DECARBURIZATION OF FERROCHROMIUM BY HYDROGEN.

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ABSTRACT.

The recent development of rustless iron—a stainless steel in which the carbon is largely eliminated—has emphasized the need of low-carbon ferrochromium. A number of patents claiming various methods of producing low-carbon ferrochromium, or of decarburizing high-carbon ferrochromium, have been granted. Among the methods proposed has been decarburization by means of hydrogen. Some preliminary tests of this method have been carried out on an 8 per cent carbon ferrochromium. The carbon content of powdered ferrochromium was slowly reduced by heating in dry hydrogen at temperatures between 1,100 and 1,350° C.; that is, below the melting point of the alloy. The decarburization was much more rapid when hydrogen was bubbled through molten ferrochromium. Patents have been granted which cover the decarburization of molten ferrochromium by blowing in a converter with the injection of gases or vapors into the blast. The tests made indicate that hydrogen could be used effectively in this manner.

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I. INTRODUCTION.

1. RUSTLESS IRON.

Considerable publicity has recently been given to the development in England of a rustless or stainless iron and the uses to which such material may be put. Stainless steel has become a familiar class of material. It contains in the neighborhood of 13 to 16 per cent chromium and usually 0.3 to 0.4 per cent carbon. Rustless iron contains about the same proportions of

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chromium but its carbon content is lower, in the neighborhood of or less than 0.1 per cent—a stainless steel with the carbon largely eliminated.

Some of the advantages claimed for rustless iron [1] over stainless steel are that the former is more ductile than the latter, more easily rolled or forged, does not require special heat treatment of the ingots before working, and machines more readily. It is said to have stainless or rustless properties close to those of stainless steel. It is also stated that marine growths will not adhere to plates rolled from rustless iron.[2]

2. NEED FOR LOW-CARBON FERROCHROMIUM.

In order to produce an iron alloy containing not over 0.1 per cent carbon and as high as 12 per cent chromium it is evident that the usual grades of ferrochromium are not suitable since they contain carbon in amounts so large as to introduce more than 0.1 per cent carbon in the finished metal. Usual grades of ferrochromium contain 60 per cent chromium and 4 to 8 per cent carbon. The ratio of chromium to carbon in the 4 per cent carbon alloy is thus 120 to 8, while in order to produce a 12 per cent chromium alloy with not over 0.1 per cent carbon the same ratio can not be greater than 120 to 1, or 60 per cent ferrochromium should contain not more than 0.5 per cent carbon.

II. PRODUCTION OF LOW-CARBON FERROCHROMIUM.

1. ALUMINOTHERMIC FERROCHROMIUM.

There are available "carbon-free" metallic chromium and ferrochromium manufactured by the aluminothermic reduction methods. These materials, however, command a much higher price per pound of contained chromium than the usual grades of ferrochromium—40 to 60 cents per pound of chromium as against about 11 cents per pound of contained chromium in the 4 to 6 per cent carbon ferro-alloy. At such rates the chromium in 100 pounds of rustless iron would cost from $4.80 to $7.20 when added as carbon-free aluminothermic alloys. Rustless iron would thus obviously be too seriously handicapped in commercial uses in comparison with ingot iron, copper-bearing steel, or many nonferrous metals.

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[1] L. Aitchison, Foundry Trade Jour., 24, pp. 418–420; 1921. Anon. Ibid, 24, pp. 413–414; 1921. Anon. Ibid, 24, pp. 435–436; 1921.

[2] Anon. Canadian Foundryman, 13, p. 31; 1922.

It is reported that an English process for manufacture of low-carbon ferrochromium worked out in connection with the development of rustless iron, enables selling an alloy containing only 0.25 per cent carbon[3] at a price of 20 cents per pound.

2. REFINING HIGH-CARBON FERROCHROMIUM.

Recent patents have described the production of low-carbon ferrochromium by subjecting crude high-carbon ferro-alloy to an oxidizing blast in a converter,[4] to electric-furnace treatment with oxides of iron or chromium[5] or of titanium[6] or by blowing molten high-carbon ferrochromium in a converter with the injection into the blast of steam or some other gas or vapor.[7] Ballantine has also patented[8] the method of production of chromium alloys by thermoreduction of oxides of chromium with calcium carbide in the presence of an alkaline-earth oxide with or without calcium silicide or aluminum. A still more recent patent[9] claims the method of producing rustless steel containing low carbon by adding to a molten decarburized steel in an electric furnace a mixture of aluminum and chrome ore.

III. DECARBURIZATION BY MEANS OF HYDROGEN.

An interesting, if not at present commercially practicable, method for the decarburization of ferrochromium by means of hydrogen was called to the attention of certain organizations investigating the claims of rustless iron. The Bureau of Standards was requested to carry out a few preliminary experiments to determine the feasibility of such a method.

1. PREVIOUS TESTS ON DECARBURIZATION BY HYDROGEN.

The use of hydrogen for the removal of carbon from iron and iron alloys has previously been suggested and demonstrated experimentally. Schmitz[10] has studied the action of hydrogen on the nonmetallic constituents of irons and steels and reviews rather completely previous work on the same lines. He showed that by

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[3] Anon. Iron Age, **109**, p. 597; 1922.
[4] W. B. Ballantine, U. S. Pat. 1386981; Brit. Pat. 159568. Chem. Abstracts, **15**, p. 2060.
[5] A. W. Clement, U. S. Pat. 1365091; Chem. Abst., **15**, p. 824.
[6] H. C. Sicard, U. S. Pat. 1341939; Chem. Abst., **14**, p. 2141.
Krupp Akt. Ges., Brit. Pat. 148456; Chem. Abst., **15**, p. 230.
[8] W. B. Ballantine, Brit. Pat., 152399; Chem. Abst., **15**, p. 667.
[9] W. B. Hamilton and T. A. Evans, Brit. Pat., 174271; Chem. Abst., **16**, p. 1737.
[10] F. Schmitz, Stahl und Eisen, **39**, pp. 373–381; 1919.

heating a cast iron in hydrogen at 1,200° C. for one-half hour the carbon content was reduced from 3.46 per cent to 2.74; by further successive heatings of 2 to 3 hours each the carbon was reduced to 2.16, 1.38, 0.53, and finally to 0.03 per cent. Plain carbon steels were appreciably decarburized in 15 to 35 minutes at 1,200° C. A 25 per cent nickel steel containing 0.99 per cent carbon was treated 3 successive times for 2 hours each. The carbon dropped to 0.61, 0.11, and 0.08 in the successive heatings. Schmitz also heated carbon alone in hydrogen. A sample of 0.05 g of "kish" heated for 15 hours at 1,100° C. in hydrogen lost 63 per cent of its weight. A 0.2 g sample of graphite heated 3 hours at 1,000° C. in hydrogen lost 8.7 per cent of its weight.

Campbell [11] has reported the decarburization of several steels by heating in moist hydrogen at 950 to 1,000° C. for periods of 4 to 12 days. The maximum decrease in carbon content in the specimens treated was the reduction of an original carbon content of 1.67 per cent in a chromium-molybdenum steel to 0.22 per cent after heating for 12 days at 950 to 1,050° C. Campbell concludes from results on plain carbon and alloy steels that pure carbides of iron are less stable when in solid solution than are the carbides which are formed if some other elements are present; for example, manganese.

Austin [12] has recently described the surface decarburization of three plain carbon steels treated in both moist and dry hydrogen at several temperatures between 400 and 1,000° C., giving data on the influence of time and temperature on the depth of the decarburized layers.

2. TESTS ON HIGH-CARBON FERROCHROMIUM.

The material used for the tests on the decarburization of ferrochromium was a commercial grade of 60 per cent ferrochromium containing 8.5 per cent carbon. The first tests were made on rather finely crushed material and at temperatures corresponding to those used by Campbell.

Ferro-alloy crushed to pass an 80-mesh screen was used for the first runs. This fine material contained 56.6 per cent chromium and 8.47 per cent carbon. The results of all tests are summarized in Table 1.

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[11] E. D. Campbell, J. Iron and Steel Inst., **100**, pp. 407–414; 1919.

[12] C. R. Austin, Jour. Iron and Steel Inst. (advance proof), May, 1922.

(a) ACTION OF HYDROGEN ON SOLID FERROCHROMIUM.

The first test was made on 20 g of the 80-mesh alloy placed in a silica boat and heated within a silica tube at 900° C. in a nichrome-wound electric combustion furnace. Temperatures in all runs in tube furnaces were controlled by the power consumption of the furnace, a calibration having previously been made with the hot junction of a chromel-alumel thermocouple placed in the usual position of the boat. The hydrogen gas used was commercial compressed hydrogen purified by passing successively through tubes containing soda-lime, platinized silica at a red heat, concentrated sulphuric acid, and phosphorus pentoxide. Carbon dioxide, oxygen, and moisture should be removed by this purification. In the first trial the pure dry hydrogen was passed over the sample of ferrochromium for one hour after the furnace tube reached the desired temperature. The rate of passage of hydrogen was 4½ liters per hour. Three quarters of an hour was required for the boat to reach 900° C. The sample was cooled in the stream of hydrogen. Analysis of the treated sample showed no loss in carbon.

The conditions in run 2 were modified to conform more nearly to those used by Campbell [13] in the decarburization of steels. The hydrogen free from oxygen was bubbled through water at room temperature before passing into the furnace tube.

TABLE 1.—Tests on the Decarburization of Ferrochromium by Heating in Hydrogen.

Run No.	Duration of run at maximum temperature.	Condition of hydrogen.	Approximate temperature Fe-Cr.	Carbon in original Fe-Cr.	Carbon in Fe-Cr after treatment.	Reduction in carbon in Fe-Cr.	Remarks.
	hr. min.		°C.	Per cent.	Per cent.	Per cent.	
1	1 0	Dry.....	900	8.47	8.57	.....	
2	1 30	Moist.....	1,000	8.47	8.14	0.33	Fe-Cr noticeably oxidized after treatment.
3	3 30	Do.....	1,000	8.47	8.14	.33	Fe-Cr oxidized.
4a	4 15	Dry.....	1,100	8.47	8.16	.31	Fe-Cr bright, indicating no oxidation.
4b	2 45	Do.....	1,100	8.16	8.14	.02	Residue from run No. 4a reheated.
4c	4 15	Do.....	1,100	8.14	7.88	.26	Residue from run No. 4b reheated.
7	4 0	Do.....	1,350	8.41	6.54 5.21	1.87 3.20	Unfused portion of Fe-Cr. Fused portion of Fe-Cr.
8	4 0	Do.....	1,350	8.41	6.80 6.23	1.61 2.18	Unfused portion of Fe-Cr. Fused portion of Fe-Cr.
9	.. 4	Do.....	1,500-1,600	8.47	7.50	.97	Hydrogen bubbled through molten Fe-Cr.
10	.. 20	Do.....	1,600-1,700	8.47	6.91	1.56	Hydrogen blown on surface of molten Fe-Cr.

[13] See note 11.

The temperature of the furnace was raised to 1,000° C. The heating period for this sample was 1 hour to reach 1,000° C. and 1½ hours at full temperature. The carbon in the sample after treatment was 8.14 per cent, a drop of 0.33.

The third test was made under conditions the same as those of the second, but the length of time the furnace was kept at 1,000° C. was increased to 3½ hours. The loss in carbon was the same as in run 2.

In both runs 2 and 3 the ferrochromium was very noticeably oxidized after treatment. The loss in carbon in these samples may have been due to oxidation of carbon by moisture rather than due to reduction by hydrogen. Consequently in trials 4a to 4c the hydrogen entered the furnace dry. At the same time the temperature of treatment was increased to 1,100° C. Tests 4b and 4c represent a second treatment of the ferro-alloy used in 4a and 4b, respectively. A small sample for carbon determination was removed between heatings. The total time of heating at 1,100° C. in dry hydrogen for runs 4a to 4c was 11¼ hours and the total loss in carbon was 0.57 per cent. The loss extended throughout the entire period of heating. The ferrochromium after treatment was bright and not oxidized.

It thus appeared that at 1,100° C. the reduction of carbon in ferrochromium by dry hydrogen became appreciable, although the reaction was slow. This reduction apparently is either initiated at some temperature between 900 and 1,100° C. or is very much accelerated by an increase in temperature from 900 to 1,100° C.

The next tests were made with a still further increase of temperature. The nichrome-wound resistance furnace used in the work up to this point was not suitable for use at higher temperatures. A platinum-wound tube furnace was used in runs 7 and 8. A porcelain tube was used to contain the boat and sample. In run 7 the boat also was of porcelain. The furnace was operated at 1,350° C. and the hydrogen was thoroughly dried as before. The sample was held at the maximum temperature for 4 hours. When the boat was removed it was found that the ferro-alloy in one end had melted while in the other end of the boat the alloy retained its originally powdered form, though slightly sintered. This condition was doubtless due to the nonuniform temperature in the tube over the entire length of the boat. Analysis for carbon showed a loss of 1.87 per cent carbon in the unfused portion and a loss of 3.20 per cent in the fused portion. There were indi-

cations of some attack of the glaze of the porcelain boat by the molten ferrochromium. The greater loss of carbon in the fused portion might have been caused by reaction with this glaze.

In the next trial all conditions were identical with those in run 7 with the exception that an alundum boat was used to contain the sample. After the completion of the heating the sample was found to have been melted only partially as in run 7. The loss of carbon was 1.61 per cent in the unfused portion and 2.18 in the fused.

The two tests at 1,350° C. pointed to the conclusion that there is a sudden and marked change in the rate of decarburization at the melting point of the ferro-alloy. The Krupp patent [14] for the decarburization of ferrochromium seems to cover the use of any gas or vapor in the blast of the Bessemer converter. The above tests would indicate that hydrogen might be used effectively in such a manner.

(b) ACTION OF HYDROGEN ON MOLTEN FERROCHROMIUM.

As a method of obtaining some indication of the effectiveness of blowing molten ferrochromium with hydrogen two tests were made in which the ferro-alloy was melted by direct induction in a high-frequency induction furnace. The alloy in the first run in the induction furnace (run 9) was melted in a magnesia crucible under a stream of hydrogen and then held somewhat above 1,500° C. and dry hydrogen bubbled through the melt by means of a fused-silica tube leading to the bottom of the crucible. This silica tube was corroded or melted slightly but not rapidly. The melt was blown in this manner for 4 minutes. The carbon content of the alloy was reduced from 8.47 to 7.50, a loss of 0.97 per cent. That this loss in carbon was not due to oxidation by silica from the small tube through which the hydrogen was introduced was indicated by the fact that the silicon in the ferro-alloy was not increased during the melting. The silicon content of the original ferro-alloy was 0.87 per cent, while in the alloy after run 9 it was 0.55 per cent.

The rapidity of the reduction in carbon by a 4-minute blowing of the molten ferrochromium with hydrogen is striking when compared with the reduction of 1.87 per cent in the unfused alloy after heating for 4 hours at approximately 1,350° C.

Molten metal heated by direct induction in the high-frequency furnace is very rapidly stirred by the magnetic flux. It was

[14] See note 7.

thought worth the trial to make a test in which hydrogen was blown only on the surface of molten and rapidly stirred ferrochromium. For run 10 the alloy was melted in a crucible of 85 per cent magnesia and 15 per cent zirconium silicate. The molten metal was unintentionally allowed to attain a temperature of 1,700° C., a much higher temperature than in run 9, and the silica tube through which the hydrogen was flowing was rapidly melted off at the end, although not touching the molten metal. Hydrogen was blown on the surface of the melt for 20 minutes.

The carbon content of the alloy in this run was reduced from the original 8.47 to 6.91, a loss of 1.56 per cent. This loss in carbon was caused in large part by the reduction of silica at this high temperature, as is indicated by the increase of the silicon content of the ferrochromium from the original 0.87 to 1.61 per cent.

IV. SUMMARY.

The recent development of stainless or rustless iron—a low-carbon stainless steel—has emphasized the need of low-carbon ferrochromium. Among several methods of refining or reducing the carbon content of commercial grades of high-carbon ferrochromium, decarburization by means of hydrogen has been proposed. Moist hydrogen at 1,000° C. reduces the carbon content of ferrochromium but also oxidizes the ferro-alloy somewhat. Dry hydrogen reduces the carbon very slowly, if at all, at 900° C.; at 1,100° C. the reduction is appreciable; at temperatures close to the melting point of 8 per cent ferrochromium the reduction in carbon is still greater and is much more rapid at a temperature slightly above than at one slightly below the melting point. The most rapid reduction in carbon was obtained by bubbling hydrogen through molten ferrochromium at somewhat above 1,500° C. At a higher temperature and in the presence of silica the loss in carbon was partly due to the reduction of silica to silicon.

The preliminary tests made indicate that while the decarburization of high-carbon ferrochromium by means of hydrogen takes place to some extent at temperatures below the melting point of the alloy, the most promising condition for refining high-carbon ferrochromium by this method is probably blowing the molten alloy with a blast of hydrogen in a converter.

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