles that of iron in that the two oxides Fe_2O_3 and Fe_3O_4 are formed, and consequently the transfer of oxygen inward and of metal outward is facilitated. In stating that there is a transfer of metal outward the authors wish to make clear that they are not inferring that there is necessarily a transfer of the metal in the metallic state, but only that there is a building up of the scale at the surface through a transfer of material outward through the scale as well as a continual formation of oxidized products at the scale-metal interface. As the chromium content of the scale increases the rate of scaling decreases and this effect is undoubtedly connected with the more stable character of the higher chromium scale. It is well known that chromium and aluminum, which form much more stable oxides than does iron, are also much more resistant to continued oxidation. This higher resistance to oxidation of the former metals is probably due to lower solubilities of the metals and of oxygen in the oxides together with the fact that oxides of a single composition are formed so that there is no possibility of oxidation-reduction reactions between oxides of different states of oxidation or between the metals and their oxides.

Some explanation must be found for the differences in composition of the scale. Preferential oxidation alone is evidently not sufficient, for chromium is more readily oxidized than iron until a definite layer of oxide is formed and the scale on the lower chromium alloy contained practically no chromium in the outer layer. It would seem that the differences in composition must be due to diffusion through the scale and the following explanation is offered. The first step of the oxidation process results in the formation of a surface layer of oxides of chromium and iron in which these metals are in the same proportions as in the original alloy. It is probable that chromic and ferric oxides are formed, since the pressure of oxygen in the furnace is greater than the dissociation pressure of either of these oxides; and furthermore, it is likely that these oxides are in the form of a solid solution since they have been shown to be completely miscible in the solid stage.^{20, 21, 22} Once this oxide layer is formed by direct oxidation then further oxidation must involve diffusion as well as chemical reactions. At the interface no oxide can be formed ex-

²⁰Wretblad, *Z. anorg. allgem. Chemie*, Vol. 189, 1930, p. 329-36.

²¹Passerini, *Gazz. Chim. Ital.*, Vol. 60, 1930, p. 544-58.

²²Forestier and Chaudron, *Comptes Rendus*, Vol. 180, 1925, p. 1264-6.

cept by reaction with the scale or with dissolved oxygen which has diffused through the scale. If the maximum possible partial pressure of oxygen from these sources is less than that of the most stable oxide of iron then there can be no reaction between either the scale or the dissolved oxygen with the iron of the alloy. Under these circumstances only chromium will be oxidized and the reaction occurring at the metal-scale interface will be strictly a preferential oxidation of the chromium. If there is no appreciable solubility of iron in chromium oxide the amount of iron that diffuses to the scale-gas interface will be small and the scale will consist largely of chromic oxide. This is evidently the situation when alloys that contain more than about 25 per cent of chromium are oxidized at temperatures up to 1100 degrees Cent. It is apparent that once the chromium content of the initial scale is sufficient to prevent continued oxidation of iron then higher amounts of chromium can not further increase the resistance of the alloys to oxidation.

Carrying this concept a step further it is seen that when the chromium content of the initial layer of scale is somewhat less it becomes possible for iron as well as chromium to be oxidized at the scale-metal interface. The presence of iron in the scale increases the ability of the latter to transmit oxygen, possibly because of a series of oxidation-reduction reactions between different iron oxides. Some chromium may diffuse outward through the scale as metal or oxide, but evidently iron or iron oxide diffuses much more readily and the portion of the scale that builds up beyond the original surface of the specimen is largely iron oxide. This is shown by the chemical composition of the scale from the 12 per cent chromium alloy, the outer layer of which was mostly iron oxide while the inner layer contains a higher proportion of chromium than did the original alloy.

The foregoing concept of the scaling process explains the form of the composition-oxidation curves shown in Fig. 5. At the higher percentages of chromium the rate of oxidation is very low and apparently does not change appreciably as the chromium content increases. As the amount of chromium decreases the rate of oxidation suddenly begins to rise rapidly until the amount of chromium reaches a certain value below which this element has very little effect. It should be remembered that these curves are for a particular temperature and that at other temperatures these particular critical values of the chromium content may be different than at the temperatures for which these curves apply.

It was concluded from the proposed mechanism of oxidation that at extremely low oxygen pressures an alloy high in chromium would oxidize more than one containing less chromium. To check this conclusion the following tests were made. Specimens of alloys containing 12 and 28 per cent chromium were heated for 150 hours at 980 degrees Cent. in a furnace that was continuously evacuated during this time. A similar test was made with the specimens packed in chromic oxide and heated in the evacuated furnace. During both these tests the pressure within the furnace was of the order of 0.0005 millimeter of mercury. It was found that the loss of weight of the higher chromium alloy due to oxidation was more than ten times that of the other. When similar tests were carried out with the specimens packed in finely powdered ferric oxide it was found that, even though the evacuation was continuous as before, the pressure within the furnace was considerably greater and in this case the lower chromium alloy oxidized fully as much as the other and both oxidized more than in the other tests. The scale resulting from these tests was not analyzed but that formed on both alloys in the first tests was distinctly green in color, indicating that it was chiefly chromium oxide, while that formed in contact with iron oxide was black in color and probably contained considerable iron oxide.

Action of Hydrogen Sulphide on Iron-Chromium Alloys—As a result of the action of hydrogen sulphide upon the alloys under discussion scale was produced that consisted principally of a single phase, and there is consequently little possibility of a series of reactions within the scale itself. The relatively high rates of scaling in hydrogen sulphide are very probably due to a high solubility of sulphur and of the metals in the scale. Both iron and sulphur are known to be quite soluble in FeS,²³ and it is probable that chromium is appreciably soluble in the FeS-CrS solid solution. Under these conditions sulphur will be readily transferred inward through the scale, and both iron and chromium as the dissolved metals or as sulphides comparatively low in sulphur, will be transferred outward. It must be concluded that the transfer of iron in this way is the more rapid, since the outer layer of scale was found to be largely FeS with excess sulphur. There must, however, also be some transfer of chromium in this manner since the second layer of scale which was outside the original surface of the specimen was found to contain a considerable

²³Benedicts and Löfqvist, "Non-metallic Inclusions in Iron and Steel," 1931, p. 14.

proportion of this element. This slower rate of diffusion of chromium may be the reason for the slightly greater resistance of the higher chromium alloy to attack by hydrogen sulphide.

Effect of Temperature and Time—It has already been shown that the temperature coefficients of reaction that were found are consistent with the hypothesis that rates of diffusion determine the rate of scaling under the conditions of this work. There are not enough data available to explain the difference in the forms of the temperature-scaling curves for scaling in oxygen and in hydrogen sulphide.

The relation of time and the amount of diffusion of a material is expressed by the relationship $dW = -D \frac{dc}{dx} dt$, that has already been given. If it be assumed that D remains constant, that x , the thickness of the layer through which diffusion takes place, is proportional to W , the amount of substance which has diffused at a given time, and that the concentration gradient, $\frac{dc}{dx}$, of the diffusing substance is inversely proportional to the thickness of the layer through which diffusion takes place, then the foregoing equation leads to the relationship $W^2 = kt$, where k is a constant under a given set of conditions. The derivation of this expression has already been given in the literature^{14, 24} and will not be repeated here. The relation of time to amount of scaling was found in the present work to follow equations of the form $W^n = kt$, where n was 2 in the case of the oxidation of a low carbon steel containing no chromium and was less than 2 in every other case. This means, of course, that in the latter cases the amount of scaling was more nearly proportional to the time than the ideal integrated form which the diffusion law requires. This does not necessarily mean that diffusion is not the determining factor, but may mean that the assumptions upon which the integration is based are not strictly true. Physical changes in the scale such as fissuring or changes in chemical composition during the process of scaling would change the value of D , and the latter factor might also change the relation of the concentration gradient to the thickness of the scale.

It is evident that there are several points in connection with the mechanism of scaling of these alloys on which more information is

¹⁴Pilling and Bedworth, Loc. cit.

²⁴Dunn, *Proceedings*, Royal Society, London, Vol. 111A, 1926, p. 210-19.



desirable, but the hypothesis that has been offered is not inconsistent with any of the results observed in the present work and seems to offer a working basis for explaining the behavior of iron-chromium alloys in atmospheres of the type studied.

SUMMARY AND CONCLUSIONS

The most important results of this investigation may be briefly summarized as follows.

1. The resistance of iron-chromium alloys to oxidation at a given temperature increases relatively slowly at first and then very rapidly as the chromium content of the alloys increases. A chromium content is finally reached beyond which further additions of this element have little additional effect.

2. The scaling of these alloys in hydrogen sulphide at temperatures of from 760 to 1090 degrees Cent. (1400 to 2000 degrees Fahr.) is much greater and the effect of increasing amounts of chromium is much less than in oxygen under similar conditions.

3. The rate of scaling in both oxygen and hydrogen sulphide decreased as the time increased and, except in the case of oxidation of a 28 per cent chromium alloy, increased rapidly as the temperature increased up to 1090 degrees Cent. (2000 degrees Fahr.).

4. The increased resistance to oxidation of the higher chromium alloys was found to be accompanied by a great increase in the proportion of chromium in the scale.

5. Observations of the character of the scale and a consideration of the published results of another investigation support the hypothesis that there is a diffusion of both the reacting gas or of higher products of reaction inward and of the metal or of lower products of reaction outward through the scale.

6. On the basis of such a hypothesis it is possible to explain the effect of chromium content on the resistance to oxidation and to attack by hydrogen sulphide, and to account for the compositions of the various types of scale. The effects of temperature and of time are not inconsistent with this hypothesis.

ACKNOWLEDGMENTS

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