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INFLUENCE OF SULPHUR, OXYGEN, COPPER AND MANGANESE ON THE RED-SHORTNESS OF IRON

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INFLUENCE OF SULPHUR, OXYGEN, COPPER, AND MANGANESE ON THE RED-SHORTNESS OF IRON

By J. R. Cain

ABSTRACT

Small ingots (approximately 900 g each) of electrolytic iron and in some cases Armco ingot iron have been prepared in such manner as to contain varying small amounts of sulphur, oxygen, copper, and manganese separately or in certain combinations. The ingots were melted under vacuum or in an induction furnace under air. Bars forged from these were tested for red-shortness by bending back and forth over a blacksmith's anvil while they cooled from approximately 1,100 to 500° C. It was found that if sulphur is below 0.01 per cent, there is no red-shortness, even when the oxygen content (as determined by the Ledebur method) is 0.2 per cent. If the sulphur be above 0.01 per cent, a manganese-sulphur ratio of 3.0 is sufficient to prevent red-shortness. The effect of copper was found to be of minor importance, but had some tendency to correct red-shortness in the low sulphur materials (0.015 to 0.021 per cent S) studied.

CONTENTS

I. INTRODUCTION

Metallurgical literature and textbooks contain many data on elements which are believed to cause or affect red-shortness of iron; that is, brittleness when worked above a red heat. Of the chemical elements usually present in commercial iron and steel, sulphur, oxygen, and copper are most often blamed. It is quite generally accepted that sulphur, in the absence of necessary amounts of manganese, causes red-shortness. The minimal percentage of sulphur at which red-shortness disappears has, however, not been accurately fixed. Many writers consider oxygen equally potent in causing brittleness during hot working, although many statements to the contrary can be found. The effect of copper is probably most disputed by various investigators.

A summary of the literature and of the views on effects of different elements on the red-shortness of iron is given by Howe.[1] The discordance of views with respect to the effect of different elements is quite evident from Howe's summary, and particularly

[1] Metallurgy of Steel, 2d ed.; 1891.

from a table given (Ref. 1, p. 92) showing working properties of various unrecarburized basic open-hearth and acid-Bessemer steels in which oxygen contents above 0.068 are reported. As stated by Howe, a great deal of uncertainty attaches to the oxygen results given in his table; in fact, many of them were admittedly only approximations because no reasonably satisfactory methods for determining this element in iron and steel had been devised at that time. Howe says, "It is stated that more than 0.1 per cent oxygen appreciably affects forgeableness, but that in smaller proportions it is often harmless; I do not, however, think we have evidence to warrant precise statements." Also, "At the end of the Bessemer process the metal usually absorbs a certain proportion of oxygen which renders it unforgeable." Ledebur [2] states that 0.10 per cent oxygen in mild steel causes red-shortness. Stoughton[3] writes, "There is probably no constituent more harmful to steel than oxygen. * * * The effect of oxygen is somewhat similar to that of sulphur, and, in common parlance, makes the steel 'rotten'."

Among other investigators of the effect of oxygen on red-shortness and other properties of iron may be mentioned W. Austin,[4] Eichhoff,[5] Becker,[6] Oberhoffer and d'Huart,[7] and Herbert Monden.[8] Fleming [9] discusses briefly the effect of oxygen content and deoxidation on the rolling properties of commercially pure irons.

Howe (loc. cit., p. 44) discusses the effect of manganese in preventing red-shortness, and states "* * * it (manganese), moreover, counteracts hot-shortness no matter at what temperature and from what cause it may arise, whether from phosphorus, sulphur, copper, silicon, iron oxide, suspended silicate of iron, or blow-holes * * *." He gives tables showing forging results on samples of steels and irons from various sources where the ratio of manganese to sulphur or other elements to which red-shortness might be attributed varies greatly, and there is also great variation

[2] Eisenhüttenkunde, 1st ed., 1, p. 296; and 3, p. 12.

[3] Metallurgy of Iron and Steel, 3d ed.; 1923.

[4] Wesley Austin, The Influence of Oxygen on Some Properties of Pure Iron, J. Iron and Steel Inst., 2, pp. 157–163; 1915.

[5] Prof. Eichhoff-Charlottenburg, Ueber die Fortschritte in der Elektrostahl Darstellung, Stahl u. Eisen, 27, p. 48; 1907.

[6] E. Becker, Ueber das Zustandsdiagramm Schwefeleisen—Eisen und den durch Schwefel hervorgerufen Rotbruch, Stahl u. Eisen, 32, pp. 1017–1021; 1912.

[7] P. Oberhaffer and K. d'Huart, Bertrage zur Kenntnis, oxydischer Schlackeneinschlüsse sowie der Desoxidationsvorgange in Flusseisen, Stahl u. Eisen, 39, pp. 165–169 and 196–202; 1919.

[8] H. Monden, Beitrag zur Metallurgie des basischen Siemens-Martin Verfahren und zur Frage des Einflusses des Sauerstaffgehaltes auf die mechanischen Eigenschaften des Flusseisen inbesondere des Rotbruches, Stahl u. Eisen, 43, pp. 745–752 and 782–788; 1923.

[9] W. R. Fleming, Oxygen in Iron and Steel; Value of Existing Methods for its Determination, Proc. Amer. Soc. for Testing Materials, 13, pp. 477–486; 1913.

in the forging results. He says "* * * as we have neither a scientific basis for calculating the quantity of residual manganese needed to prevent hot-shortness under given conditions, nor even trustworthy empirical data, the steel maker has to proceed tentatively when under unusual conditions."

Among those who have investigated the effect of copper on red-shortness may be mentioned Eggertz,[10] Wasum,[11] Choubley,[12] Stead and Evans,[13] and Campbell,[14] all of whom regard copper, per se, as of minor significance in causing red-shortness, although some of them believe that, in combination with a high sulphur content, copper may help to cause red-shortness. On the other hand, Brustlein,[15] Howe (loc. cit., p. 82), Ruhfus,[16] Sargent,[17] and Richardson and Richardson[18] are inclined to regard copper as an element likely to cause red-shortness in iron and steel, regardless of other elements present. Aupperle, in discussing Richardson's paper, states that if the sulphur content is low, amounts of copper up to 0.5 per cent do not cause red-shortness.

II. EXPERIMENTAL METHODS

In reviewing the work of previous investigators one is impressed by the difficulty of their problem in that, although they usually attempted to determine the effect of one element on iron, they were constrained to use commercial steels for their experiments. However careful the selection of these specimens, it was, and still is, almost impossible to select compositions in which only one element at a time varies in a regular manner. Considerations such as these led to the research described herein, which differs from most of the preceding work on the subject in that the samples were made specifically for the investigation in small electric furnaces which could be kept under fairly good control. Electrolytic iron was used as raw material except for certain experiments on manganese-sulphur ratios (see Table 1). The advantages of such raw material with its well-known low content of copper,

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10 Jahresbericht, Wagner, p. 9; 1862.

11 Stahl u. Eisen, p. 193, 1882. Abstract in J. Iron and Steel Inst., 1, p. 369; 1882.

12 Bul. Soc. Industrie Minerale 23, p. 205; 1884. Abstract in J. Iron and Steel Inst. 1, p. 248; 1884.

13 J. E. Stead and John Evans, The Influence of Copper on Steel Rails and Plates, J. Iron and Steel Inst., 1, pp. 89–100; 1901.

14 Manufacture and Properties of Iron and Steel, p. 358; 1907.

15 See Howe (loc. cit., p. 368).

16 A. Ruhfus, Der Einfluss des Kupfers auf Eisen, Stahl u. Eisen, 20, pp. 691–692; 1900.

17 George W. Sargent, Iron-Copper Alloys, Metallurgical and Chemical Engineering, 20, p. 68; 1910.

18 E. A. Richardson and L. T. Richardson, The Influence of Copper, Manganese, and Chromium, and Some of Their Combinations on the Corrosion of Iron and Steel, Trans. Amer. Electrochem. Soc., 38, pp. 221–223; 1920.

manganese, and sulphur is obvious. The analysis of the electrolytic iron used was, in percentages, C, 0.004; S, 0.004; Si, 0.001; Cu, Ni, and Co together, 0.014; phosphorus, trace.

In planning this investigation the intent has been to limit the study, for the present, to the effect of sulphur, oxygen, copper, and manganese on red-shortness of iron, in such manner that the major effect of an element could be studied alone or in the presence of a desired amount of another element. It is practically impossible, of course, to have only one of these elements combined with iron to the complete exclusion of the others; it is also impracticable, without an undue amount of work, to study all the possible combinations of these elements with iron, nor does this seem necessary in view of what follows.

The samples were melted in the carbon resistor vacuum furnaces described in a previous investigation by Neville and Cain,[19] and in a high-frequency induction furnace. The former type of furnace enabled samples to be melted with practical exclusion of air, hence permitted a fairly good control of oxygen content, although there was occasional slight contamination of the melts by silicon from impurities in the crucible material and carbon. On the other hand, the melts made in the induction furnace under air are generally characterized by high content of oxygen, but contain only very small percentages of carbon, silicon, and manganese. Magnesia crucibles were used as containers in both furnaces. Melts made in the Arsem furnace were allowed to solidify in the crucible under vacuum. Melts made in the induction furnace sometimes solidified in the crucible, and others were poured into chill molds. The average weight of the ingots used was approximately 900 g. Ingots which solidified in the crucible were about 3.5 cm diameter, and 10 cm long with a slight taper. Ingots made in chill molds were about 3.5 cm square and 8 to 9 cm long.

The electrolytic iron used for the work has been described in the paper last cited. The manganese was that produced commercially by aluminum reduction and was over 98 per cent pure. The copper was over 99.9 per cent pure.

Preparatory to making the red-shortness test the ingots were forged to one-half-inch round bars. The test for red-shortness consisted in heating the bars to approximately 1,100° C. in a gas-fired or coke-fired forge, withdrawing the bars quickly from the fire and bending them back and forth rapidly through 180°

[19] R. P. Neville and J. R. Cain, Preparation and Properties of Pure Iron Alloys: I. Effects of Carbon and Manganese on the Mechanical Properties of Pure Iron, B. S. Sci. Paper No. 453, Oct. 16, 1922.

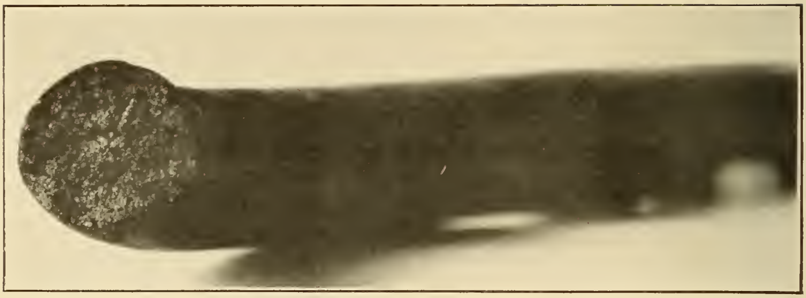

FIG. 1.—*Typical red-short fracture* (× 100)

Per cent C = 0.017; per cent O_2 = 0.034; per cent S = 0.033

over the sharp edge of an anvil while they cooled rapidly to a dull red heat. The bending was done with a hammer heavy enough to apply the necessary force, but light enough so that the operator could make the bends very quickly. In this way a sample could be subjected to perhaps a dozen bending cycles, provided it did not break because of red-shortness. A sample free from red-shortness stands such a test without breaking; one which is red-short breaks off with a fracture like that shown in Figure 1. The temperature at which the fracture takes place varies probably within a range of 100 to 200° C. for different specimens of variable composition, but no attempts were made during this work accurately to fix the temperature of breaking, since this would have necessitated the devising of special mechanism.

It was observed that the samples would usually stand the bending test above and below the brittle range where any brittleness existed. During the preliminary forging of the bars to one-half-inch sections (whether the ingots were worked under a press or a hammer) it was found that samples which afterwards proved red-short in the anvil bending test could, in many cases, be worked throughout the brittle range without serious cracking or breaking.

Chips from the broken test bars were analyzed for the ordinary constituents by the methods of the American Society for Testing Materials, or slight modifications of these. Oxygen was determined by the Ledebur method from unsieved chips cut at slow speed on a milling machine. The work of Cain and Pettijohn [20] and of others has shown that the Ledebur method can be applied with a fair degree of accuracy to pure irons or commercially pure irons. These investigations have shown that in a low-carbon iron the iron oxide inclusions are determined with a fair degree of accuracy, provided necessary precautions are taken to secure fine chips free from surface oxidation, and a rapid current of pure hydrogen is used. On the other hand, the limitations of such a method as applied to ordinary steels should be noted (particularly as applied to specimen 85, Table 1).

Micrographs of specimens 543 (fig. 2, 0.09 per cent C and 0.018 per cent O) and 587 (fig. 3, 0.02 per cent C and 0.176 per cent O) show the irregular distribution and size of the oxide particles in the latter.

[20] J. R. Cain and Earl Pettijohn, A Critical Study of the Ledebur Method for Determining Oxygen in Iron and Steel, B. S. Tech. Paper No. 118, Jan. 11, 1919. See particularly p. 23 as to cutting samples in air.

TABLE 1.—Composition of Samples and Results of Forging Tests

No.	C	Si	Mn	Cu	S	O_2	Forging test	Ratio Mn/S	Remarks
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.			
12	0.010	0.01	0.012	0.007	0.009	0.051	O. K.	1.3	Electrolytic iron used for preparing these ingots.
543	.090	.08	.006	.006	.006	.018	do	1.0	
544	.110	.08	.001	.004	.004	.034	do	.2	
73–1	.050	.04	.006	.003	.007	.037	do	.9	
587	.020	.00	.001	.005	.003	.176	do	.3	
588	.020	.00	.001	.005	.004	.147	do	.2	
231	.020	.00	.002	.005	.005	.200	do	.4	
75–1	.025	.02	.006	.003	.014	.036	Broke	.4	
77–1	.045	.02	.004	.002	.022	.036	do	.2	
74–1	.060	.05	.001	.045	.016	.028	O. K.	.06	
31	.018	.02	.008	.060	.018	.040	do	.4	
32	.022	.06	.018	.168	.015	.020	do	1.2	
33	.015	.05	.027	.365	.015	.023	do	1.8	
34	.031	.08	.021	.526	.017	.021	do	1.2	
85	.490	.04	.020	.045	.021	.038	Broke	1.0	
A 510	.066		.033	.022	.015	.030	O. K.	2.2	Commercially pure iron used for preparing these ingots.
A 511	.033	.05	.031	.023	.011	.027	do	2.8	
3	.034	.10	.160	.033	.029	.028	do	5.5	
76–1	.060	.05	.120	.099	.034	.027	do	3.5	
A	.010	.01	.090	.040	.023	.085	Broke	3.9	
B	.010	.00	.160	.037	.050	.109	do	3.2	

Note.—Only traces of phosphorus were present in these samples.

III. DISCUSSION

Samples 543, 544, and 73–1 of Table 1 contained less than 0.01 per cent each of manganese, sulphur, and copper, with oxygen less than 0.04 per cent in each; these samples were free from red-shortness. On the other hand, samples 75–1 and 77–1, with about the same content of manganese, oxygen, and copper as those just mentioned, but with 0.014 per cent and 0.022 per cent of sulphur, respectively, both broke on the red-shortness test. This indicates that sulphur, and not oxygen, is the cause of the red-shortness in these samples, and that the percentage of sulphur where red-shortness disappears lies between 0.014 and 0.007 per cent.

Samples 12, 587, 588, and 231 carry less than 0.01 per cent of copper and sulphur and (except sample 12 with 0.012 per cent Mn) less than 0.01 per cent Mn each; that is, they contain well below the limiting percentage of sulphur for causing red-shortness; however, it will be noted that they carry very large percentages of oxygen (0.05 to 0.20 per cent). Nevertheless, none of them broke on the red-shortness forging test. This indicates that a very high oxygen percentage in pure iron does not cause red-shortness if the sulphur content is below 0.01 per cent. There is, however, an apparent effect of oxygen when manganese has been added to correct red-shortness, due to sulphur, as stated below.

The samples with increasing copper content: 74–1 and 31 to 34, inclusive, contain small percentages of manganese, oxygen, and

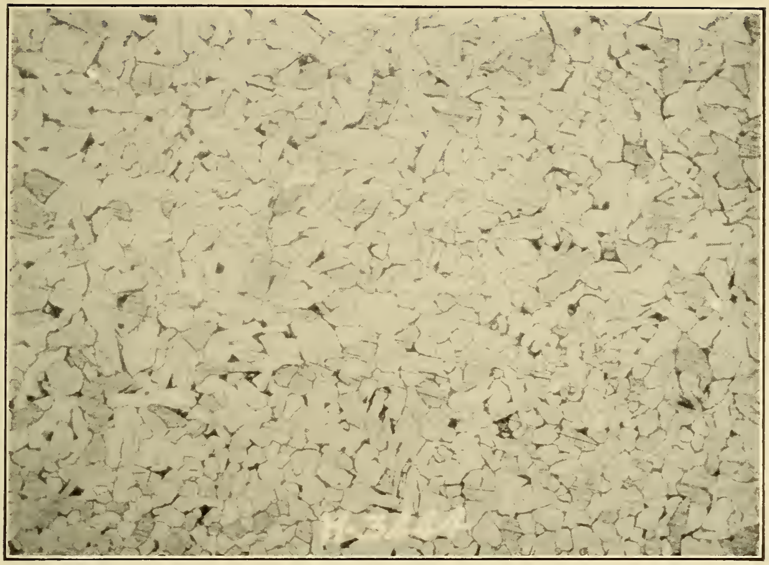

FIG. 2.—*Specimen 543* (× *100*). *Absence of iron oxide inclusions*

Per cent C = 0.09; per cent O_2 = 0.018; per cent S = 0.006

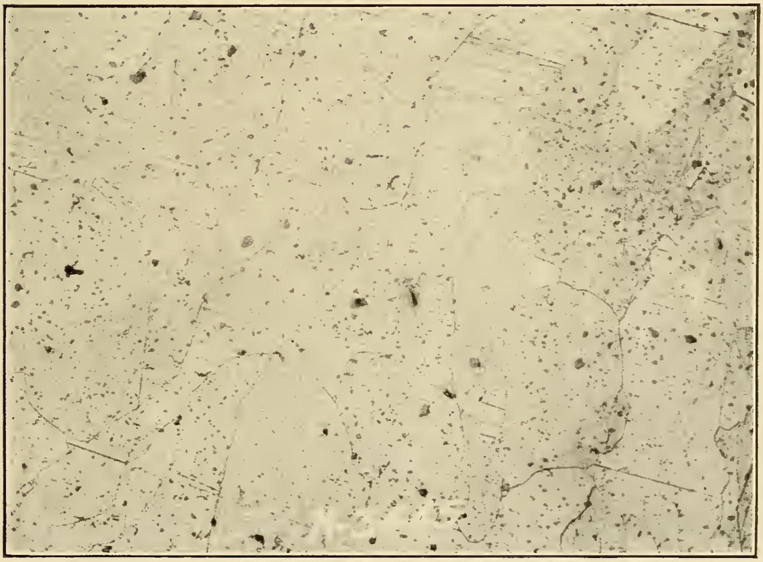

FIG. 3.—*Specimen 587* (× *100*). *Iron oxide inclusions*

Per cent C = 0.020; per cent O_2 = 0.176; per cent S = 0.003

FIG. 4. *Specimen 587* (× 100). *Unetched*

FIG. 5.—*Specimen 543* (× 100). *Unetched*

sulphur (0.015 to 0.018 per cent of the latter). Although sulphur is present in these samples considerably in excess of the amount that has been mentioned as the safe limit for preventing red-shortness (below 0.01 per cent), nevertheless none of these samples broke during the anvil test for red-shortness. Examination of the manganese content of these samples shows, in the light of what follows, that the red-shortness could not have been prevented by manganese, since the latter element was present in such small amounts. It would seem, then, that copper up to 0.5 per cent in such material tends to prevent red-shortness. It will be noted, however, that sample 85 is an exception; this sample contains a large amount of carbon in comparison with the other samples of Table 1, and this may explain the exception, since it has been found by most investigators that amounts of carbon, such as found in steels, profoundly affect the properties of the iron-copper system. Evidently, considerably more investigation would be needed if it were desired to ascertain whether copper tends to correct red-shortness when the percentage of sulphur and carbon vary considerably from the samples herein described.

Among the samples containing varying amounts of manganese relative to sulphur, where the sulphur is above 0.01 per cent, the lowest ratio found at which red-shortness was absent was Mn/S = 2.2 (sample A 510). Specimen A 511, with a ratio of 2.8, checks this result. Both of these ingots contained low percentages of oxygen and copper. Sample 3 had a considerably higher percentage of sulphur than the two specimens just mentioned, and with a manganese-sulphur ratio of 5.5 was not red-short. As yet no complete series has been made with wide variations in the percentage of sulphur or in the manganese-sulphur ratios. This may be studied in another phase of this investigation.

The recent work of Feild [21] shows that a Mn/S ratio of 3.6 is necessary in order to secure satisfactory hot-rolling properties (per cent C, 0.42; per cent S, 0.075; per cent Mn, 0.28; per cent Cu, not given); with ratios lower than this the rolling results were unsatisfactory on 10 other compositions. Feild also refers in this paper to the necessary Mn/S ratio of between 3 and 5 established by the work of Hackney [22] and to the researches of McCance [23] on

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[21] Alexander L. Feild, Effect of Zirconium on Hot-rolling Properties of High Sulphur Steels and the Occurrence of Zirconium Sulphide; Preprint 1306-S (17 pp.); February, 1924, meeting of Amer. Inst. of Mining and Metallurgical Engrs.

[22] Hackney; Discussion of paper by M. F. Gautier, The Use of Ferro-Manganese, J. Iron and Steel Inst., p. 63; 1876.

[23] Andrew McCance, Nonmetallic Inclusions; Their Constitution and Occurrence in Steel, J. Iron and Steel Inst., 97, pp. 239-286; 1918.

the equilibrium of the reaction between ferrous oxide and manganese, which is supposed to represent what takes place in deoxidation by manganese.

Samples A and B were highly oxidized, owing to exposure to air in melting, and both broke in the anvil test, even though the manganese-sulphur ratio was considerably higher than was the case for A 510 and A 511. A possible explanation is that part of the manganese found by analyses in these samples was present as oxide and hence would not be effective for preventing red-shortness. It is not impossible also in oxidized samples such as these that "oxysulphides" of iron, such as described by E. D. Campbell [24] (or eutectics of oxides of iron with sulphides of iron or manganese (see Becker, loc. cit.), are present, and the phenomena in such cases with respect to red-shortness or with respect to manganese added as a corrective for red-shortness might be quite different. The views advanced by Sargent (loc. cit.) as to the possible effect of oxides of copper on red-shortness in low-carbon irons and steels are also of interest in considering these results.

In applying the results of this work to ordinary irons and steels, it should be noted that most of the compositions given in Table 1 are quite different from any commercial product. This is particularly true of those samples having sulphur contents below 0.01 per cent, since it is very difficult and expensive to manufacture such a product commercially. The samples with very high oxygen content (0.10 per cent and above) are also abnormal in comparison with the oxygen content of commercial irons and steels reported in recent investigations. These deviations from commercial practice were made intentionally during this investigation in order to establish the various points in respect to the effect of composition on red-shortness, but it is not intended to imply thereby that the compositions herein described are practical or even advantageous. It should be noted, also, that such factors as the mass law, the rate of cooling, segregation, and slag cleansing action may profoundly affect the distribution, crystallographic habit, and form of chemical combination of the elements investigated, so that the relationships in large masses of metal, such as are used industrially, might be quite different in some cases from those described in this paper. With these qualifications, however, it is believed that the experiments described will help to throw light on some of the disputed matters affecting red-shortness.

[24] E. D. Campbell, On the Diffusion of Sulphides Through Steel, Amer. Chem. J., 18, pp. 707–719; 1896.

IV. SUMMARY

The effects of sulphur, oxygen, copper, and manganese on the red-shortness of pure iron have been investigated in a series of small experimental ingots. The results of this investigation indicate that:

1. Sulphur is the principal element responsible for red-shortness. In order to avoid red-shortness in iron not more than 0.01 per cent sulphur should be present.

2. Oxygen in amounts up to 0.20 per cent does not cause red-shortness in pure iron if the sulphur is below 0.01 per cent.

3. Manganese may prevent red-shortness in iron when present to the extent of three times the sulphur percentage, if the oxygen percentage is not above 0.04.

4. The presence of considerable amounts of oxygen in irons (0.10 per cent and above) tends to reduce the efficiency of manganese in preventing red-shortness. The hypothesis is advanced that this is because some of the manganese reported in such irons is present as oxide.

5. Copper (0.05 to 0.5 per cent) is of minor importance in its effect on red-shortness of pure iron, but in some of the specimens described in this paper it tended to decrease the red-shortness.

The author wishes to express appreciation for cooperation and assistance in this investigation from his associates in the divisions of metallurgy and chemistry of the Bureau of Standards and from the research department of the American Rolling Mill Co.

WASHINGTON, April 15, 1924.