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DETERIORATION OF STEELS IN THE SYNTHESIS OF AMMONIA

BY

J. S. VANICK, Consulting Metallurgist
Fixed Nitrogen Research Laboratory
W. W. de SVESHNIKOFF, Assistant Physicist
Bureau of Standards
J. G. THOMPSON, Associate Chemist
Fixed Nitrogen Research Laboratory

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211	2	"3.4" (not "4.3") in footnote.
223	1	"shallow" (not "shadow") in fo

DETERIORATION OF STEELS IN THE SYNTHESIS OF AMMONIA

By J. S. Vanick,[1] W. W. de Sveshnikoff,[2] and J. G. Thompson [3]

ABSTRACT

The introduction, in the United States, of nitrogen fixation by means of the synthesis of ammonia from its gaseous elements hydrogen and nitrogen at a temperature of 500° C. and a pressure of 100 atmospheres (1,500 lbs./in.^{2}) revealed a lack of information of the effect of the gas mixtures upon metals.

The plain carbon steels quickly showed their susceptibility to deterioration. Early work found some degree of success in a chrome-vanadium steel of the 0.30 per cent C, 1.0 per cent Cr, 0.18 per cent V type and this steel was used up to the time the work described in the following pages was undertaken. An acceptable steel should be easily made, readily forged and machined, and obtained at a cost that would justify its use.

Ten commercial steels, subjected to the working conditions of 500° C., 100-atmosphere pressure, and 8.3 per cent ammonia, on a laboratory scale, yielded results which indicated that—

(*a*) The carbon content should be low.

(*b*) Increasing chromium was helpful.

(*c*) Tungsten was useful.

A second test was made upon a series of chrome-vanadium steels in which carbon was varied from 0 to 1.15 per cent, chromium from 0 to 14 per cent, and vanadium from 0 to 1.65 per cent. The test showed that—

(*a*) Low carbon content was desirable.

(*b*) Vanadium contributed no perceptible improvement.

(*c*) Chromium in the amount of 2.25 per cent stopped selective penetration and intergranular fissuring and limited the depth of penetration. More chromium reduced the depth of attack, but not in proportion to the amount added, and at the risk of reducing the forgeability and machinability, with the certainty of increasing the expense.

An explanation of the mechanism of the deterioration of the steels is advanced. From the facts that oxides are reduced, carbides are decomposed, and nitrides formed in the chromium steels after a slight decarburization has been achieved, an explanation of the mechanism of the deterioration is advanced which regards ammonia as the active corrosive agent, and the metal as a porous filter which permits an ammonia enrichment to a destructive concentration.

[1] Consulting metallurgist, Fixed Nitrogen Research Laboratory.

[2] Formerly assistant physicist, Bureau of Standards.

[3] Associate chemist, Fixed Nitrogen Research Laboratory.

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I. INTRODUCTION

During the period of the war when efforts were made to manufacture synthetic ammonia by the high-pressure, high-temperature processes, the problem was faced of providing materials capable of withstanding such severe service conditions. The failure of tubes in service demonstrated a lack of information regarding the suitability of readily available materials, and the danger attending the use of unproven materials for high-pressure bombs, converters, and autoclaves was keenly felt.

During 1917 and 1918, Watertown Arsenal undertook an investigation of the problem, but the data obtained [4] were largely qualitative and further work was obviously necessary. Accordingly, a joint investigation was started in which the Fixed Nitrogen Research Laboratory planned the work, prepared the specimens, and exposed them to the conditions under which deterioration would take place, after which metallurgical inspection and tests of the steels were made at the Bureau of Standards.

Data on the physical properties of certain structural materials at elevated temperatures are available [5] to show that the tensile strength and proportional limit of ordinary structural steels decrease markedly with increase in temperature above 300° C., and that at 500° C. this loss of strength is so great as to impair seriously the value of the steels in the construction of high-pressure apparatus. The question of resistance to corrosion, to conserve the remaining strength of the steels, becomes increasingly important as the strength decreases. This investigation is concerned, therefore, with the deterioration of metals exposed to gases containing ammonia at

[4] H. E. Wheeler, Trans. A. I. M. and M. E., **67**, p. 257; 1922.
[5] B. S. Tech. Paper No. 205.

high pressure and elevated temperature, particularly under conditions representative of ammonia synthesis.

Very little quantitative information is available regarding the action on metals of gas mixtures containing moderate concentrations of ammonia. Wheeler [6] records the superiority of a chromium-vanadium steel to three other commercial steels exposed in ammonia at 500 to 600° C., and 1,500 lbs./in.^{2} Preliminary results of the present investigation have been published in two papers dealing, respectively, with the deterioration of steel and wrought-iron tubes in hot gaseous ammonia,[7] and with the deterioration of some metals in hot reducing ammonia gases.[8] Microscopic examination, supplemented by tensile tests before and after exposure, showed that ingot iron, wrought iron, mild steel, copper, "oxygen-free" copper, nickel, and its common alloys all deteriorated rapidly when exposed to gaseous mixtures of nitrogen, hydrogen, and ammonia under the conditions which prevail in either the synthesis or cracking of ammonia.

The synthesis of ammonia from hydrogen and nitrogen is the phase of the equilibrium reaction which is of primary interest, not only from the standpoint of practical application but under the conditions for synthesis (that is, with low concentrations of ammonia in the gas phase) there is little or no visible change in the metallic surface to serve as a warning of deterioration of the metal, while the cracking of high concentrations of ammonia is usually accompanied by the formation of considerable amounts of readily detectable metallic nitrides. In this early work on the synthesis of ammonia practically all of the metals tested were seriously impaired through intergranular fissuring which resulted in a dangerous loss of tensile strength and ductility in the specimens. These failures and the one noteworthy case of resistance to attack, shown by a chromium-nickel-silicon-iron alloy, led to tests on other chromium steels.

II. EXPERIMENTAL PROCEDURE

Test conditions were chosen to simulate operating conditions in the synthesis of ammonia, namely, 500° C., 100 atmospheres pressure, and an ammonia concentration of 8.3 per cent (near but somewhat below equilibrium concentration) in a gas composed of nitrogen and hydrogen in the proportions of $N_2 : 3H_2$. The test specimens for each steel or alloy were cylinders as shown in Figure 1, of such size that 2 tensile, 2 Charpy impact, and 2 corrosion specimens of the shape shown in Figure 2 could be placed in them. Each set of speci-

[6] See footnote 4, p. 200.
[7] J. S. Vanick, Trans. Am. Soc., Steel Treating, **4**, p. 62; 1923.
[8] J. S. Vanick, Proc. A. S. T. M., **24**, II, p. 348; 1924.

mens had the same composition and was given the same preliminary heat treatment as the corresponding cylinder. These specimens were exposed on all sides to the action of the hot gases, but were not subjected to the constant stress of 100 atmospheres pressure, as were the

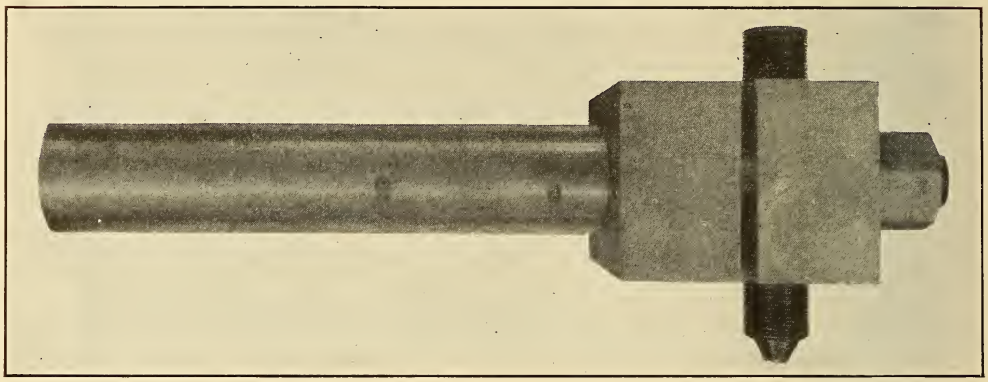


FIG. 1.—*Test cylinder*
Approximately one-half size

test cylinders. Each material was to be exposed until failure of the cylinder occurred or until metal deterioration had progressed to a point where further exposure would yield little additional information.

The cylinders were arranged in a series of 5 parallel layers, 5 cylinders to a layer. The assembly of specimens with electrical heating

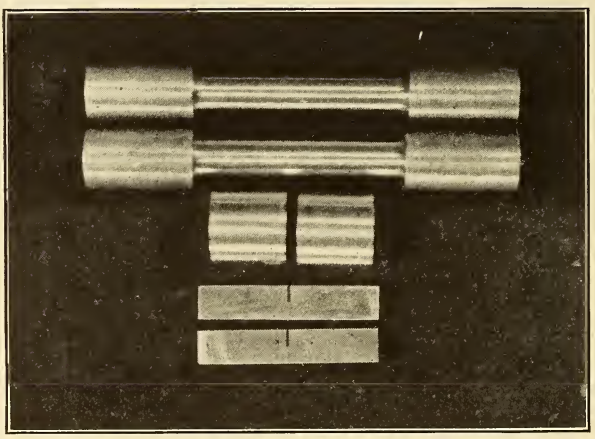


FIG. 2.—*Charge of specimens of test cylinder*
Top, tensile specimens; center, corrosion specimens; bottom, impact specimens. Approximately one-half size

coils and outer shell of boiler plate (raised to show the interior of the assembly) and the complete apparatus are shown in Figures 3 and 4. In addition to the heating coils shown in the illustration, grids at the top and bottom of the assembly provided for the heating of the nest

of cylinders from all sides. The temperature was controlled by means of iron-constantan thermocouples, the outer shells were jacketed with magnesia, and these heating arrangements were found to give very satisfactory and uniform temperature throughout the assembly.

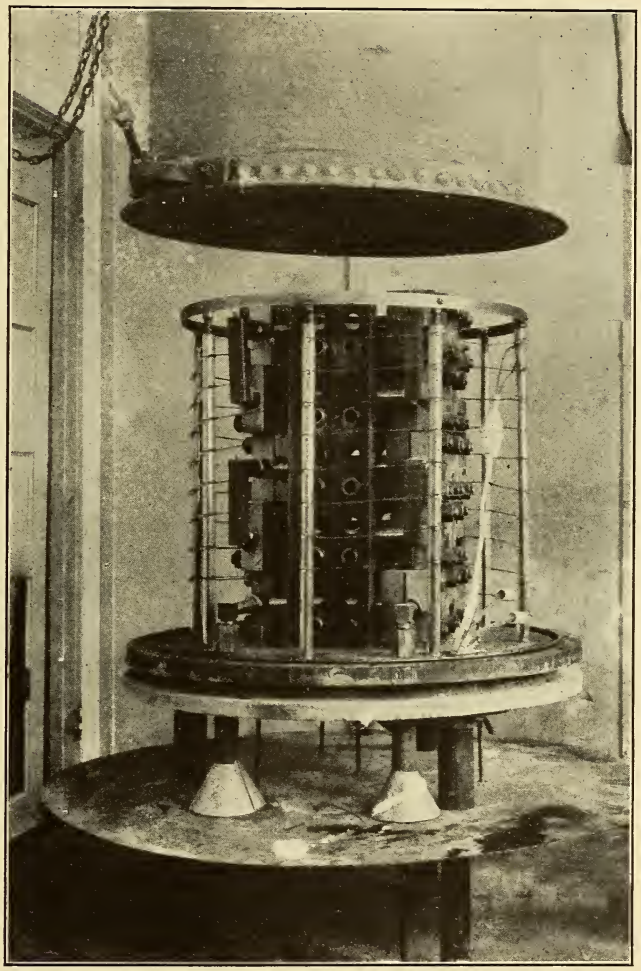


FIG. 3.—*Nest of test cylinders ready for exposure*

The auxiliary furnace, shown in the foreground of Figure 4, consisted of a steel cylinder, capped at the top and bottom with heavy flanged joints, electrically heated. Duplicate corrosion specimens exposed in this auxiliary furnace were examined periodically to indicate the probable condition of the specimens in the main test assembly.

The requisite concentration of ammonia, 8.3 per cent, in the test gases was obtained by first passing the gases under pressure through one of the two catalyst bombs shown between the two insulated

furnaces of Figure 4. The construction of these catalyst bombs and the generation, purification, and compression of the gases have been described in detail elsewhere.[9] The ammonia concentration in the gases was determined at the exit of each catalyst bomb and steel specimen furnace. Apparatus for the sampling and analysis of the gas is shown at the left of Figure 4. A flow meter indicated the amount of leakage from the high-pressure cylinders and connections

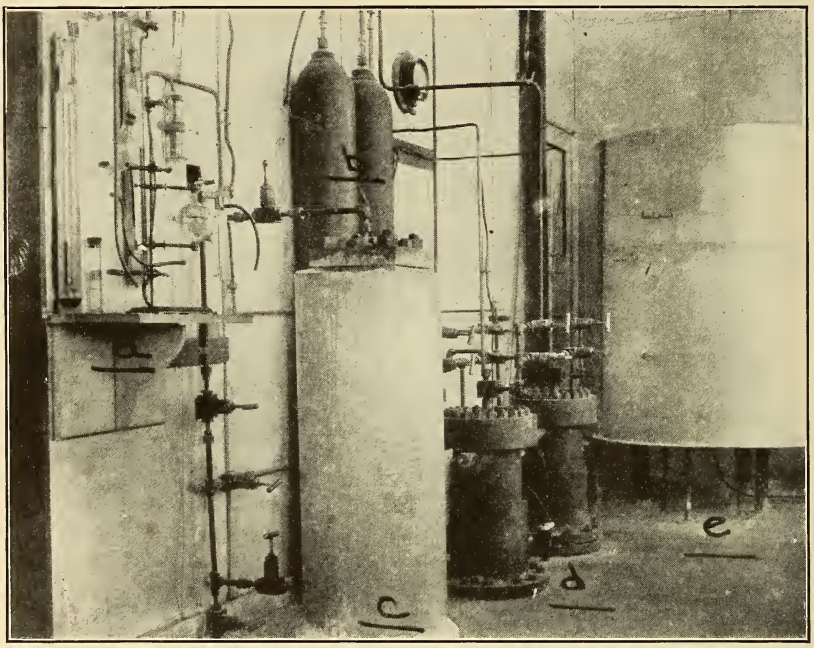


FIG. 4.—*Apparatus for exposure tests*

a, Apparatus for gas analyses, leakage pressure, flow meter, etc. *b*, Storage tanks for N_2 and H_2. *c*, Auxiliary furnace containing specimens used to determine rate of deterioration. *d*, Catalyst bombs (2) synthesizing a mixture of $N_2 \times H_2$ to desired NH_3 content. *e*, Assembled nest of test cylinders, shown in Figure 3. Direction of gas flow: From supply lines to *b*, to *d*, to *e*, to *c*, to *a*, and discharged

into the furnace shell. A mercury trap provided for the release of the pressure from accumulated leakage or from failure of connections or rupture of a test cylinder. Emergency storage cylinders, whose tops appear in back of the corrosion specimen furnace, in Figure 4, were used in case of any interruption in the gas supply.

The first set of steel samples, listed in Table 1, may be classified as follows:

[9] R. S. Tour, Chem. Met. Eng., **26**, p. 538; 1922.

Steel No.	Description	Usual purpose
31	Low carbon	Carburizing.
32	High carbon	Tools (lathe).
33 and 40	Nickel	Forging-carburizing.
35 and 36	Nickel-chromium	Forging.
37 and 38	Chromium, high and medium carbon	Bearing-forging.
34	Chromium-vanadium	Forging.
39	Tungsten-chromium	Do.

TABLE 1.—*Composition of 10 steels*

Serial No.	S. A. E. specification No.	C	Mn	P	S	Si	Cr	Ni	V	W
31	1020	0.19	0.43	0.008	0.033	0.17				
32	1095	1.01	.40	.007	.036	.16				
33	2330	.24	.52	.008	.032	.03		3.43		
34	6130	.30	.68	.012	.024	.26	0.93		0.18	
35	3335	.39	.70	.011	.044	.29	.84	3.56		
36	3230	.27	.59	.014	.022	.13	1.00	1.60		
37	52100	.93	.30	.010	.014	.21	1.47			
38	5140	.48	.79	.030	.029	.23	.60			
39	7260	.58	.36	.004	.017		.55	.21		1.62
40	2512	.10	.31	.008	.023	.31		4.87		

Before being made up into bombs and specimens, the steels were all annealed, by allowing them to cool in the furnace from a temperature of 1,650° F. (900° C.), except steels 34 and 32, which were furnace cooled from 1,600 and 1,500° F., respectively. Mechanical tests were made upon a set of samples and duplicate samples were then exposed to the $N_2 : 3H_2$ gas mixture, containing 8.3 per cent ammonia, at 100 atmospheres and 500° C., for four months. During this period additional specimens were removed from the auxiliary furnace at intervals of 1, 2, and 4 months to trace the rate of deterioration. After exposure, specimens cut from the bomb walls and those which comprised the charge inside the bombs were tested in tension and impact. In addition to the physical tests, macroscopic and microscopic examinations were made of bomb sections and corrosion specimens, and in a few instances chemical analyses of the affected zones were made to check microscopic observations.

III. RESULTS OF TESTS UPON PLAIN CARBON STEELS AND OTHERS CONTAINING USUAL AMOUNTS OF NICKEL, CHROMIUM, TUNGSTEN, AND VANADIUM

1. MECHANICAL TESTS

The data presented in Tables 2 and 3 and graphically in Figure 5 are arranged in order, an average being taken of the four values for each sample in Table 3. In general, a marked decrease in strength and ductility results from exposure to the gases. The decreased resistance to impact also testifies to the brittleness produced by the

exposure. The loss in tensile strength and the depth of penetration (shown, respectively, in columns A and C of Table 2) are of primary importance in evaluating the steels, but unfortunately they do not always run parallel, as will be explained subsequently. Column D is a composite of A and C, and serves as an aid in the interpretation of column C, which is based on microscopic inspection. If an homogeneous material were completely disintegrated for the depth of

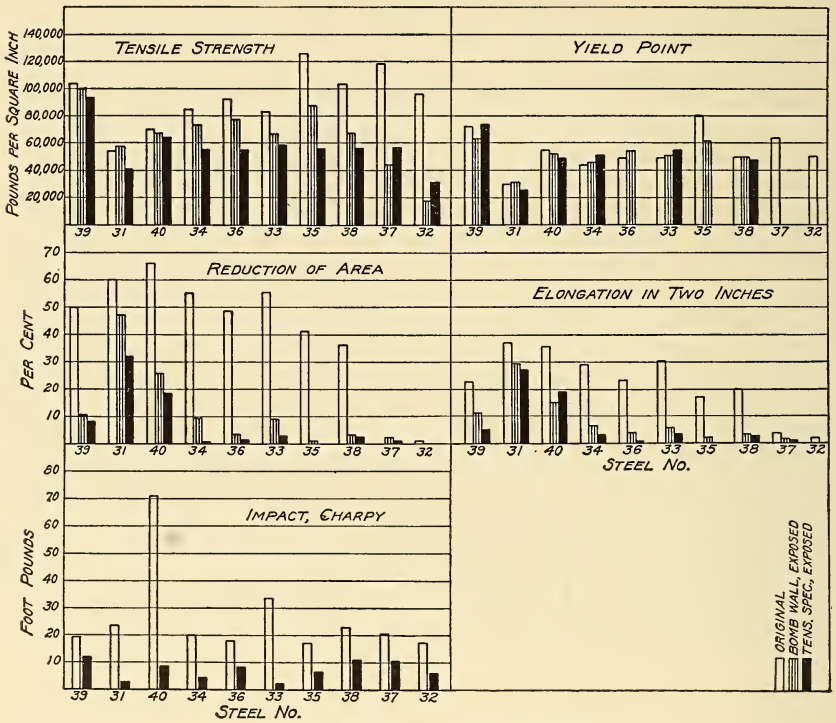


FIG. 5.—*Properties of 10 steels*

penetration microscopically observed, and no further, the residual strength per unit area would correspond with the original strength per unit area and the value in column D would be unity. Where this factor exceeds unity it is evident that the effects of the gas had penetrated the metal beyond the observed limits, and conversely, if the value is less than unity, destruction has not been complete within the observed area.

TABLE 2.—*Effect of four months' exposure on 10 commercial steels*

Steel No.	Type	Percentage of original tensile strength retained		Percentage of thickness of bomb wall affected	Loss of strength per unit of affected area $\frac{100-A}{C}$
		Bomb walls	Tensile specimen		
		A	B	C	D
39	Cr-W	96.3	89.8	None.	----------
31	Plain, low C	105	76	18	----------
40	Ni (5 per cent)	95.8	91.3	42.9	0.098
34	Cr-V	86	65.7	9.6	1.46
36	Ni-Cr	84.5	59.4	8.7	1.78
33	Ni (3½ per cent)	81	71	49.7	.383
35	Ni-Cr	69.6	44.4	10.9	3.59
38	Cr (low)	65.1	54.3	27.8	1.255
37	Cr-high C	47.7	36.9	17.0	3.08
32	Plain, high C	18.7	32.7	73.5	1.105

TABLE 3.—*Order of merit of steels*

[Four months' exposure]

Steel No.	Type	A	B	C	D
39	Cr-W	2	2	1	2
31	Plain, low C	1	3	6	1
40	Ni (5 per cent)	3	1	8	3
34	Cr-V	4	5	3	6
36	Ni-Cr	5	6	2	8
33	Ni (3½ per cent)	6	4	9	4
35	Ni-Cr	7	8	4	9
38	Cr (low)	8	7	7	7
37	Cr, high C	9	9	5	10
32	Plain, high C	10	10	10	5

In all cases a final evaluation of the steel can be reached only on the basis of a composite of all the available data. The tensile strength determinations seem to be the most consistently reliable of the mechanical tests, but the limited number of specimens throws doubt on some of the results; for example, the bomb wall of steel No. 31 apparently is stronger after exposure than it was originally. The brittleness of the specimens, localized fissuring (see fig. 6), and the possibility of distortion made the determination of mechanical properties difficult and reduced the security with which the results could be interpreted. Macroscopic and microscopic observation of the affected areas furnish valuable information to supplement and explain the mechanical tests data, but such observations are difficult to evaluate quantitatively.

A summary of the data separates the steels into groups where steels Nos. 39, 31, and 40 show the least deterioration, steels Nos. 34, 36, 33, 35, and 38 occupy an intermediate position, and samples 37 and 32 bring up the rear. In the first group steel No. 39 (Cr-W)

is manifestly the best. Steel No. 40 (Ni, 5 per cent) shows a small loss in tensile strength accompanied by deep penetration. This anomaly is explained by the microstructure which reveals the pres-

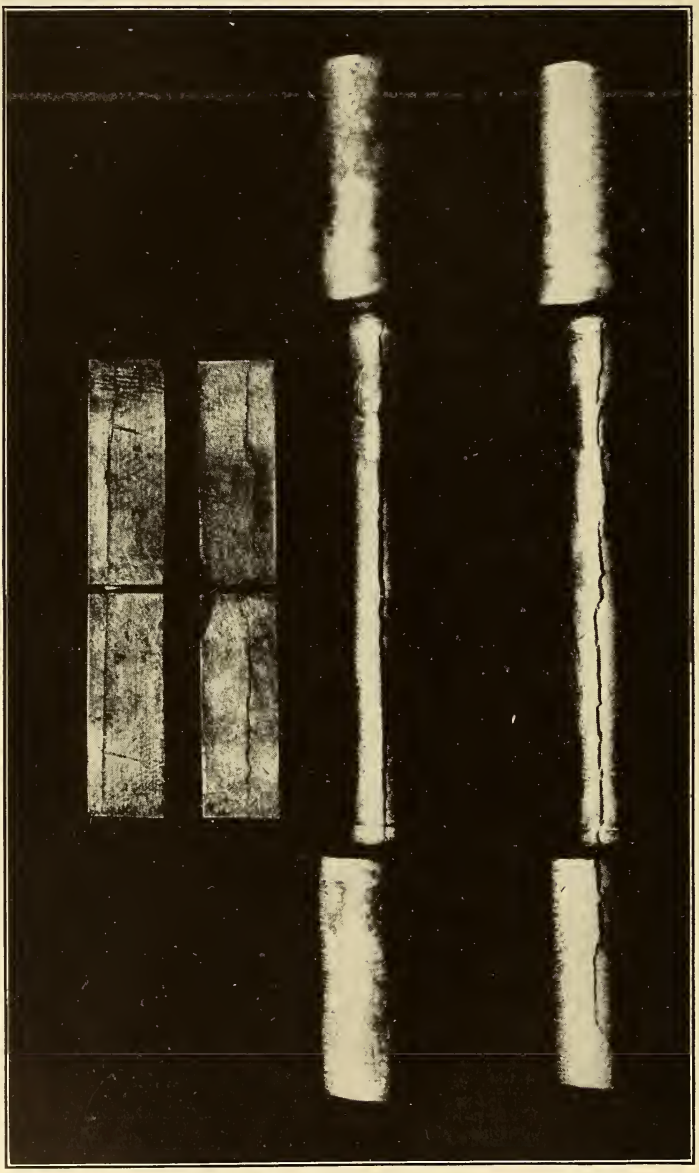


FIG. 6.—*Surface cracks in specimens*
Steel No. 9. Ten months' exposure

ence of short fissures parallel to the longitudinal dimension. Tensile tests in the longitudinal direction consequently indicate comparatively small losses in strength. Steel No. 31 (low C) in contrast to steel No. 32 (high C) clearly demonstrates the advantage of a low-

carbon content. The low original tensile strength of No. 31 must be weighed against the indicated resistance to deterioration.

In the second group the steels possess nearly equivalent tensile properties after exposure, with the differences between individual members traceable to variations in structure and penetration. Steel No. 33 (low Ni) is deeply penetrated by concentric fissures similar to those shown by sample No. 40 (high Ni). Steels Nos. 34 (Cr-V) and 36 (Cr-Ni) show residual strengths indicating decided resistance to deterioration. Steel No. 35 (Cr-Ni) stands somewhat apart on account of its complex composition. A decrease in strength produced by the loss of carbon and directional deterioration enhanced by the presence of nickel and retarded by the presence of chromium, complicate the evaluation of its merits. It is, perhaps, best compared with steel No. 36 to illustrate the added resistance which accompanies an increase in chromium and a decrease in carbon. Steel No. 38 (low Cr-low C) shows a decided decrease in strength and an appreciable depth of penetration. Steel No. 32 (high C) shows a large loss of strength accompanied by a deep zone of deterioration. Steel No. 37, comparatively rich in both chromium and carbon, shows a severe decrease in strength notwithstanding the resistance to deterioration which the higher chromium content offered.

The data show that the presence of chromium tends to resist, while the presence of a high-carbon content tends to facilitate penetration and deterioration, even in the presence of the higher chromium contents. This is further evidenced by aligning the carbon-chromium steels in the order of decreasing resistance to penetration and noting the accompanying decrease in the Cr/C ratio, as follows:

Steel No.	Cr/C ratio
36	3.7
34	3.1
35	2.15
37	1.58

The importance of this chromium to carbon relation is clearly shown in subsequent exposures of chromium-vanadium steels.

2. METALLOGRAPHIC EXAMINATION

Figure 7 illustrates the penetration of the gases into specimens as revealed in the macrostructure of polished cross sections after etching. The three specimens of each steel represent exposures of 2 weeks, 1 month, and 4 months, respectively. Gradual decarburization is distinctly shown in the microstructure of the outer areas of the specimens, though not visible in the photographs of the macrostructure. The depth of penetration shows a distinct increase for samples

35 and 36, with increasing time and an even more pronounced rate of increase for samples 37 and 38. In four months' exposure the gases have penetrated to the very center of sample 38.

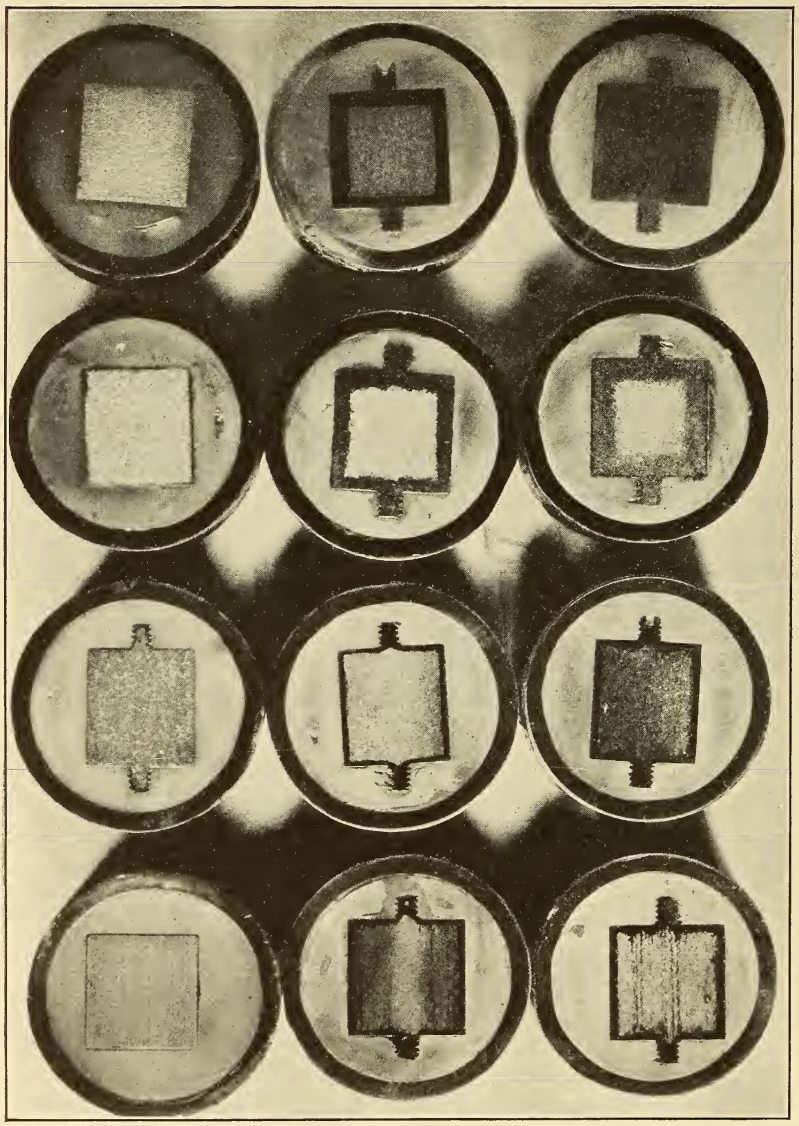


FIG. 7.—*Penetration of specimens by gases*

Top row, steels 35 (Ni, Cr), 36 (Ni, Cr) 37 (Cr, high C), and 38 (low Cr) after two weeks' exposure. Middle row, same steels after one month's exposure; bottom row, same steels after four months' exposure

The specimens are rectangular, transverse sections of corrosion specimens, mounted in solder and incased by an iron ring

Attention may be called to the thin, dark, longitudinal streaks found in steel No. 35 after the longer exposures. Under the microscope these streaks were found to be decarburized tendrils pierced by very fine fissures. This effect, most noticeable in the two high-nickel steels Nos. 35 and 40, is not produced solely by an attack from

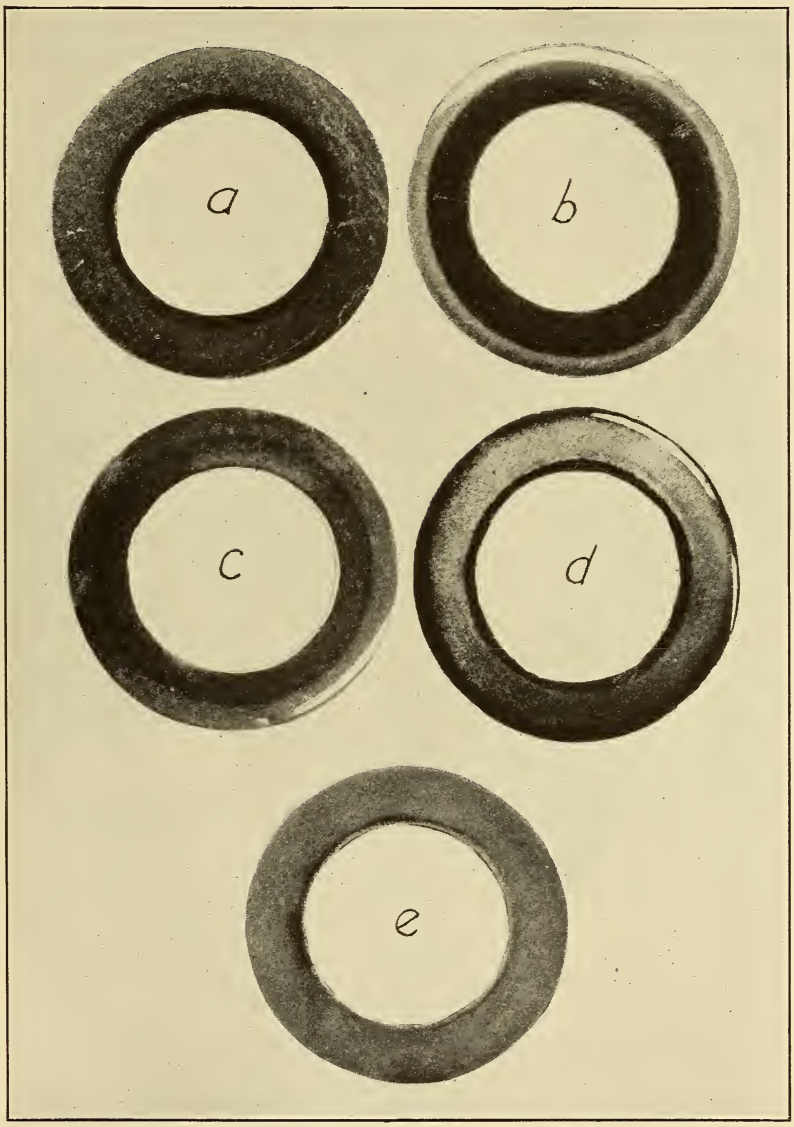


FIG. 8.—*Cross sections of bombs after four months' exposure, illustrate the improvments inherent in chromium and low-carbon steels*

a, Low-carbon steel 31, 0.2 per cent C. *b*, High-carbon steel 32, 1.0 per cent C. *c*, Nickel steel 33, 0.25 per cent C, 4.3 per cent Ni. *d*, High-carbon, chromium steel 37, 0.9 per cent C, 1.5 per cent Cr. *e*, low-carbon, chrome-vanadium steel 34, 0.3 per cent C, 0.9 per cent Cr, 0.2 per cent V

the ends of the specimens, although sections cut from various bombs indicate somewhat greater accessibility of the gas to the interior of the metal along longitudinal than along transverse fibers.

Figure 8 illustrates the appearance of sectioned bombs after four months' exposure. The structure is developed by etching with boiling concentrated hydrochloric acid. The shading shows the depth of attack of the more thoroughly penetrated zone. The differences between the high carbon, low carbon, chromium, and nickel steels are clearly shown. However, macroscopic evidence is only qualitative and may even be misleading on account of the occurrence of microscopic fissures which sometimes precede and sometimes follow the decarburization and coarse fissuring recorded in the macrostructure.

The steels initially possessed the structure typical of annealed material, namely, a mixture of pearlite and ferrite corresponding to the carbon content, subject to the slight modifications in texture imposed by the presence of the alloys. An exception was the chromium-tungsten steel, sample 39, which had a sorbitic structure after annealing. The principal microstructural features, after exposure, consisted of the following, in the order of their importance: (*a*) Fissuring, (*b*) decarburization, (*c*) reduction (deoxidation) of inclusions, and (*d*) recrystallization.

Very little change occurred in any of the steels with two weeks' exposure. With longer exposures, the various effects appear, but in different combinations and proportions for the various steels. Fissuring, which may be either continuous as in Figure 9, *a*, or intermittent as in 9, *b*, is not limited to the decarburized zones. Many examples of fissures in undecarburized zones were recorded, not only for the carbon steels but for all the steels of this group. In addition, decarburized fissures often penetrate the undecarburized interior. Such fissures are usually continuous and are bounded by narrow, decarburized walls. This tendril type of penetration will be referred to as "selective" in contrast to the "uniform" penetration sometimes observed. Decarburization is readily detectable by the presence of ferrite which on etching remains white, instead of pearlite which etches dark.

The two carbon steels, Nos. 31 and 32, after four weeks' exposure showed fissuring and decarburization. After four months both steels were deeply penetrated, with thorough decarburization of the high-carbon steel and only partial decarburization of the low-carbon sample. The net results indicate less deterioration of the low-carbon steel, a conclusion supported by a comparison of the condition of the bomb walls.

The nickel steels, Nos. 33 and 40, both showed a distinctive type of selective fissuring, illustrated in Figure 9, *c*, parallel to the axis and

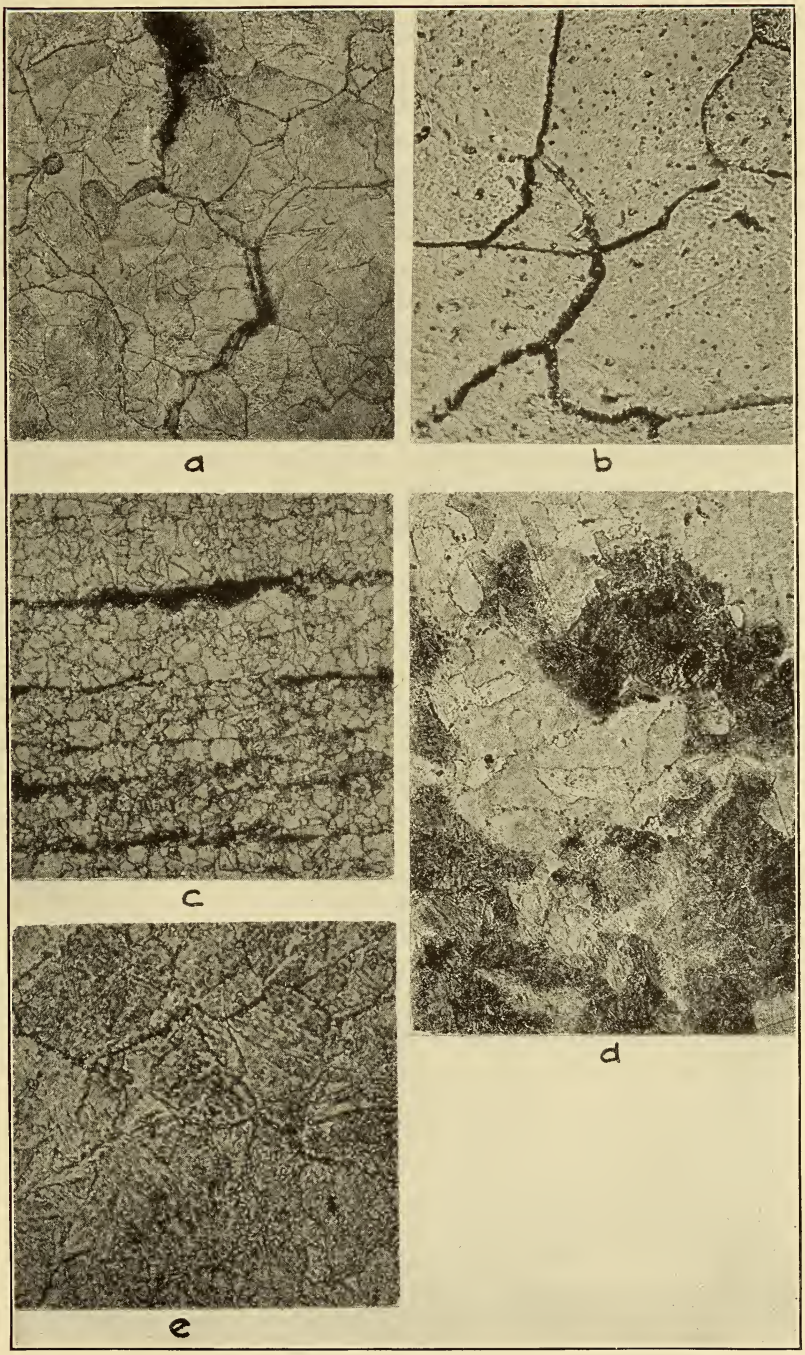


FIG. 9.—*Typical example of fissuring and decarburization*

a, Intergranular fissures and coarsened grains filled with veinlike markings. Steel 32, high carbon, one month's exposure. ×100. *b*, Fissures in a completely decarburized zone. Steel 31, low carbon, four months' exposure. ×500. *c*, Parallel, longitudinal fissures in high-nickel steel 40, four months' exposure. ×50. *d*, Intergranular perforations in a partially decarburized zone. Steel 37, high-carbon, chromium, one month's exposure. ×100. *e*, Intergranular fissures in undecarburized martensitic matrix. Steel 39 tungsten-chromium, one month's exposure. ×500
Etched in 2 per cent nitric acid in alcohol

concentric with respect to the cylindrical surface. These fissures increased in number and size with time until, with four months' exposure, the specimens were fissured to the core. These parallel rows of fissures indicate a selective penetration longitudinally along the "fibers." The apparent lack of transverse connecting fissures explains the surprising amount of longitudinal tensile strength retained by these specimens.

The structure of the chromium steels, Nos. 34, 37, and 38, after exposure is characterized by selective and intermittent fissures accompanied or preceded by decarburization. Fissures may be exaggerated by slight overetching, as in Figure 9, *b*. Figure 9, *d*, shows a decarburized vein invading the interior from the completely decarburized outer zone. Submicroscopic fissures presumably direct the progress of the gas inward from the decarburized outer zone. Occasionally the delicate outlines of fissures can be traced in the decarburized tendrils. These fissures reduce the carbon content in the interior. The tendril form of penetration by the irregularity of its invasion into the metal, both with respect to the direction and rate of penetration, is a treacherous form of deterioration.

Microscopic evidence supports the statement previously made, that an increase in the chromium to carbon ratio results in an increase in resistance to deterioration. It appears that the degree of deterioration in the affected areas increases with increasing carbon content, as it did for the plain carbon steels, and the depth of penetration or the extent of the affected area decreases with increasing chromium content. The medium carbon content of steel No. 34, and its comparatively high Cr/C ratio together with the fact that it could be obtained as a commercial product, led to its tentative adoption for general service in converters and other parts exposed to hot ammonia or its constituent gases. In longer exposures, as will be subsequently described, this steel displayed a tendency toward selective fissuring which led to its replacement by a steel higher in chromium.

The nickel-chromium steels, Nos. 35 and 36, reflect the influence of both elements. The fissured area was greater for steel No. 35 (Ni, 3.5 per cent), but the fissures were of the intermittent type and preceded decarburization. In steel No. 36 (Ni, 1.6 per cent) the fissured area was less deep, but the fissures were coarse and continuous and followed the decarburization which took a selective path. The resistance to penetration of steel No. 36 may be attributed to the chromium content, or to the higher value of the Cr/C ratio.

The tungsten-chromium steel No. 39 is apparently the least affected of the steels in this group. Except for intergranular fissures close to the surface, there is very little evidence of attack by the gases. Figure 9, *e* illustrates the course of a typical fissure through the undecarbur-

ized, martensitic matrix. Tables 2 and 3 show the undisputed superiority of this steel over its companions, notwithstanding the rather high-carbon content.

IV. TESTS UPON SPECIAL CHROMIUM-VANADIUM STEELS CONTAINING RELATIVELY LARGE AMOUNTS OF CHROMIUM AND VANADIUM

1. SELECTION AND PREPARATION

The apparent tendency of chromium to resist the penetration of the gases, the satisfactory showing of an ordinary chromium-vanadium steel, and the ready availability of steels of this type suggested further experiments to see if even better results could not be secured by a manipulation of the chromium, vanadium, and carbon contents. With this in view, the ordinary 0.30 per cent carbon chromium-vanadium steel was chosen as a base and the three principal constituents were varied to form three main series as shown in Table 4. In each series one of the principal constituents varies while the other two remain constant. Two steels of the stainless type (Nos. 27 and 28) were added to the 14 first chosen, to expand the chromium series to steels containing 21 per cent of that element. Samples of the commercial 0.30 per cent carbon chromium-vanadium steel used in earlier tests were included with each series for comparative purposes.

TABLE 4.—*Composition of chromium-vanadium steels used in second series of tests*

Serial No.	C	Mn	P	S	Si	Cr	V
CHROMIUM SERIES							
1	0.37	0.39	0.017	0.022	0.27	0.04	0.19
2	.29	.53	.015	.011	.16	.51	.28
3	.30	.68	.012	.024	.26	93	.18
4	.31	.48	.011	.011	.12	2.01	.34
5	.32	.37	.028	.013	.26	7.70	.18
6	.42	.35	.025	.009	.06	14.40	.18
27	.25	.40	.020	.020	.60	13.50	----------
28	.48	.09	.018	.014	.43	21.10	.07
VANADIUM SERIES							
7	0.40	0.53	0.018	0.013	0.18	1.05	0.02
8	.37	.52	.018	.018	.20	1.05	.07
9	.35	.37	.020	.013	.20	1.02	.14
10	.37	.55	.018	.019	.18	1.07	.31
11	.27	.34	.025	.011	.29	1.24	.65
CARBON SERIES							
12	0.16	0.55	0.023	0.023	0.34	1.03	0.20
13	.58	.68	.011	.017	.23	.73	.18
14	1.16	.55	.022	.018	.20	1.06	.20

Four lots of the 0.30 per cent carbon chromium-vanadium steel were heat treated to represent different typical conditions. The rest of the samples were double annealed by furnace cooling from about 900° C. to release strains and then all of the samples were machined into bombs and other specimens. These were exposed for 10 months to 8.3 per cent ammonia in hydrogen-nitrogen gas at 500° C. and 100 atmospheres pressure, as before. Periodic examinations of auxiliary specimens and final mechanical and metallographic tests of the exposed specimens were carried out as in the preceding experiments. An attempt was made to determine changes in weight

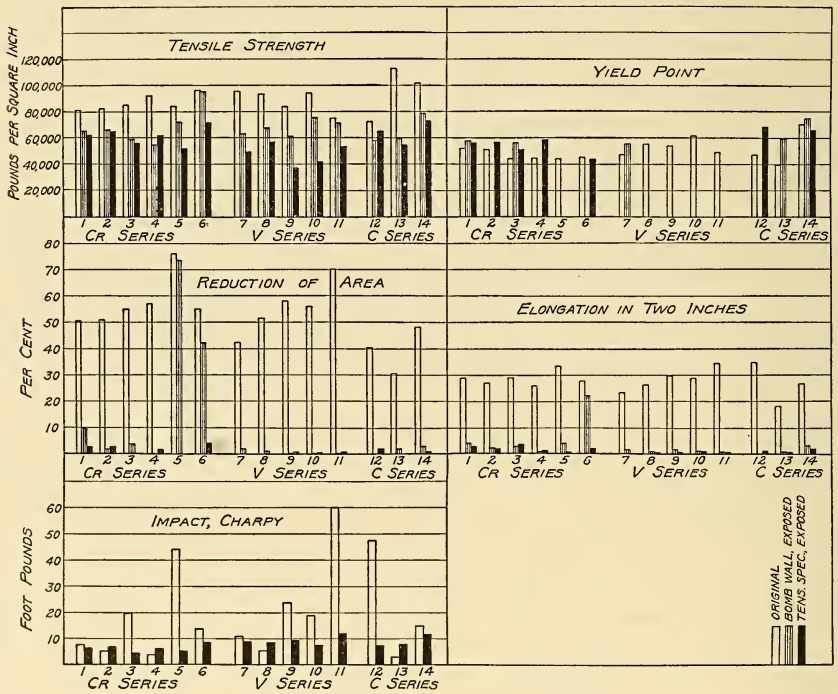


FIG. 10.—*Properties of Cr V steels*

of the corrosion specimens during exposure, but any changes which occurred were obscured by the diffusion into the steel specimens of copper from the copper washers used as end spacers.

2. MECHANICAL TESTS

The results of the tests for the 14 major specimens, before and after 10 months' exposure, are shown graphically in Figure 10. As before, a marked decrease in strength and ductility resulted from the exposure, but again, cracks and fissures which developed at the surfaces of the specimens interfered with the tests and made the reliability of single determinations open to question. The embrittlement of the steels by the action of the hot gases was especially

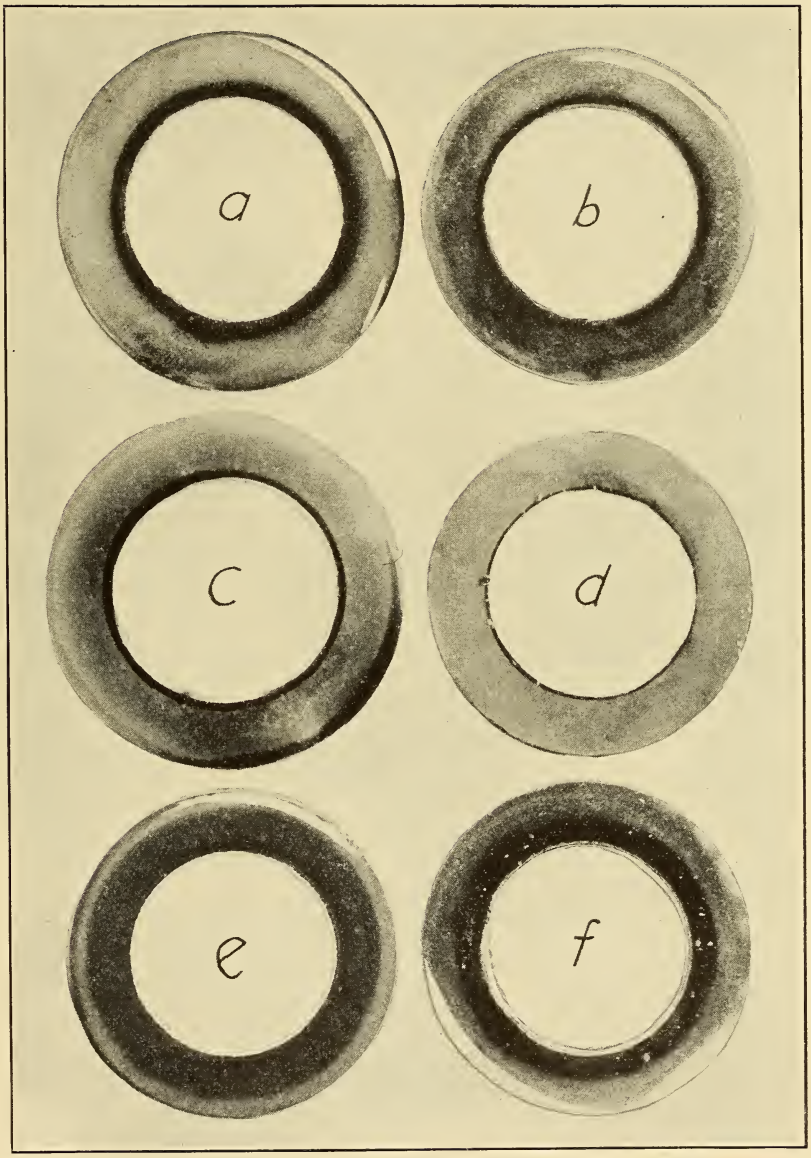


FIG. 11.—*Cross sections of chrome-vanadium steels after 10 months' exposure*

a, Chromium series, steel No. 1, 0.04 per cent Cr, 0.19 per cent V, 0.37 per cent C. *b*, Chromium series, steel No. 3, 0.93 per cent Cr, 0.18 per cent V, 0.30 per cent C. *c*, Chromium series, steel No. 4, 2.01 per cent Cr, 0.34 per cent V, 0.31 per cent C. *d*, Chromium series, steel No. 6, 14.40 per cent Cr, 0.18 per cent V, 0.42 per cent C. *e*, Vanadium series, steel No. 11, 1.24 per cent Cr, 0.65 per cent V, 0.27 per cent C. *f*, Carbon series, steel No. 13, 0.73 per cent Cr, 0.18 per cent V, 0.58 per cent C.

noticeable; usually the elongation after exposure was less than 2 per cent and in many cases practically zero. However, it is possible that at higher temperatures, such as those of the test run, some ductility is retained which is lost upon cooling to room temperature.

Figure 11 shows the appearance of some of the specimens after exposure and reveals the extent of coarse fissuring and most severe destruction. The coarse fissuring macroscopically observed, may be either of the uniform concentric or the selective type. Figure 12 shows the increasing depth of penetration with time for the different steels.

The results in Table 5 show the lack of agreement between the strength values for the tensile specimens and bomb walls after exposure. Consistent results for the percentage of affected area appear only for the chromium-rich steels and these were the only ones which did not reveal microscopic fissures extending beyond the observed affected zones.

Specimens containing more than 7 per cent chromium were colored blue after exposure, in contrast to the dull gray of the remaining steels. This blue coloration is attributed to a nitride of chromium, dissolved or in solid solution in the skin of the specimen. In long exposures the blue color penetrated measurable distances into the specimens.

TABLE 5.—*Effect of 10 months' exposure on chromium-vanadium steels*

Steel No.	Percentage of original tensile strength retained		Coarse fissured zone in bomb walls		Loss of strength per unit of affected area $\frac{100-A}{D}$
	Bomb walls	Tensile specimen	Average depth	Area affected	
	A	B	C	D	E
			mm	*Per cent*	
CHROMIUM SERIES					
1	81	86.5	2.94	31	0.62
2	80	79	3.58	38	.53
3	70	66	2.17	23	1.32
4	59.5	67	1.20	13	3.24
5	93	62	.52	6	1.27
6	97.5	----------	0	0	----------
VANADIUM SERIES					
7	66.5	51.5	2.82	30	1.13
8	72.5	61	4.23	44	.62
9	73	44	5.98	63	.42
3	70	66	2.17	23	1.32
10	79	44	2.07–7.15	22–71	0.94–0.29
11	95	71.5	1.96–7.94	21–84	.24–.06
CARBON SERIES					
12	81	91	3.26	34	0.56
3	70	66	2.17	23	1.32
13	59	49	5.11	53	.77
14	78	72	4.02	42	.56

3. METALLOGRAPHIC TESTS

Most of the information relative to the effect of the gases on the microstructure of the steels was obtained from the inspection of midsections of the small, cylindrical, corrosion specimens which were removed at periodic intervals from the corrosion furnace. No appreciable change in the basic structure occurred as a result of the prolonged heating at 500° C., except the decarburization of pearlite. The steels containing less than 2 per cent chromium possessed a typical pearlite plus ferrite structure. The 2 per cent chromium

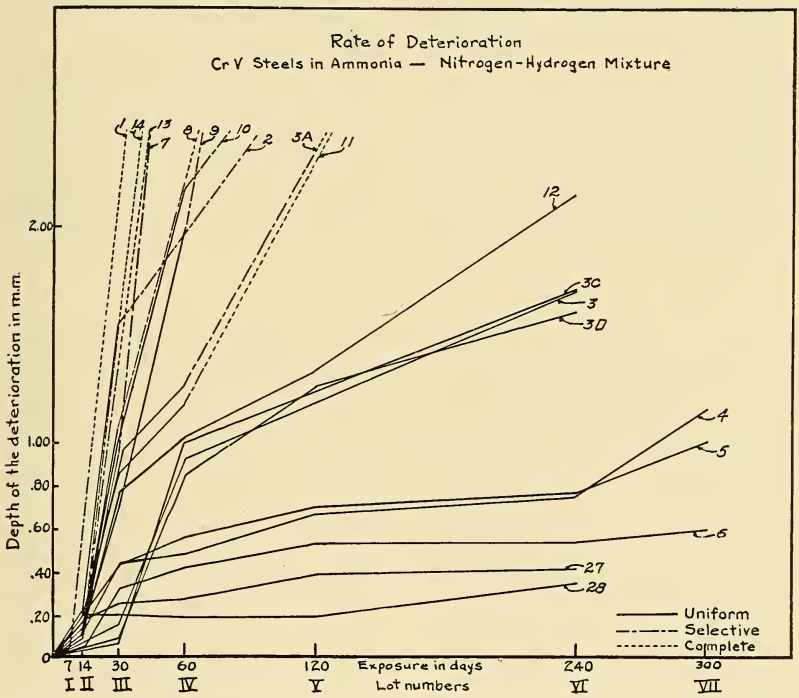


FIG. 12.—*Rate of deterioration, Cr V steels in ammonia, nitrogen-hydrogen mixture*

steel had a sorbitic structure bordering on martensite. The 7.7 per cent chromium steel possessed a troostitic structure in an austenitic matrix, while the structure of the steels which contained 14 per cent or more chromium consisted of carbides embedded in austenite.

The relative merits of the members of the carbon series, steels Nos. 3, 12, 13, and 14 are shown in Figure 12. The rapid penetration of the high-carbon steels, Nos. 13 and 14, is evident, and the character of the penetration is shown in the micrographs of Figure 13, *a* and *b*. Decarburization is first manifested in a whitening in the pearlitic areas. Complete decarburization follows, evidenced by the disappearance of the pearlite. It is interesting to note that for exposures

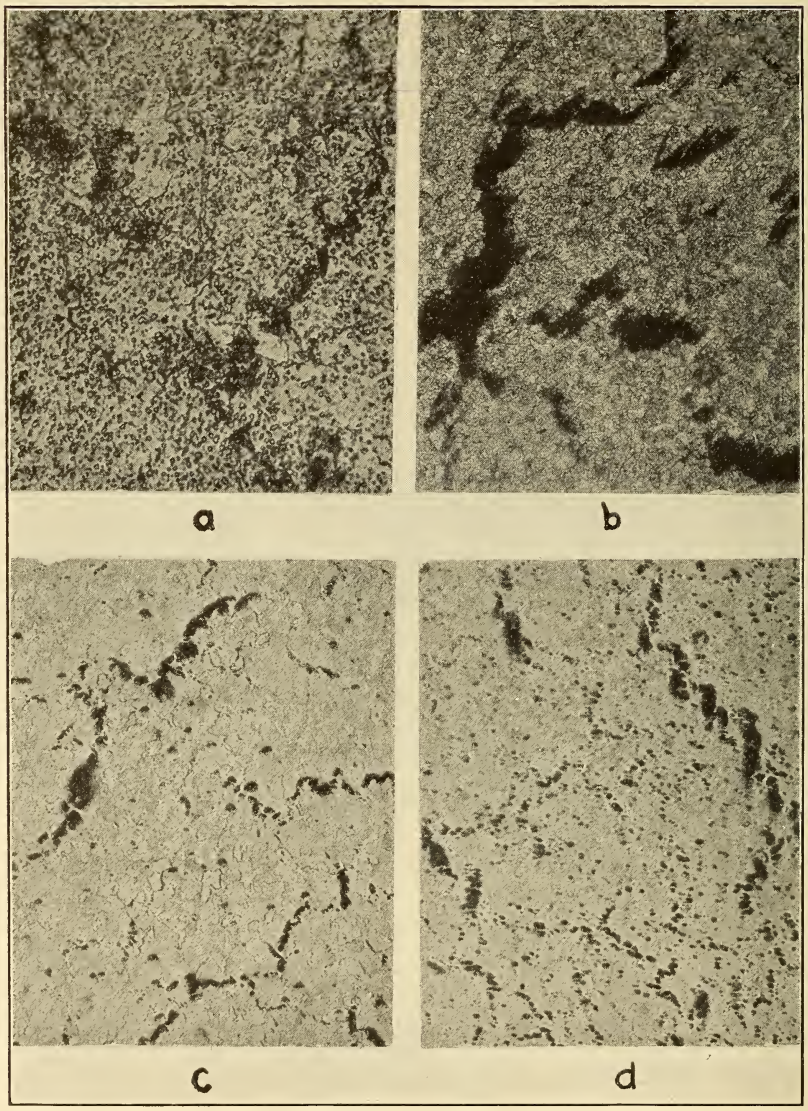


FIG. 13.—*Fissuring and decarburization in the carbon and vanadium members of the chromium-vanadium steels*

a, High-carbon steel 14; partly decarburized and badly fissured. ×500. 1.16 per cent C, 1.06 per cent Cr, 0.20 per cent V. *b*, High-carbon steel 13, thoroughly fissured and decarburized. ×50. 0.58 per cent C, 0.73 per cent Cr, 0.18 per cent V. *c*, Vanadium steel 7, completely decarburized and severely fissured. ×50. 0.40 per cent C, 1.05 per cent Cr, 0.02 per cent V. *d*, Vanadium steel 10, illustrating pitting and porosity. ×50. 0.37 per cent C, 1.07 per cent Cr, 0.31 per cent V

of 14 days or less, the high-carbon steels showed less penetration than the low-carbon members of the series. However, after 14 days, selective fissuring began to appear in the high-carbon steels and thereafter destruction proceeded rapidly. The penetration of the low-carbon steels remained more gradual throughout the test, and destruction in the affected zones was less complete than in the case of the high-carbon steels. It is evident that exposures of short duration, 14 days or less, are unreliable and may be definitely misleading. In this connection Wheeler [10] mentions the remarkable resistance of washed metal to deterioration, based on a 24-hour exposure at 750° C. From this one might conclude that a high-carbon content would be desirable, but while this is unquestionably true for very short periods of time, it would not apply for long exposures.

In the vanadium series steels Nos. 3, 7, 8, 9, 10, and 11 it appears that a threefold increase over the ordinary vanadium content in a 1.0 per cent chromium steel failed to improve significantly the resistance of the steel to attack. In Figure 12, the steels arrange themselves in order of increasing vanadium, but all were susceptible to selective penetration and fissuring and most of them were completely penetrated within 60 days. The appearance of steels Nos. 7 and 10 after eight months is shown in Figures 13, *c* and *d*. The slight improvement with larger amounts of vanadium consists of a refinement in the coarseness of the fissures rather than a retardation of their rate of formation or an obstruction to their depth of advance. Any improvement contributed by the vanadium is entirely obscured when the chromium content reaches or exceeds 2 per cent.

The chromium series, steels Nos. 1, 2, 3, 4, 5, 6, 27, and 28, aptly illustrates the influence of increasing chromium in retarding the penetration of a 0.30 per cent carbon steel. From the data on which Figure 12 is based, it is apparent that steels containing 1 per cent or less of chromium are subject to rapid selective penetration as illustrated in Figure 14, *a*. With 2 per cent or more of chromium, the rate of penetration is retarded and the extent is confined to that area near the surface, which is readily detectable by macroscopic inspection. Furthermore, microscopic cracks and fissures do not exist in advance of the macroscopically detectable zone, as shown in Figure 14, *b*, *c*, and *d*. These are very important features in favor of the 2 per cent or higher chromium steels. The presence of more than 2 per cent chromium retards the penetration still more, as shown in Figure 11, but not in proportion to the amount of chromium. Figure 12 shows that steel 5, containing 7.7 per cent chromium, is only slightly better than steel 4, containing 2.0 per cent, and that only slight differences exist between the steels containing still higher amounts of chromium.

[10] Wheeler, Trans. A. I. M. and M. E., **67**, p. 287; 1922.

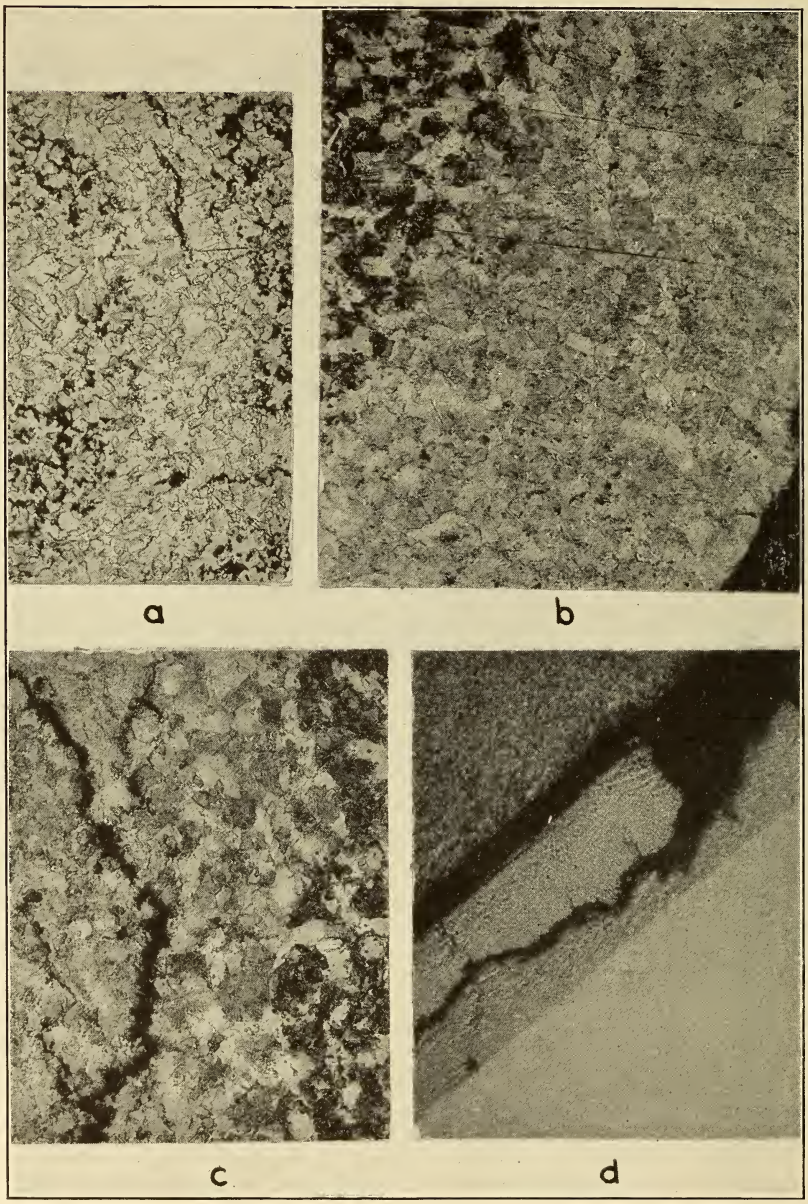


FIG. 14.—*The character at the deterioration changes as the chromium content increases*

a, Selective penetration of low-chromium steels; steel No. 1. ×50. 0.37 per cent C, 0.04 per cent Cr, 0.19 per cent V. *b*, Uniform penetration to limited depth characteristic of steels containing more than 2 per cent chromium; steel 4. ×100. 0.31 per cent C, 2.01 per cent Cr, 0.34 per cent V. *c* and *d*, Fissuring in the high-chromium steels is confined to the thin penetrated zones; steels 4 and 27. ×100. No. 27=0.25 per cent C, 13.50 per cent Cr. Etched in 2 per cent nitric acid in alcohol

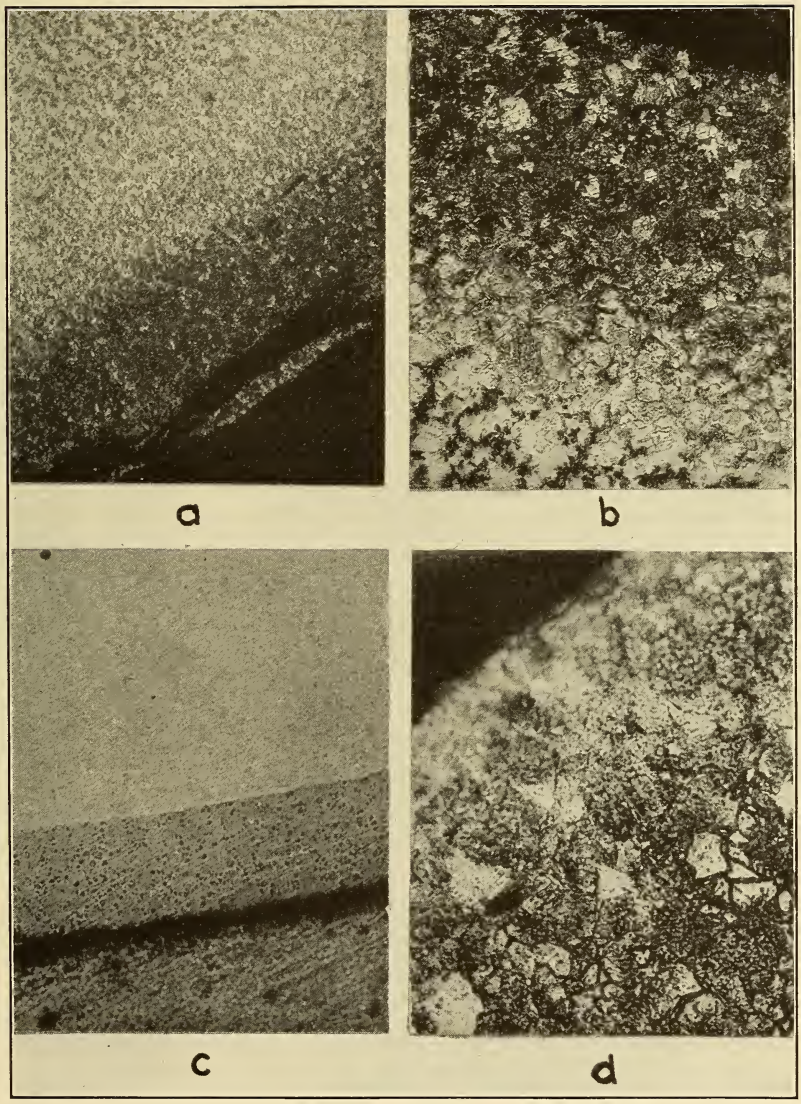


FIG. 15.—*Nitride formation in high-chromium steels*

a, *b*, and *c*, Dark colored, nitrogen-rich layer, at or near the surface, overlies a shadow zone of partial decarburization; steel 4. ×50. Steel 5. ×100. Steel 28. ×100; *d*, Structure of the nitrogen-rich layer; apparently a nitride in solid solution; steel 5. ×500; *a*, *b*, and *d*, etched with 10 per cent nitric acid in alcohol; *c*, Unetched; No. 4 contains 0.31 per cent C, 2.01 per cent Cr, 0.34 per cent V; No. 5 contains 0.33 per cent C, 7.70 per cent Cr, 0.18 per cent V, No. 28 contains 0.48 per cent C, 21.10 per cent Cr, 0.07 per cent V

A secondary feature which may be of considerable importance is the development, in the penetrated zone, of a protective layer which probably consists of a solid solution of nitrogen in the chromium-iron matrix. Typical examples of this protective layer overlying a partly decarburized zone, are shown in Figure 15. This structure could be created if ammonia penetrated the surface skin of the metal and was then cracked catalytically into its component gases, the nitrogen going into solid solution while the more fluid hydrogen penetrated further into the metal and accomplished the decarburization. The presence of increased amounts of nitrogen in this protective layer was definitely shown by chemical analysis of thin layers machined from the specimens. For steel No. 5, an original value of 0.016 per cent combined N_2 rose to 0.59 per cent after six months' exposure, and steel No. 6 showed 0.18 per cent N_2 after six months. Apparently the nitrogen-rich layer is less permeable to gases than was the original steel. Consequently the progressive penetration of the gases, which causes an increase in the thickness of the nitrogen-rich layer and produces the decarburization, is materially delayed.

The samples of chromium steel No. 3 which were heat-treated in various ways to test the effect of such treatments on the resistance to penetration, did not yield much useful information. All of the heat-treated specimens were severely attacked and the resulting data are so irregular that the only conclusion which can be drawn is that heat treatment does not improve the resistance of a poorly resistant steel. Fortunately, the high chromium steels in the annealed state, and without resort to special heat treatments, possess a fair degree of resistance to ammonia synthesis gases.

V. DISCUSSION OF THE CHEMICAL REACTIONS PROMOTING OR RETARDING THE DETERIORATION

The chemical reactions which are known or assumed to occur during the progress of the penetration and deterioration of the steels offer an interesting field for speculation. These reactions have been discussed [11] to some extent in connection with the deterioration of nonferrous and other metals, where the following reactions were suggested to explain the observed facts:

1. The combination of impurities or alloying elements in the metal with the gases of the gas mixture.

2. The activity of hydrogen cracked from its compounds and the probable catalytic influence of the metallic surfaces upon the components of the gas mixture, regardless of the state of the equilibrium in the bulk of the gas phase.

3. The more rapid diffusion of hydrogen through the steels leading to the presence of more than the equilibrium amount of ammonia in

[11] J. S. Vanick, Proc. A. S. T. M., **24**, II, p. 164; 1924.

the residual gases, with consequent decomposition of ammonia and formation of nitride.

The discussion also applies to the steels with the following reactions proposed for consideration:

$$FeO + H_2 \rightleftharpoons Fe + H_2O$$
$$Fe_3C + 2H_2 \rightleftharpoons 3Fe + CH_4$$
$$Fe_3C + H_2O \rightleftharpoons 3Fe + CO + H_2$$
$$2NH_3 \rightleftharpoons N_2 + 3H_2$$
$$NH_3 + Fe \rightleftharpoons Fe_xN_y + H_2$$
$$NH_3 + Fe_xCr_y \rightleftharpoons Fe_xCr_yN_z + H_2$$

In the consideration of these reactions, the effects of temperature and pressure are important in the stress exerted on the metal fibers, in increasing the diffusivity of the gases, and in affecting the equilibrium conditions in the $H_2 : N_2 : NH_3$ gas phase. Consideration of the reactions is simplified by the assumption that the reactions for the synthesis and cracking of ammonia occur simultaneously, particularly at the surfaces of contact between the gases and the metal. The metal is mildly catalytic for both reactions under various conditions of temperature, pressure, and ammonia concentrations. Among other reasons, this assumption of dynamic equilibrium is convenient in that it accounts for the presence of hydrogen and nitrogen in an active or atomic form.

The reduction of iron and other oxides in a reducing atmosphere at elevated temperature is well known. It is customary to reduce the catalyst, used in the synthesis of ammonia, which is usually a granulated fused mixture of iron and other oxides, by passing a current of 3:1 hydrogen-nitrogen gas at a few ounces pressure and at moderate temperature over the oxides until water vapor is no longer evolved. The ability of reducing gases to penetrate metals and remove oxygen or oxides dissolved in the metal is also known and was discussed in the earlier work on nonferrous metals, particularly copper. Microscopic evidence of the reduction of occluded oxides, such as slag particles, was frequently encountered in the study of the steels.

Decarburization can occur under the same conditions as deoxidation and the fact that it does occur is established by chemical analysis as well as by microscopic examination. For instance, steel No. 38 of the first series, on microscopic evidence was reported completely decarburized after a four months' exposure. Chemical analysis showed that the carbon content had dropped from 0.48 to 0.04 per cent while the Mn, P, S, Si, and Cr remained unchanged. Another analysis of the 0.30 per cent carbon chromium-vanadium steel showed a decrease in carbon from 0.34 to 0.07 per cent during six months' exposure. Decarburization might occur through the reaction of carbides with the water formed in the reduction of FeO. Decarburiza-

tion from this cause, however, is relatively unimportant and rather improbable in view of the isolation of the oxide particles from the carbide particles in the matrix, and the probability that any water vapor formed is washed out by infiltering hydrogen before the water vapor can react with the carbide. Hydrogen apparently is the prime factor in the deoxidation and decarburization reactions.

These facts and the absence of nitrides in the microstructure of most of the steels would suggest that all of the deterioration was caused by the hydrogen, and that nitrogen or ammonia do not participate in the destruction of the steel. No prolonged exposures were made in hydrogen alone. From comparisons with short exposures and from a study of the literature, it is doubtful whether deterioration approaching in severity that shown for these steels has been observed with hydrogen alone. The fact that conditions within the bomb approximate equilibrium for the NH_3:H_2:N_2 system, that simultaneous cracking and synthesis of ammonia may occur, aids in accounting for this increased severity of attack. It is significant that the outer surfaces of the bombs, exposed to the escaping gas at atmospheric pressure, were but slightly attacked. Lowering the pressure reduced the severity of the attack and rendered the gas mixture almost harmless.

The formation of iron nitride occurs [12] in the cracking of ammonia at temperatures above 400° C. in an ammonia-rich atmosphere, but above 450° C. the nitride is unstable. In the tests described a localized enrichment of ammonia may occur in the pores of the steel, due to the faster diffusion of hydrogen, until conditions arise favoring the cracking of ammonia, with accompanying formation of iron nitride. The nitride would be unstable and would decompose readily when fresh gas filtered in to restore the normal concentration in the gas phase. The absence of nitrides in the microstructure of most of the steels indicates that if iron nitride is formed at all, it is formed in some temporary and unstable manner, but to assume this cyclic formation and decomposition assists materially in explaining the severity of the deterioration of the steels.

Nitrification of the high chromium steels was observed as a band of dark solid solution in the microstructures. This was confirmed by chemical analysis. Where nitrification was not detected it must have been very slight, since the presence of 0.18 per cent N_2 was readily apparent. The fact that nitrides are found to exist in the high chromium alloys while they are not found in the low chromium or chromium-free samples exposed to the same conditions, indicates a stabilizing influence of the chromium toward the nitride.

[12] J. S. Vanick, Trans. Am. Soc. Steel Treating, 4, p. 62; 1923.

Many of the physical features which mark the progress of the attack support the explanation proposed. These are: (*a*) Loss in strength and ductility, (*b*) decarburization, and (*c*) fissuring.

The temperature and pressure during exposure affect the strength and ductility of the steel, beside affecting the equilibrium conditions and activity of the gases. Internal stresses may be mentioned as a possible factor in quenched or high-alloy steels, but its importance is slight as the high temperature of exposure would largely eliminate stresses.

All of the 16 steels in the second series were tested in tension at 550° C. and several were tested at 100° C. intervals in the range of

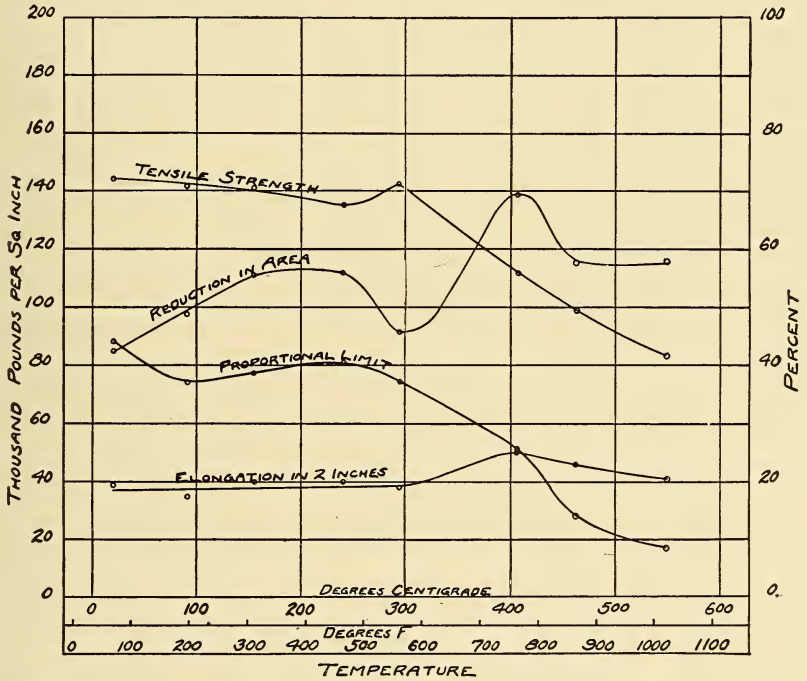


FIG. 16.—*Properties of a chromium-vanadium steel at high temperatures*

100 to 600° C. The data are not included in this report as the results of similar tests have already been published.[13] The behavior of the 0.30 per cent carbon chromium-vanadium steel at higher temperatures, shown in Figure 16, is typical of the results given in this paper. None of the steels in the present tests seemed to possess properties which would favor some particular alloy composition for this special purpose. The rapid falling off in strength above 300° C. offers a strong inducement toward the design of apparatus to operate at or below this temperature. On the other hand, increased catalytic activity at high temperatures and greater yields of ammonia at high

[13] B. S. Tech. Paper No. 205.

pressures, are incentives to operate the process at the utmost capacity of the steel. In the design of bombs or pressure cylinders, current formulas[14] show that 75 per cent of the elastic limit is the maximum available for holding pressure. This limits the maximum pressure at 500° C., for the steel shown in Figure 16, to approximately 15,000 pounds or 1,000 atmospheres, without allowance for the usual factor of safety. Furthermore, the elastic or proportional limit in this temperature range falls rapidly with temperature, thereby inviting attention to the possibilities of "creep," or slow deformation. In view of these facts, it is not surprising that the "superpressure" and "supertemperature" processes employ alloys of high elastic ratio and low ductility at high temperatures. Such alloys possess very little ductility at room temperature and are usually difficult to machine. Their properties are obtained by the use of large quantities of alloying elements which are inherently resistant to corrosion or high-temperature deterioration.

That the proportional limit lies so near the tensile strength in the exposed specimens and bomb walls is probably due to—

1. A disintegration of the granular aggregate or solid solution through decarburization.
2. Dilation of the metal due to infiltration of hydrogen.
3. The probable presence of compounds which are end products in the gas-metal reactions.

The very low ductility of the exposed specimens is undoubtedly due to the same causes, but at the temperature of the exposure it is quite probable that they were appreciably ductile. The exposed specimens when tested at high temperatures showed some ductility.

The influence of alloying elements, particularly chromium, is apparent in the restricted decarburization of the higher chromium steels. Similar results have been reported by Campbell[15] and Austin.[16] Some of the resistance to deterioration may be ascribed to the great stability of chromium carbides in the hydrogen-rich atmosphere, but the position of the whitened band in the high chromium steels indicates that the solid solution of chromium iron and carbon offers greater resistance to the diffusion of hydrogen than the carbides and suggests the probable superiority of a low-carbon chromium-rich steel. For example, steel No. 4 containing about 2.0 per cent chromium and 0.30 per cent carbon showed slow and uniform deterioration, while steel No. 37 with about 2.0 per cent chromium and 1.0 per cent carbon showed rapid and severe penetration. Annealing the steels in which the carbides were already in the lamellar or granular pearlitic form, afforded ample

[14] Ernst, Reed, and Edwards, Ind. Eng. Chem., **17**, p. 775; 1925.
[15] Campbell, Ross, and Fink, J. Iron Steel Inst., **108**, p. 173; 1923.
[16] C. R. Austin, ibid., **105**, p. 93; 1922.

opportunity for the concentration of chromium in the carbides. In the high chromium steels, the structure was an austenitic solid solution. The superior resistance to decarburization which this structure offered, indicated that the chromium in solution was a more effective barrier than the precipitated chromium carbides. This should not be interpreted to mean that the chromium carbides were not resistant. Figure 15, *c*, illustrates their practically unaltered appearance in the affected zone of a high chromium steel. However, it appeared that the chromium most directly concerned in obstructing the infiltration of hydrogen was that portion in solid solution in the steel. This suggests that in the vanadium series an improvement might result from the combination of vanadium with carbon, thus liberating some of the chromium. However, all of the vanadium steels in these tests were severely fissured and decarburized, but this may have been due to the low chromium content of about 1.0 per cent.

Where a steel possessed a well-defined grain structure, fissuring developed along the grain boundaries. Fissuring was usually associated with the decarburization and may be described in similar terms, such as continuous, intermittent, radial, concentric, selective, and so forth, according to the appearance as shown in the various illustrations. The descriptive terms of course apply only to the predominant character of a particular specimen; in many cases practically all of the various types of fissures could be identified in the same sample, and as previously mentioned in the discussion of decarburization the type of deterioration changes in some specimens with different lengths of exposure. For example, specimens frequently show only uniform penetration at first, but with longer exposures the selective type may appear and later become predominant.

The question whether decarburization and fissuring occurred independently of each other remains a matter for speculation. It is certain that fissures can occur without decarburization, since they were so clearly developed in practically carbonless iron and nonferrous alloys in earlier experiments.[17] Fissures were equally detectable in decarburized and in undecarburized zones, and sometimes in the center of a decarburized tendril. It was frequently impossible to prove the presence of a fissure in one of the decarburized tendrils microscopically, but it seems certain that the localized decarburization marking the course of the tendril must have required a fissurelike passage to conduct the decarburization products from the deep and narrow penetrated area. The presence of gas pits, reducible oxide inclusions, decomposable carbides, or free carbon, would contribute toward fissure development. The reaction products may expand in the cavities formed, in a manner analogous to the explanation for the fissuring of oxide-bearing copper by

[17] J. S. Vanick, Proc. A. S. T. M., **24**, II, p. 348; 1924.

reducing gases It is quite possible that hydrogen, or hydrocarbons formed by the infiltration of active hydrogen, produced fissures which preceded the decarburization.

The concentric fissures, especially apparent in the nickel steels, are of interest in that their presence may be considered less harmful, as regards tangential stress, than the selective or radial types. The "sleeve in sleeve" structure of concentric intermittent fissuring may not appreciably reduce the tangential or longitudinal strength of a cylindrical body. In tube shapes the separate sleeves, like the

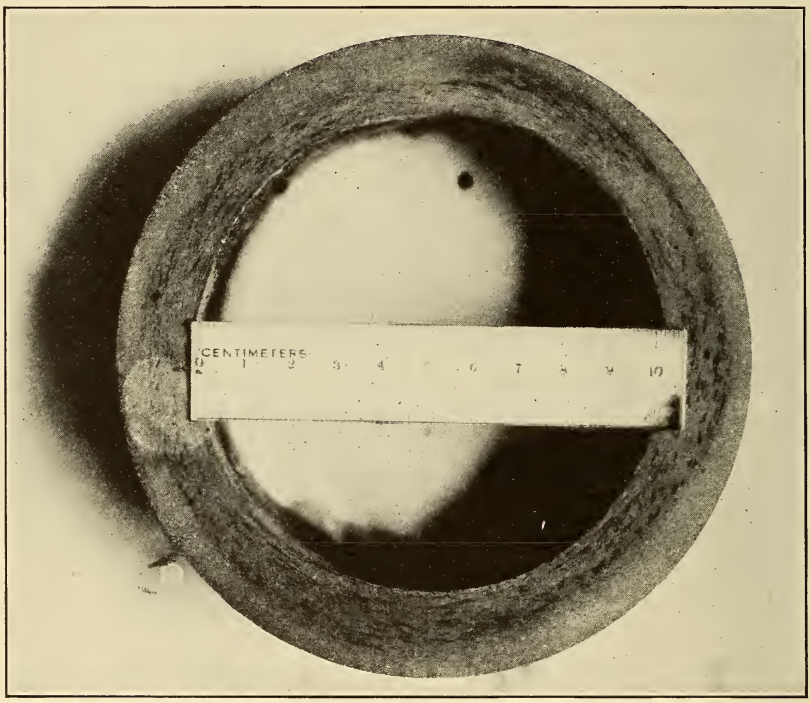


FIG. 17.—*Concentric fissues in a low-carbon steel*

individual plies of a rubber tire, may each be able to assume a share of the load. The high strength of a low-carbon steel tube which developed concentric fissures in low temperature service as a catalyst bomb may be mentioned. A seamless tube of approximately 0.25 per cent carbon was in service for two years at operating temperatures not in excess of 300° C. Penetration of 75 per cent of the wall thickness resulted, as shown in Figure 17, but in spite of this penetration longitudinal specimens showed very little loss in tensile properties as compared with the original values. An average of eight tests showed 55,000 lbs./in.^{2} tensile strength and 28,750 lbs./in.^{2} yield point, both within 2,000 lbs./in.^{2} of the original values, and an elonga-

tion of 34.5 per cent in 4 inches and reduction of area of 58.5 per cent both within two units of the original figures.

Selective fissuring obviously is the least desirable and the most treacherous form. In the low chromium (including vanadium) and the high carbon steels of Table 4 selective fissuring appeared to be the rule rather than the exception. In some of the steels selective penetration began immediately, in others it was evident only after exposures of 30 days or longer. Initial radial fissures usually forked during their development and finally formed a connecting network of fissures. In general, all specimens of any individual steel fissured to about the same degree, but the quantity or coarseness of fissuring did not always increase with time uniformly for companion specimens. The release of internal stresses after fissuring or local unfavorable distribution of fissure-inducing elements may account for differences in rate of individual specimens. Such stresses may be developed as has been suggested by the interatomic absorption of hydrogen, by the infiltration of permeable gas, or by the expansion of impermeable gases formed in reactions with inclusions. That stresses were developed in the specimens during exposure, was indicated by the fact that most of the exposed tensile specimens increased 0.002 to 0.005 inch in diameter, and several were split by longitudinal fissures extending over their entire length.

VI. SUMMARY

Results are presented of an investigation of the resistance to deterioration of steels for service as primary containers in the synthesis of ammonia at elevated temperatures and high pressures.

The apparatus consisted of test specimens in the form of bombs, arranged in nests in series and exposed to test conditions. Each bomb contained tensile, impact, and corrosion specimens. The temperature was adjusted manually, the pressure automatically, and the ammonia concentration by passing the gas over seasoned catalysts before it reached the test bombs. The ammonia concentration in the test bombs (8.3 per cent) is near but somewhat below equilibrium concentration (10.4 per cent).

Practical experience and early experimental work showed that plain carbon forging steels were liable to rapid deterioration. The present work confirmed these earlier findings and also showed that experimental exposures should extend over a period of two months or more in order to allow deterioration to develop.

A group of 10 commercially available forging steels exposed for four months showed that all of the steels were susceptible to deterioration, the severity of which was made evident by the different degrees of decarburization and fissuring. The tensile strength and

ductility were lowered, usually less in the less affected steels. The true relation in mechanical properties between the exposed specimens and the original material was obscured by irregular changes in cross section of the test specimens, which accompanied the deterioration. More emphasis, consequently, was placed upon the results of macroscopic and microscopic examinations. It was found that—

1. Carbon steels decarburized and fissured readily.
2. Nickel steels were deeply penetrated, but showed a high residual strength in spite of parallel longitudinal fissures.
3. Chromium steels deteriorated rapidly if they were of high carbon content but were quite resistant if they were of low carbon content.
4. Tungsten and nickel increased the resistance to deterioration of chromium steels if the latter were of low carbon content.

A group of 14 steels chosen to cover variations of carbon, chromium, and vanadium contents within the limits of 0 to 1.20 per cent C; 0 to 14.0 per cent Cr; and 0 to 0.65 per cent V, showed that—

1. The carbon content must be low.
2. Two per cent or more chromium is necessary to confine the fissuring and decarburization to smooth and uniform penetration.
3. A suitable steel should contain at least 2.25 per cent chromium with not more than 0.30 per cent carbon.
4. Larger quanties of chromium further improve the resistance, but not in proportion to the increase in chromium content.
5. High chromium and nickel-chromium steels of the "stainless" type are most resistant, but are difficult to forge or machine.
6. Heat treatment was useful in dissolving the alloying elements in steels inherently resistant, but did not appreciably improve steels which were not very resistant.
7. Vanadium adds no appreciable improvement.

The chief features of the attack of the gases upon the steels were represented by decarburization; sharp increase in combined nitrogen, principally in the chromium steels; fissuring; porosity in the affected zones; lowered strength and ductility.

Evidence that carbon was eliminated during exposure was secured. Decarburization, fissuring, and the presence of combined nitrogen in some of the steels are accounted for; first, by the presence in the gas mixture and the penetration into the steels of molecular hydrogen; second, by the injection of activated hydrogen released from catalyzed reactions; third, by the inflation of the crystal lattice by hydrogen "activated" during its infiltration into the steels; fourth, by the more rapid diffusion of hydrogen as the gas mixture passes through the steel, causing localized enrichment of ammonia which causes the formation of nitrides, which are, in turn, decomposed. Internal decarburization, and the presence of nitride layers in the chromium

steels, in spite of their being in contact with gases which decompose nitrides, would be accounted for in a cyclic reaction which is proposed of nitride formation and decomposition.

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