INFLUENCE OF OXIDE FILMS ON THE WEAR OF STEELS

By Samuel J. Rosenberg and Louis Jordan

ABSTRACT

The effect of oxygen-free atmospheres (nitrogen and hydrogen) upon the wear of a hypoeutectoid, a eutectoid, and a hypereutectoid carbon steel was studied. It was found that when these steels were hardened and subsequently tempered at low temperatures, the rates of wear were comparatively low; the wearing surfaces were smooth and were covered by a thin oxide film and the abraded particles consisted of Fe₂O₃ and Fe₃O₄. When these steels were tempered above certain temperatures, the rates of wear were extremely high; the worn surfaces were very rough and bright and the abraded particles were metallic iron.

Microscopic examination showed that those steels which had rough, film-free worn surfaces had severely distorted structures adjacent to these surfaces. In the case of steels which showed only the filmed, worn surfaces, the structures adjacent to these surfaces were not greatly changed by the wear test and the worn surfaces themselves were smooth. The severely distorted structure was also observed in the case of certain steels which showed characteristics of both types of wear. Numerous cracks intersecting or approximately parallel to the worn surfaces were observed in the microexaminations of both types of surfaces.

These tests indicated that a film of either ferric or ferroso-ferric oxide on the wearing surfaces of carbon steels results in a certain degree of protection against wear, probably by preventing actual metal-to-metal contact. When these films are absent, severe wear of a galling type takes place.

I. Introduction ........................................................................................................................................ 267
II. Methods of testing .................................................................................................................................. 269
III. Repetition of Fink’s experiments ........................................................................................................... 269
IV. Effects of atmosphere and heat treatment on the wear of steels ...................................................... 270
   1. Wear of a eutectoid carbon steel ......................................................................................................... 270
      (a) Comparison of type and rate of wear in different atmospheres ...................................................... 270
      (b) Comparison of type and rate of wear after different tempering treatments .................................. 271
   2. Wear of a hypoeutectoid and a hypereutectoid carbon steel ............................................................. 274
   3. Summary of the wear tests .................................................................................................................. 274
V. Microstructural characteristics of the steels adjacent to the worn surfaces ........................................... 275
VI. Nature of the particles abraded from the specimens ............................................................................ 276
VII. Discussion ............................................................................................................................................ 277
VIII. Summary and conclusions .................................................................................................................. 279

I. INTRODUCTION

Marked advances in many phases of the testing of metals have taken place in recent years, yet little or no real progress in developing the fundamentals of the wear testing of metals has been achieved. This is probably because of the complexity of this particular problem, the difficulty in separating the numerous factors of service conditions which influence wear, and the consequent difficulty in properly understanding and evaluating the individual effects of these factors upon the mechanism and nature of wear.

267
The logical method of attacking the general problem of wear of metals is to attempt to separate these factors which occur in service and to study the effect of each upon the wear. The factor selected for study and reported in this paper is that of the effect of the presence or absence of oxygen in the atmosphere surrounding the wearing surfaces of metals.

The appearance of films upon the wearing surfaces of metals has frequently been observed. It has been accepted that these films influenced the results obtained in wear testing; in some cases attempts have been made to minimize or prevent the formation of films by mechanical means, while in other cases the films have been allowed to form and remain on the assumption that they are a natural phase of the wearing process.

An hypothesis as to the effect of oxide films upon the wear of metals has been advanced by Fink, as a result of tests on steel in oxygen-free atmospheres. The wearing surfaces at the conclusion of his tests were very smooth and shiny and the specimens had suffered no wear. When the same steels were tested in air, the surfaces were covered with oxide films and an appreciable amount of wear took place. This phenomenon of film formation Fink terms "wear oxidation" and, according to his theory, oxygen is essential if wear is to take place between two metallic surfaces.

---

II. METHODS OF TESTING

An Amsler wear-testing machine (the same type as used by Fink) was used for the tests described in this paper. In this machine wear takes place on the circumferences of 2 specimens 2 in. in diameter and 0.4 in. thick, mounted on parallel horizontal shafts as shown in figure 1. An oval cell to inclose the specimens and maintain the desired atmosphere during test was constructed as also shown in figure 1.

The cell was closed for each test with a strip of lead foil about 0.006 in. thick. This foil was pressed tightly against the grooved circumference of the brass side walls of the cell by means of two rubber gaskets and two brass strips which could be tightened by means of a screw. The lapped joint in the lead envelope was sealed with a mixture of beeswax and rosin.

Hydrogen was used for the oxygen-free atmosphere in the majority of the tests. Nitrogen was used in a few tests. Both gases were purified in the train shown in figure 2. The rate of flow of gas, observed from the bubbles through the sulfuric acid, was kept fairly rapid in order to maintain a pressure slightly above atmospheric within the cell. The purified gas was allowed to flow through the cell for at least 15 minutes before starting each run. Gas analyses, sensitive to 0.03 to 0.04 percent oxygen, failed to indicate the presence of oxygen in the gas leaving the cell.

The test specimens were washed in carbon tetrachloride, dried, and weighed before and after each test; the losses in weight were used as a measure of the wear. The oscillating motion of the upper head of the Amsler machine was not used in any of the tests.

III. REPETITION OF FINK’S EXPERIMENTS

An effort was first made to duplicate the results reported by Fink. He tested a 0.65 percent carbon steel, having an ultimate tensile strength of approximately 115,000 lb/in.² in an atmosphere of nitrogen under a load of 59 kg and with 1 percent slip. Of the steels available, that most nearly approximating 0.65 percent carbon had the following composition:

\[
\begin{array}{ll}
\text{C} & 0.58 \\
\text{Mn} & 0.29 \\
\text{P} & 0.014 \\
\text{S} & 0.018 \\
\text{Si} & 0.27
\end{array}
\]

Slip of approximately 1 percent between the wearing surfaces was obtained by mounting a specimen of 2.186 in. diameter on the upper shaft of the machine and one of 2.0 in. diameter on the lower shaft.
All of the specimens were normalized at 825 C, water quenched from 800 C and tempered at 625 C. This heat treatment gave a Brinell hardness number of 230, which corresponds to a tensile strength of approximately 110,000 lb/in.².

Results of tests made under these conditions in atmospheres of hydrogen, nitrogen, and air are summarized in table 1.

### Table 1 — Wear of 0.58 percent C steel in different atmospheres under 50 kg load and 1 percent slip

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Specimen</th>
<th>Rate of wear — Loss in grams per 10,000 revolutions of lower specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Upper</td>
<td>0.06</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Lower</td>
<td>0.05</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Upper</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
</tr>
</tbody>
</table>

The rates of wear of all these specimens were appreciable and there was no significant difference between the tests in hydrogen, nitrogen, or air. The surfaces of the specimens tested in hydrogen and in nitrogen were light gray in color, while the surfaces of the specimens tested in air were dark gray. All of the surfaces had a characteristic rippled appearance as shown in figure 3.

These results were not in agreement with Fink’s observation that wear occurred only in the presence of oxygen.

### IV. EFFECTS OF ATMOSPHERE AND HEAT TREATMENT ON THE WEAR OF STEELS

#### 1. WEAR OF A EUTECTOID CARBON STEEL

(a) COMPARISON OF TYPE AND RATE OF WEAR IN DIFFERENT ATMOSPHERES

Eutectoid carbon steel (0.81 percent carbon) was chosen for further study of the effect of atmosphere upon wear. The first tests of this steel in atmospheres of hydrogen and of nitrogen were made under 60 kg load and 10 percent slip and with specimens which had been hardened and subsequently tempered at 260 C (details of composition and heat treatment are given in table 4).

Worn surfaces which were smooth and covered by a reddish-brown film, sometimes streaked with black, were produced by these tests. The frictional torque was high, about the same as when identical specimens were tested in air, and the rate of wear was generally somewhat lower than when similar specimens were tested in air. (See table 2.) It was rather surprising that the wearing surfaces were covered with films, apparently of oxides, when tested in “oxygen-free” hydrogen or nitrogen. A probable explanation of this phenomenon is advanced in a later section of this paper.

In all these cases both the upper and lower specimens had been tempered at 260 C. In a subsequent test, however, a specimen which had been tempered at 400 C was inadvertently tested against one tempered at 260 C. The results in this case were markedly different.
Figure 3.—Worn surfaces of steels tested in hydrogen under 50 kg load and 1 percent slip. × 1 3/4.
The wearing surfaces of both specimens were bright with no trace of film; they were also very rough and the wear of the specimen tempered at 400 C was relatively enormous. The wear rates per 10,000 revolutions were as follows:

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper specimen (tempered at 400 C)</td>
</tr>
<tr>
<td>Lower specimen (tempered at 260 C)</td>
</tr>
</tbody>
</table>

Additional tests, in both oxygen-free hydrogen and in moist hydrogen, of specimens tempered at 400 C gave excessively high wear rates and rough, film-free surfaces. When specimens tempered at 260 C were tested in air, the wear rate was 0.03 gram and when both were tempered at 400 C, the rate was 0.06 gram. In both of these cases the surfaces were smooth and filmed. The frictional torque developed during the tests in hydrogen was lower than when specimens of the same steel treated in the same way were tested in air. A photograph of specimens showing the "smooth, filmed" type of worn surface and the "rough, bright" type of worn surface after testing in hydrogen is shown in figure 4. These two groups of specimens (one tempered at 260 C and the other at 400 C) were also tested in oxygen.

Table 2 summarizes the results of all of these tests. There were no significant differences between the effects of any of the media surrounding the specimens tempered at 260 C. The wear rates of these specimens were low in all five atmospheres; the worn surfaces were smooth and filmed. In the case of the specimens tempered at 400 C the results of the tests in air were similar to the results obtained in all types of atmospheres with the specimens tempered at 260 C, i.e., the surfaces were smooth and filmed and the wear rates were low. When specimens tempered at 400 C were tested in hydrogen atmospheres, however, the wear rates were high and the surfaces were rough and bright. This effect was noted in both moist and dry hydrogen.

Table 2.—Tests of 0.81 percent carbon steel in different atmospheres

<table>
<thead>
<tr>
<th>Tested in—</th>
<th>Wear rate—Loss in grams per 10,000 revolutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen.</td>
<td>Tempered at 260 C: 0.001-0.005 (18 determinations). Tempered at 400 C: 0.4-1.0 (8 determinations).</td>
</tr>
<tr>
<td>Moist hydrogen.</td>
<td>0.01 (2 determinations).</td>
</tr>
<tr>
<td>Nitrogen.</td>
<td>0.004-0.006 (2 determinations).</td>
</tr>
<tr>
<td>Oxygen.</td>
<td>0.03 (2 determinations).</td>
</tr>
<tr>
<td>Air.</td>
<td>0.03 (2 determinations).</td>
</tr>
</tbody>
</table>

Note.—Each value represents the slope of a weight-loss-revolutions curve of a separate specimen determined by a series of wear tests, each of which ran for 10,000 revolutions. The values given are the minimum and maximum obtained.

(b) COMPARISON OF TYPE AND RATE OF WEAR AFTER DIFFERENT TEMPERING TREATMENTS

The marked change observed in the preceding tests in both the type and rate of wear raised the question whether this change occurred gradually with increasing tempering temperature, or whether the transition occurred abruptly. A series of specimens tempered at various temperatures was therefore tested in hydrogen and in air. All these specimens were 0.81 percent carbon steel except the specimens tempered at 150 C, which were 0.88 percent carbon steel. The results of these tests are summarized in table 3.
### Table 3.—Effect of tempering temperature on the wear of carbon steels in different atmospheres

[60 kg load—10 percent slip]

**0.81 PERCENT CARBON STEEL**

<table>
<thead>
<tr>
<th>Tested in</th>
<th>Not tempered</th>
<th>Tempered at 150 C</th>
<th>Tempered at 200 C</th>
<th>Tempered at 250 C</th>
<th>Tempered at 300 C</th>
<th>Tempered at 350 C</th>
<th>Tempered at 400 C</th>
<th>Tempered at 500 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.008-0.02 (4 determinations). Smooth, filmed.</td>
<td></td>
<td></td>
<td>0.001-0.02 (4 determinations). Smooth, filmed.</td>
<td>0.01-0.02 (4 determinations). Smooth, filmed.</td>
<td>2.0-4.0 (2 determinations). Rough, bright.</td>
<td>0.2-0.4 (2 determinations). Rough, bright.</td>
<td>0.4-16.0 (8 determinations). Rough, bright.</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**0.43 PERCENT CARBON STEEL**

<table>
<thead>
<tr>
<th>Tested in</th>
<th>0.002-0.016 (4 determinations). Smooth, filmed.</th>
<th>0.10 (2 determinations). Rough, bright during first run. Smooth, filmed during succeeding runs.</th>
<th>0.12 (2 determinations). Type of wear alternated between rough, bright and smooth, filmed.</th>
<th>0.23-0.31 (2 determinations). Rough, bright during first few runs. Smooth, filmed during last two runs.</th>
<th>0.34-0.44 (2 determinations). Rough, bright during first few runs. Type of wear alternated during last three runs.</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>0.04-0.06 (2 determinations). Smooth, filmed.</td>
<td>0.07-0.09 (2 determinations). Smooth, filmed.</td>
<td>0.06-0.09 (2 determinations). Smooth, filmed.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.007-0.014 (2 determinations)</td>
<td>Smooth, filmed.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01-0.1 (4 determinations)</td>
<td>No films during first run in each test. Film formed during second run and remained.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03-0.1 (2 determinations)</td>
<td>Smooth, filmed.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 This steel contained 0.88 percent carbon.
They show that a "critical" range of tempering temperatures exists in the 0.81 percent carbon steel between 290 and 320°C. Specimens tempered above this temperature range and tested in hydrogen had rough, bright worn surfaces and the rate of wear was extremely high as compared with the rate in air. Specimens tempered below this temperature range and tested in hydrogen had smooth, filmed worn surfaces; the rate of wear was usually lower than that obtained upon testing in air and the films formed were usually considerably lighter in color.

2. WEAR OF A HYPOEUTECTOID AND A HYPEREUTECTOID CARBON STEEL

Similar tests were made on a hypoeutectoid carbon steel (0.43 percent carbon) and a hypereutectoid carbon steel (1.26 percent carbon) to determine whether the wear phenomena observed in the eutectoid steel would also be evident in steels of lower and higher carbon content.

The data obtained in the tests on these steels are also given in table 3. The same general effects of atmosphere and tempering temperature were evident in these steels, that is, a critical range of tempering temperatures existed in each steel. The "critical" tempering range was lower (between 200 and 230°C) for the hypoeutectoid steel and was higher (between 400 and 500°C) for the hypereutectoid steel than for the eutectoid steel. As in the case of the eutectoid steel, the rates of wear of these steels in air increased but slightly with increase of tempering temperature; the type of wear remained the same in all tests in air.

3. SUMMARY OF THE WEAR TESTS

A general summary of the significant features of the wear tests in oxygen-free hydrogen is presented in table 4. The compositions and heat treatments of the steels are also given in this table.

Table 4.—Summary of the wear of steels in hydrogen

<table>
<thead>
<tr>
<th>Composition (percent)</th>
<th>Heat treatment</th>
<th>Tempering temperature °C</th>
<th>Rockwell &quot;C&quot; number</th>
<th>Type of worn surface</th>
<th>Rate of wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 0.43……………..</td>
<td>Water quenched from 835°C</td>
<td>None.</td>
<td>58</td>
<td>Smooth, filmed</td>
<td>Low.</td>
</tr>
<tr>
<td>Mn .03………….</td>
<td></td>
<td>200</td>
<td>53</td>
<td>Borderline</td>
<td>High.</td>
</tr>
<tr>
<td>P .03……………</td>
<td></td>
<td>290</td>
<td>52</td>
<td>Rough, bright, clean</td>
<td>Do.</td>
</tr>
<tr>
<td>Si .28……………</td>
<td></td>
<td>320</td>
<td>48</td>
<td>do</td>
<td>Do.</td>
</tr>
<tr>
<td>C 0.81……………..</td>
<td>Normalized 810°C; water quenched from 770°C</td>
<td>150</td>
<td>64</td>
<td>Smooth, filmed</td>
<td>Low.</td>
</tr>
<tr>
<td>Mn .30……………</td>
<td></td>
<td>290</td>
<td>56</td>
<td>Borderline</td>
<td>Do.</td>
</tr>
<tr>
<td>P .024……………</td>
<td></td>
<td>290</td>
<td>54</td>
<td>Rough, bright, clean</td>
<td>High.</td>
</tr>
<tr>
<td>Si .28……………</td>
<td></td>
<td>320</td>
<td>47</td>
<td>do</td>
<td>Do.</td>
</tr>
<tr>
<td>C 1.26……………..</td>
<td>Normalized 925°C; annealed 760°C</td>
<td>39</td>
<td>59</td>
<td>Smooth, filmed</td>
<td>Low.</td>
</tr>
<tr>
<td>Mn .30……………</td>
<td></td>
<td>400</td>
<td>48</td>
<td>Borderline</td>
<td>Do.</td>
</tr>
<tr>
<td>P .024……………</td>
<td></td>
<td>500</td>
<td>39</td>
<td>Rough, bright, clean</td>
<td>High.</td>
</tr>
<tr>
<td>Si .28……………</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Steel used for this treatment contained 0.88 percent C.
Figure 4.—Worn surfaces of steels tested in hydrogen under 60 kg load and 10 percent slip. × 1\(\frac{1}{3}\).

a and b, Smooth, filmed surfaces; c and d, bright, rough, film-free surfaces.
Figure 5.—A, Structure adjacent to rough, film-free, worn surface of a specimen tested in hydrogen.

Note cold-worked surface layer. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 230° C. Rockwell C number 52.6.) × 100.

B, Same specimen as A, but another area.

Note cracks beneath the surface outlining a lenticular area in the initial stages of separating from the wearing surface. × 500.

Both etched with 1 percent nitric acid in alcohol.
Figure 6.—A, Structure adjacent to the smooth, filmed, worn surface of a specimen tested in hydrogen.
The martensitic needles are deformed just below the surface. (Steel—0.43 percent carbon, water quenched from 835° C and not tempered. Rockwell C number 58.2.)

B, Structure adjacent to the wearing surface of a specimen tested in hydrogen.
This specimen had a rough film-free surface during the first test. In subsequent tests, the surface became filmed. Note cracks beneath and parallel to the wearing surface. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 290° C. Rockwell C number 56.2.)

C, Structure adjacent to the smooth, filmed, worn surface of a specimen tested in air.
Note cracks beneath and parallel to the wearing surface. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 320° C. Rockwell C number 54.1.)

All × 500. All etched with 1 percent nitric acid in alcohol.
Figure 7.—A, Structure adjacent to the worn surface of a specimen tested in hydrogen.
The part of the surface shown here was roughened, but filmed. Note cold-worked layer. *(Steel—0.81 percent carbon, water quenched from 770°C and tempered at 260°C. Rockwell C number 59.1.) \( \times 100. \\

B, Same location as A.
Note cracks in cold-worked layer. \( \times 500. \\

C, Same specimen as A, but showing structure adjacent to the smooth filmed surface.
All etched with 1 percent nitric acid in alcohol. \( \times 500. \\

J o u r n a l  o f  R e s e a r c h  o f  t h e  N a t i o n a l  B u r e a u  o f  S t a n d a r d s  \\
R e s e a r c h  P a p e r  7 0 8
It is worthy of note that under the conditions of loan and slip employed in these tests, steels treated to a Rockwell "C" number of about 56 or higher invariably showed the smooth, filmed type of worn surface in oxygen-free atmospheres. Steels softer than this value had either a border line or a rough, film-free type of worn surface.

V. MICROSTRUCTURAL CHARACTERISTICS OF THE STEELS ADJACENT TO THE WORN SURFACES

Several representative specimens were subjected to a microscopic examination after the wear tests. In the following discussion of the microstructural characteristics the phrase "structure at the surface" is used to indicate not only the regularity of the contour of the actual surface but also the structure of a relatively thin layer of metal immediately below the surface; the phrase "interior structure" designates the structure of the steel at a distance below the worn surface, where it was not affected by the wear test.

Two characteristic types of structures were found adjacent to the worn surfaces. Specimens having the rough, film-free type of worn surface after testing in oxygen-free atmospheres had severely cold worked surface layers. Numerous cracks, evidently caused by the stresses developed during the wear tests, were present at and just below the wearing surfaces. Areas of severely distorted metal frequently lenticular in section and outlined by cracks, were characteristic of the surface structure (see fig. 5).

Specimens having the smooth, filmed type of worn surface after testing either in air or in oxygen-free atmospheres showed a relatively smooth contour of the wearing surfaces under the microscope (see fig. 6 a and c). There was but little evidence of distortion of the layers immediately below the surfaces except for some cracks approximately parallel to the wearing surfaces.

Some specimens started wearing with rough, film-free surfaces but as the tests progressed formed surface films. This type of wear is designated as a borderline type. Micro examinations of such specimens showed that the surface structures characteristic of wear producing a rough, bright surface were still very evident after the surfaces had become covered with films (see figs. 6 b, 7 a and b).

The structures shown in figure 7 a and b were rather unusual with respect to the type of surface developed in the wear tests. All the way around the specimen in the middle of the wearing surface there was a somewhat roughened, although filmed, area. On both sides of this roughened surface was a relatively smooth, filmed surface. This specimen might have been expected, on the basis of the preceding tests, to have had a smooth, filmed, worn surface because of its low tempering temperature. The interior structure of this specimen etched somewhat darker below the rough surface (fig. 7 b) than below the smooth surface (fig. 7 c). This suggests that for some reason the interior structure was more troostitic and therefore slightly softer below the rough, worn surface than below the smooth, worn surface. This may have been the reason for the two different types of wear observed on this specimen.

A very interesting phenomenon developed during the tests of the 0.88 percent carbon steel in hydrogen. After the first test in hydro-
gen, four heavily worn areas appeared on the wearing surface of one of the specimens. Whereas this specimen, due to its low tempering temperature, had the smooth, filmed type of worn surface, these spots were rough, even though they were covered by a thin film. Their appearance was quite similar to that of specimens which normally exhibited film-free, heavily worn surfaces at first and then formed a film either because of an imperfection in the hydrogen gas train or for other causes which will be discussed later. The locations of these rough spots were marked, the specimen was resurfaced and tested again. The spots reappeared in the same locations and with the same shapes as before. Their appearance is shown in figure 8. Rockwell "C" scale readings, made at the locations indicated, are given in this figure.

Apparently these four areas were soft spots, the hardnesses of which were about equal to or lower than the hardness of the eutectoid steel specimens which showed the borderline type of wear in hydrogen. This lower hardness was apparently the cause of the development of the rough areas in an otherwise smooth, worn surface.

Figure 9 shows the structures at the wearing surface of a section cut through one of these rough areas. The worn surface is irregular and shows a thin layer of severely deformed material containing cracks. The interior structure consists of troostite, tempered martensite and free carbides. The presence of the troostite explains the lowered hardness. Figure 10a shows the transition from the rough to the smooth worn surface; it is evident that this transition coincides with the disappearance of the troostitic areas. The structure at the wearing surface of the material which is free from primary troostite is shown in figure 10 b. The wearing surface here was smooth.

VI. NATURE OF THE PARTICLES ABRATED FROM THE SPECIMENS

The abraded particles produced during each test varied with the type of wear. When smooth, filmed surfaces resulted from wear, the amount of abraded particles was small and the color was very dull gray or brownish-black, usually the latter. When bright, rough, film-free surfaces were formed, the amount of abraded particles was large and the color was a very bright gray with no trace of either red or black.

Two samples of abraded particles were examined by X-rays using the powder method and Mo Kα radiation, to determine whether they were iron or iron oxide. One sample (A) consisted of the red and reddish-black particles from the smooth and slightly filmed surfaces formed in testing in an atmosphere of hydrogen 2 specimens of 0.81 percent carbon steel tempered at 200 C. The other sample (B) consisted of bright, light-gray particles from the extremely rough and bright surfaces formed in testing in an atmosphere of hydrogen 2 specimens of 0.81 percent carbon steel tempered at 320 C.

Sample A consisted of Fe₃O₄ and Fe₂O₃. Neither free FeO nor free iron was detected. Sample B gave the pattern of highly distorted iron; no lines representing iron oxides were present. This was not

---

The authors are indebted to F. Sillers, jr., Research Associate at the National Bureau of Standards for these X-ray examinations.
FIGURE 8.—Specimen showing heavily worn areas after testing in hydrogen.
(Steel—0.88 percent carbon, water quenched from 770° C and tempered at 150° C. Rockwell C number 64.1.) X 3.
Figure 9.—A, Structure adjacent to the worn surface of a section through one of the rough areas of the specimen shown in figure 8.

The presence of primary troostite is evidence of incomplete hardening. Note the rough, deformed surface layers. × 100.

B, Same location as A.

Note the metallic particle partially separated from the wearing surface. × 500.

Both etched with 1 percent nitric acid in alcohol.
Figure 10.—A, Same specimen as figure 8, showing the transition from the rough to the smooth, worn surface.

This transition zone is also marked by the disappearance of the troostitic areas.  X 100.

B, Same specimen as figure 8; showing the structure adjacent to the smooth, filmed, worn surface.

The structure is tempered martensite with a few free carbides.  X 500.

Both etched with 1 percent nitric acid in alcohol.
evidence, however, that very thin oxide films were not present on the surfaces of these particles, since such thin films would not be detected by the X-ray examination.

These results confirmed the supposition that the films formed in "oxygen-free" atmospheres under conditions producing smooth, filmed, worn surfaces were indeed oxide films.

VII. DISCUSSION

Evidence has been gathered during this work definitely contradictory to Fink's conclusion that no wear takes place between two metallic surfaces unless oxygen is present in the surrounding atmosphere. On the contrary, the absence of appreciable amounts of oxygen in the atmosphere surrounding many of the steel specimens tested was conducive to greatly increased wear. The apparent explanation is that there is no opportunity for the wearing surfaces to become covered with a protective oxide film which prevents actual metal-to-metal contact.

It is to be noted that the carbon steels tempered at the lower temperatures formed oxide films even when tested in gases (hydrogen or nitrogen) substantially free from oxygen. It was impossible to remove all traces of oxygen from the interior of the cell used in the wear tests by flushing the cell with purified gas. When 2 specimens are worn against each other, as in the Amsler machine, a fresh, chemically active surface is probably produced which combines readily with any traces of oxygen in the cell. The frictional heat generated at the surfaces of contact naturally tends to assist this reaction. Thin oxide films can, therefore, form on the specimens even in the "oxygen-free" gas.

The question arises why the same process does not occur with the carbon steels tempered at the higher temperatures. It probably does, but apparently the film which forms on these steels is not able to prevent seizing and galling and the resultant excessive wear. The lack of protective action of the oxide film in such instances may be dependent on the physical properties of the steels.

It has been pointed out that the steels which developed smooth, filmed surfaces in an atmosphere of hydrogen were those which had high hardness numbers and the steels which developed rough, bright, film-free surfaces had lower hardness numbers. In the discussion of the microstructures it was shown that a rough surface contour with a very severely distorted layer beneath was a characteristic of the film-free, worn surface. The softer steels, when subjected to wear, deformed under the influence of the various stresses and it is postulated that the oxide film which initially formed was immediately ruptured because of the deformation of the surface on which it formed. The ruptured film permitted actual metal-to-metal contact, seizure over small local areas, and finally, galling and excessive wear.

This deformation was not so apparent in the steels having a smooth, filmed, worn surface. Here it is postulated that the steel had sufficient strength to resist the stresses developed during the wearing action and the oxide film had a firm base upon which to form. Once formed, this film maintained its continuity and further wear, as a rule, failed to destroy it. True metal-to-metal contact was prevented
by the oxide film between the two specimens and as a result wear was relatively low.

In certain tests rough, though filmed, areas were observed on specimens which were expected to show smooth, filmed surfaces (see figs. 7 a and b, 8, 9 a and b, and 10 a). It has been pointed out that this might be attributed to the presence of troostite, i.e., the strength of the steels was lower in these spots. It has also been noted that frequently a specimen had a bright, rough, film-free surface during one or more tests and then changed to a filmed surface. This phenomenon may be caused by work-hardening of the surface. Initially these areas may have been too soft to support a film; after a certain amount of wear, however, they work-hardened to such an extent that they were able to support a film. This delayed film formation was noted on many of the specimens in the so-called "border-line group". As the tempering temperature increased this tendency became less marked.

It has just been mentioned that this film, once formed, was not removed ordinarily by subsequent wear tests in an oxygen-free atmosphere. Only two exceptions to this statement were noted; these were tests made on specimens of the 0.43 percent carbon steel tempered at 230 C and at 320 C. In both of these cases the type of wear was initially film-free and rough and the rate of wear was high; after several tests of 10,000 revolutions each, films appeared and the wear rate decreased very greatly; after a few further tests the films disappeared and the rate of wear increased at once to its original high value. This behavior is illustrated in detail in figure 11.

The breakdown of the oxide film in these cases may possibly be explained on the basis of excessive deformation of the surface layer, resulting in its disintegration from severe overwork and its subsequent complete removal. A new surface was thus produced which was relatively free of any strengthening effect from cold work. As a consequence the wearing surfaces again became film-free and severe wear took place.

It has been pointed out that the carbon steels tempered below certain temperatures had smooth, filmed, worn surfaces. It is suggested that the presence or absence of severe deformation at the surfaces of the specimens, that is, the relation of the strength and hardness of the steel and the stresses developed during the wearing action, determine the type of wear. On the basis of this hypothesis,
if steels having smooth, filmed surfaces were tested under higher loads, the stresses developed might deform the surface to such an extent as to cause the breakdown of the protective oxide film. This might then result in the transition to film-free surfaces and severe wear. This was tried in the case of the 0.81 percent carbon steel tempered at 260 C, but although the load was raised in steps from 60 to 150 kg, it was impossible to secure film-free surfaces with this steel. The microstructure adjacent to the wearing surface of a specimen of this steel tested under a load of 150 kg showed no more distortion than in the same steel tested under a 60 kg load.

The microscopic study of the structures adjacent to the worn surfaces indicated how wear took place. Deformation of the surface layers of the metal was particularly severe in the case of specimens which had film-free surfaces and severe wear. This severely deformed metal was characterized by numerous lenticular areas which were partially, at times almost completely, outlined by cracks resulting from the severe overwork suffered by the surface metal. These cracks were gradually enlarged and formed paths for the fracture of metallic particles which were then considered to be "worn off." This process is especially well illustrated in figures 5 b, 6 b, 7 b, and 9 b.

Deformation of surface layers of metal was much less noticeable in specimens which had smooth, filmed surfaces and light wear. Severe cold work of the surface frequently took place as evidenced by numerous cracks below the surface. In these specimens, however, the fissures produced by overwork were generally more or less parallel to the wearing surface and did not outline lenticular areas such as were characteristic of the type of wear producing rough, film-free surfaces.

VIII. SUMMARY AND CONCLUSIONS

A study has been made of the influence of oxygen in the atmosphere surrounding specimens of carbon steels subjected to metal-to-metal wear. This work has been undertaken as the initiation of a series of studies of the fundamental factors involved in the wear of metals. These factors have hitherto received too little attention.

An Amsler machine was used to make wear tests on specimens of a hypoeutectoid, a eutectoid and a hypereutectoid carbon steel. Tests were made, both in air and in oxygen-free atmospheres (hydrogen or nitrogen), on specimens which had been given different heat treatments. Microscopic examinations were made of the structures below the wearing surfaces of the specimens after wear tests.

The data obtained indicated:

1. The rates of wear of all the steels when tested in air were low and the worn surfaces were smooth and covered with oxide films.

2. The rates of wear of the steels tempered at low temperatures and tested in an oxygen-free atmosphere were also low and the surfaces were smooth and filmed with oxides. These films, however, were lighter in color and apparently thinner than the films formed during tests in air.

3. The rates of wear of the steels tempered at higher temperatures and tested in an oxygen-free atmosphere were very high and the surfaces were very rough and free from film.
4. Microscopic examinations of the specimens having smooth, filmed, worn surfaces showed that the structures adjacent to these surfaces were somewhat distorted and occasionally contained cracks approximately parallel to the wearing surface. The contours of the worn surfaces appeared smooth even under the microscope.

5. The microstructures adjacent to rough, film-free, worn surfaces were very severely distorted. Numerous cracks, frequently outlining lenticular areas of distorted metal, were characteristic of this type of wear. The contours of these surfaces appeared extremely irregular under the microscope.

6. The results of this study are contradictory to Fink's conclusion that no wear takes place between metallic surfaces if oxygen is absent from the surrounding atmosphere. On the contrary, at least under certain conditions, the absence of oxygen is conducive to greatly increased rates of wear.

Washington, June 18, 1934.