the semi-crystalline mass extracted with ether, the ethereal solution evaporated to dryness, crystals formed freed from oily substance by washing with ligroin, and recrystallized from benzene.

Of the products theoretically possible, acetophenone pinacone, or diphenyl dimethyl glycol, forms large colorless prisms, melting at 120° C. The product obtained melts at 120° C., and in every particular corresponds to the above. The yield was excellent.

It is our intention to further pursue the investigations with nitriles, ketones, oxynitriles, and amido-nitriles.

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TWO DEFINITE CARBIDES OF IRON WITH CHROMIUM (MOLYBDENUM AND TUNGSTEN).

BY JAMES S. DE BENNEVILLE

Received September 6, 1895.

A PREVIOUS paper[1] described in detail the results of a chemical examination of some ternary alloys of iron with chromium, molybdenum, and tungsten. In the course of the experiments there described two definite carbides were separated and it is proposed to give additional details obtained later. The physical description of the crystals is taken from Professor F. Lynwood Garrison's discussion of the paper cited.[2] The alloys described were made by taking pairs of the elements: tungsten chromium irons, molybdenum chromium irons, and molybdenum tungsten irons. The proportions taken were not based on equal weights but on quantities taken in the ratio of the atomic masses of the constituents. They were 1:1, 5:1, and 1:5. A lump of cast iron weighing fifty grams was imbedded in the mixture and melted, a white heat being maintained for an hour. The aggregations to be described were found in the chromium alloys and only in the two alloys (Nos. II and V) in which chromium was the predominant metal. These two alloys showed well individualized crystals differing in form and reactions from the matrix in which they were imbedded.

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[1] Iron and Steel Institute, May meeting, 1895.

[2] *Ibid.* I take this opportunity of expressing my indebtedness to Professor Garrison, through whose kind offer I was enabled to present this paper to the council of the Institute.

Berthier and also Percy[1] have noted the presence of needle-shaped crystals in ferrochromium and in chromium steels. Further details are not given. Behrens and Van Linge, in a recent paper, have described at length the physical and chemical properties of segregations in ferrochromium. On treating the alloy with acid they obtained bayonet or rod-shaped crystals, three to four millimeters in length, a few being eight to ten, non-magnetic, of hardness 7.5. The composition, however, varied with the ferrochromium from which they were obtained; ferrochromium with 13.8 per cent. chromium, eighty-one per cent. iron, and five and one-half per cent. carbon, giving the compound $Cr_2Fe_7C_3$, whereas with fifty per cent. chromium, the composition was approximately Cr_2FeC_2. They point out the relation of the first compound to Fe_3C, chromium replacing a part of the iron, and consider that chromium forms "double carbides less soluble in iron than the ferrocarbides, at the same time facilitating the crystallization of the latter."[2]

Considering the marked development of the segregations in the ternary alloys it appears to me doubtful whether they are to be referred, as to origin, to the iron carbides. The prismatic form is not a dominant one with the iron carbides, although it is found under certain conditions. Howe, citing Sorby, notes three successive crystallizations in hard cast-steel. I quote him in *extenso*: he says, "First we have the large prismatic columnar crystals, normal to the cooling surface, and conspicuous on fracture. They apparently represent the first crystallization, be it of hardenite, be it of the hypothetical mother-of-pearlyte, which in this case has expelled the excess of cementite present, distributing it as an elongated meshwork between the crystals. Secondly, these columns or crystals are chiefly composed of groups of pearlyte, disposed with little or no relation to the columnar structure, indeed shooting from one column into another, and apparently formed from the substance of the primary crystals of a second crystallization. Finally, by a third crystallization, each of the individual members of the radial

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[1] Percy, *Iron and Steel*, p. 186. Berthier from Percy not the original.

[2] Recuil trav. chim. Pays-Bas., 13, 155-181. From the abstracts in *J. Soc. Chem. Ind.*, 14, 275, *1895*, and *J. Chem. Soc.*, **64**, 452, *1894*.

groups of pearlyte has split into parallel layers of cementite and ferrite, which apparently occupy the space previously occupied by a simple undivided crystal.'' Again, ''the exterior columnar structure is clearly due to the rapid escape of heat from the shell of the ingot into the mold. We may suppose that the metal naturally tends to crystallize in equiaxed grains: that there is a struggle between this tendency and the tendency to crystallize in indefinitely long prisms which the rapid cooling sets up. As the walls thicken and the flow of heat outward slackens, the prismatic tendency weakens: the sudden transition from the prismatic to the equiaxed formation suggests that no resultant, no compromise is possible, so that from the moment when the equiaxial tendency outweighs the prismatic it reigns alone, as if its rival were not.''[1] This is the only mention of prismatic structure in ordinary carbon steel that I find in the ''Metallurgy.'' If the intense hardness of ferrochromium, ferrotungsten, and ferromolybdenum is to be ascribed to the conversion of the carbon present into hardening carbon and its retention in that form—although from the researches of Riche and especially of Moissan this hardness can just as well be attributed to carbides of chromium, tungsten, or molybdenum—the alloys under discussion can be justly compared to hard cast-steel containing a large excess of carbon and the prismatic form of the crystals in II and V could be attributed to a structure found in such steel as described above. However, the conditions are by no means identical. The crystals in II and V are present throughout the mass forming a network with the interstices filled in by the equiaxial granular material. There is no line where the equiaxial tendency has overcome the prismatic and so sharply differentiated the alloys into an external prismatic shell surrounding an interior of equiaxed grains. Also, the crystals show a marked increase in density as compared with the granular material and the alloys in which they are found differ in hardness from the rest of the series. In fact, the crystals give every evidence from their sharpness of outline of having a higher freezing-point and as having separated out from the mass of the alloy at a time when it was not liquid enough to effect their

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[1] Metallurgy of Steel, p. 182, 183.

segregation into any one portion of the alloy, but liquid enough to secure their own crystalline form at the expense of compounds crystallizing later. For when a mass of iron is allowed to cool uniformly, from the resultant structure it would appear that the constituent compounds have freezing points not so far removed from each other as to effect the segregation of any one of them into a part of the mass. This has no reference to the microstructure of iron and steel in which the compounds identified appear to be somewhat unstable in nature, passing readily from one form to the other even by cold working. The columnar structure is only stable under the limited conditions existing for its formation and by slight alteration of the method of cooling or of working passes readily into other forms. Also, the columns are often distinctly a mere structural arrangement of the granular material with radial lines forming prismatic aggregations in which the granular components are distinctly manifest. There is in the micro structure of steel a compound to the development of which might be attributed the prismatic and needle-like form when found in iron alloys. This has been described by Osmond[1] and named by him martensite. It is found in steel of 0.45 carbon heated to 825° and tempered at 720° in a cooling mixture of —20°. It occurs "in groups of needles or rather of rectilinear fibers lying parallel and separated or not by a granular or vermicular filling." From the grouping of three systems of fibers respectively parallel to the three sides of a triangle he regards them as crystallites of the cubical system. In the absence of any other source the form of the prismatic needles found in ferrochromium and in these tungsten chromium irons (II) and molybdenum chromium irons (V) could be attributed to the development of the microstructural element, to the fixation of the prismatic columnar structure, or to the rod-shaped fiber structure of Abel's carbide Fe_3C. As to the two first, in despite of their instability and the absence of any boundary line between the prismatic and granular formations, it seems to me better to attribute the form to the carbide of chromium isolated by Henri Moissan.[2] This carbide, of formula CCr_4, he describes

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[1] Bull. de la Soc. d'Enc. pour l'Ind. Nat., May, *1895*.

[2] Bull. Soc. Chim. Paris, 11, 1016, *1894*.

as forming needles one to two cm. in length lining the cavities found in the melt. He also isolated a carbide C_2Cr_3 occurring in brilliant lamellae. Of the two the lamellar carbide was the harder, scratching topaz but not corundum, whereas the prismatic carbide scratched glass readily, but quartz only with difficulty. Both carbides were very stable compounds and were chemically inert. The crystals found in the ternary alloys were confined to the high chromium compounds in which the ratio of chromium to tungsten or molybdenum was as five to one. The alloys, II and V, were much softer than the other alloys, which would be the case if hardness is dependent on the carbide of chromium present. For comparison, Table I gives the composition of the series of alloys.

If now the prismatic segregations in ferrochromium be compared it will be found that, with the exception of the compound $Fe_7Cr_3C_2$, chromium is the dominant constituent in the carbide. For example :

TABLE II. SEGREGATIONS IN FERROCHROMIUMS.

	B. and Van L. $Fe_7Cr_2C_3$.	B. and Van L. $FeCr_2C_2$.	V. Analysis 1 $Fe(CrMo)_8C_4$.	V. Analysis 2. $Fe(CrMo)_8C_4$.	II. $Fe(CrW)_6C_4$.	II B. $Fe(CrW)_8C_4$
Iron	0.8100	0.3030	0.4639	0.4650	0.4724	0.4723
Chromium ..	0.1380	0.5671	0.4623	0.4606	0.3542	0.3682
Molybdenum	....	....	0.0201	0.0194	....	....
Tungsten ...	....	....	....	....	0.1139	0.1007
Carbon	0.0550	0.1299	0.0553	0.0559	0.0595	0.0599

$Fe_7Cr_2C_3$, on the contrary, could fairly be classed as derived from an iron compound—Fe_3C. This compound, isolated by Abel and subsequently by Muller, is described as a dark-grey residue ; Osmond and Werth obtained it in the form of bright plates ; Behrens and Van Linge treating Dannemora iron, obtained it as bright spangles and rods ; and Arnold and Read obtained it in two forms, as bright silver plates and as a grey black powder in microscopic granules.[1] The segregations in the ternary alloys are to be compared with the " brilliant white radial needles" described by Behrens and Van Linge and which

[1] Abel—Proc. Inst. Mech. Eng., *1895*, p. 30 ; Muller—Stahl und Eisen, No. 5 ; Osmond and Werth—Annales des Mines *1895* ; Behrens and Van Linge—as cited, *1894* ; Arnold and Read—*J. Chem. Soc. Trans.*, 65-788, *1894*. Also Ledebur Jour. Iron aud Steel, Inst. 1893, II. 53. The quotations following are from the abstract of Behrens and Van Linge's paper.

TABLE I. COMPOSITION OF THE ALLOYS. *J. Iron and Steel Institute*, I, 1895.

ALLOY	I	II	III	IV	V	VI
Total carbon	0.0317	0.0299	0.0311	0.0323	0.0312	0.0323
Carbon evolved by hydrochloric acid	0.0122	0.0074	0.0127	0.0104	0.0084	0.0130
Carbon in hydrochloric acid residue	0.0195	0.0225	0.0184	0.0219	0.0228	0.0193
Carbon in nitric acid residue	none	Table VIII	none	none	Table VIII	none
Silicon evolved by hydrochloric acid	0.0033	0.0142	0.0072	0.0075	0.0055	0.0022
Silicon in hydrochloric acid residue	0.0193	0.0083	0.0130	0.0103	0.0119	0.0051
Phosphorus evolved by hydrochloric acid	0.0019	0.0025	0.0012	0.0014	0.0020	0.0003
Phosphorus in hydrochloric acid residue	0.0009	0.0007	0.0003	0.0006	0.0005	0.0020
Manganese	0.0004	0.0043	0.0049	0.0013	0.0027	0.0004
Sulphur	——	.....	.....	.....	.....	.....
Chromium	0.0846	0.1207	0.0211	0.0802	0.2257	0.0485
Tungsten	0.3382	0.0440	0.2125	.....	.....	.....
Molybdenum	——	.....	.....	0.1184	0.0735	0.3065
Iron	0.5197D	0.7754D	0.7087D	0.7531	0.6470D	0.5999
Specific gravity	11.010	7.995	10.257	7.571	7.300	8.410
Formula	$Fe_{45}Cr_7W_8$	$Fe_{62}Cr_{10}W$	$Fe_{34}CrW_3$	$Fe_{46}Cr_6Mo_4$	$Fe_{65}Cr_{23}Mo_4$	$Fe_{25}Cr_2Mo_7$
Condensation from composition difference	2.051+	0.453+	1.869+	0.089+	0.054−	0.963+

ALLOY	VII	VIII	IX	Cast iron used.	Chromium for steel.	Tungsten for steel.
Total carbon	0.0335	0.0289	0.0290	0.0331	0.0773	0.0343
Carbon evolved by hydrochloric acid	0.0162	0.0126	0.0147	0.0039	.....	0.0014 nitrogen
Carbon in hydrochloric acid residue	0.0173	1.0163	0.0153	0.0292	.....	.....
Carbon in nitric acid residue	none	none	none	0.0286	.....	.....
Silicon evolved by hydrochloric acid	0.0073	0.0184	0.0023	0.0030	total	total
Silicon in hydrochloric acid residue	0.0097	0.0067	0.0049	0.0194	0.0144	0.0039
Phosphorus evolved by hydrochloric acid	0.0014	0.0017	0.0018	0.0020	total	total
Phosphorus in hydrochloric acid residue	0.0006	0.0013	0.0006	0.0004	0.0012	trace
Manganese	0.0003	0.0019	0.0034	0.0071	trace	none
Sulphur	.....	.....	.....	0.0003	.....	.....
Chromium	.....	.....	.....	.....	0.8995	.....
Tungsten	0.1471	0.1940	0.3066	.....	.....	0.9593
Molybdenum	0.0949	0.1346	0.0379	.....	.....	.....
Iron	0.7012	0.6086	0.6189	0.9347D	0.0079	0.0007
Specific gravity	11.154	11.384	12.365	7.474	5.103	15.175
Formula	$Fe_{68}Mo_5W_4$	$Fe_{34}Mo_4W_3$	$Fe_{120}Mo_4W_{17}$	.....	.....	.....
Condensation from composition difference	2.898+	2.942+	3.438+	.....	.....	.....

D=by difference.

are characteristic of ferrochromium, attaining a very marked development which places them entirely outside the category of micro or sub-micro structure. I am in doubt as to whether the formula $Fe_7Cr_2C_3$ is meant to represent the needles, for this compound is described as "a coarse brownish grey lustrous powder, made of small bars, of which many are three to four mm. in length." The data are confessedly very scanty but against the iron derivation of the needles is to be placed the three compounds found in the ternary alloys whose constancy can hardly be ascribed to the constituent tungsten or molybdenum, metals chemically to be classed with chromium; and the existence of Moissan's carbide Cr_4C, an analogous compound. This is more clearly understood from Professor Garrison's description given later. That, however, the constitution of such compounds would be dependent on the composition of the mixture and would only be fairly constant within certain limits can be readily understood, as, for example, with double salts crystallizing in varying proportions; and hence when the iron becomes an unimportant factor in the composition of the alloy its influence would correspondingly wane in the compound crystallizing from the mixture, and vice versa. It is to be noted, moreover, that very little is known of the valence or combining power of the elements in metallic alloys and not only is this lacking for iron and chromium, but if the composition of the crystals is dependent on the composition of the alloy and the temperature at which they separate there may also be an alteration in the ratio in which iron and chromium combine, for valency may well be dependent on the temperature. Note that alloy II contains 12.07 per cent. of chromium but has a much greater content of chromium in the separated crystals than the compound of formula $Fe_7Cr_3C_2$.

The separation of the crystals from the granular material was readily effected by the comparatively slight action of nitric acid which left the crystals as residue intermixed with a little silica. This was volatilized as silico-fluoride and after washing with water and subsequently with ninety-five per cent. alcohol the crystals were obtained free from impurity. Their reactions show them to be chemically very inert compounds. As stated, they are but little attacked by nitric acid, strong or dilute.

Hydrochloric or hydrofluoric acid does not attack them. Strong sulphuric acid slowly decomposes them leaving a black residue which still retains the form of the crystals. The solvent is useless as a means of analysis. By themselves the crystals are attacked but slowly by strong aqueous solution of bromine or of iodine and only on heating. However, in the residue obtained by treating the allow with these reagents no trace of the crystals could be observed, using a lens magnifying fifty diameters. With reflected light the residues showed granular masses of irregular shape with brilliant metallic luster. From the mode of occurrence of the crystals in the alloy they could hardly have been absent from the samples examined. At a red heat chlorine, bromine, and iodine readily decompose them, but their analysis is best effected by fusion with an oxidizing mixture of sodium carbonate and saltpeter with addition of caustic soda.

Professor Garrison, in his discussion,[1] gives the form and dimensions of the crystals as follows: "I have examined under the microscope the segregations obtained from alloys II and V and find them to consist of well developed prismatic hexagonal crystals, more or less corroded by the nitric acid solvent. I was not able to detect any of the crystals with pyramidal terminations; most of them appeared to have been broken, leaving ragged ends, as would be observed in Figs. 1 and 2. The general appearance of the crystals from the different alloys is similar. Those from II averaged 0.03 to 0.04 of an inch in length, and 0.003 of an inch in diameter; those from V were 0.03 to 0.04 in length and 0.005 of an inch in diameter. The aspect of the crystals under a magnification of thirty-five diameters is well shown by the micro-photographs; Fig. 1 being from alloy II, and Fig. 2 from V. I was able to detect a slight difference in color between the two varieties when they were heaped in masses and held in the proper light. II had a decided yellowish metallic luster; V a dark steel grayish-blue color and luster. The slight difference in thickness was not appreciable to the naked eye, neither would the color or luster be apparent to a casual observer. I experienced some difficulty in making the specific gravity determinations of these crystals, owing to

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[1] Iron and Steel Institute, May meeting, [illegible]

the extremely small quantities. On the whole, I think those mentioned are nearly correct, although that of II might be a light one." Of II specific gravity is 12.80; of V 7.473 (Garrison).[1]

The analytical results obtained were:

Alloy V.—Ferromolybdenumchromium Carbide. The analysis was made as follows: Half a gram of pure crystals were fused with the oxidizing mixture with addition of caustic soda. The melt was cooled, lixiviated in water, and the solution containing chromate and molybdate filtered from the residual ferric hydroxide. The solution was acidified with hydrochloric acid and boiled to dryness with addition of alcohol to ensure reduction of the chromic salt. The residue was then dissolved in a little dilute hydrochloric acid, diluted and brought to boiling. Chromium was precipitated by ammonia in excess, the boiling being continued for at least half an hour. The precipitated chromic hydroxide was filtered off, washed twice with hot water, dissolved in dilute hydrochloric acid, and reprecipitated by ammonia. This solution was filtered, the filtrate being added to the first but not the washings. The chromic hydroxide was now thoroughly washed by boiling up with water, decanting, finally throwing on the filter, and washing with boiling water. It was then dried, ignited, and weighed as Cr_2O_3. In analysis 1 (table II) the filtrate containing the molybdenum was boiled until the odor of ammonia had to a great extent disappeared. The solution was then acidified with sulphuric acid, poured into a separatory funnel containing zinc and, after reducton, titrated with permanganate (Pisani's method). In analysis 2 the molybdenum was determined gravimetrically. The ferric hydroxide was examined for silica but the quantity found checked closely with that present in the alkali salt used for fusion. After removal of platinum, iron was converted to sulphate and titrated in acid solution by permanganate. The chromic oxide was fused with bisulphate and the solution examined for phosphorus with nega-

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[1] In some experiments carried out by Professor Garrison and myself with highly phosphoric titaniferous pig iron, prismatic needles were obtained lining the cavities and blow-holes. Their form could not be made out with certainty but they were well developed and in no sense belonged to the micro structure of the alloy. They have not yet been isolated. The prismatic form is of frequent occurrence in Ferromanganese.

tive results. If silicon or phosphorus were important constituents of the crystals they would readily be detected in a half gram sample. The carbon of analysis 1 was determined by direct combustion of the crystals with the lead and potassium chromate mixture. The carbon of 2 was determined by combustion of the residue obtained after first decomposing in chlorine at a red heat.

TABLE III. FERROMOLYBDENUMCHROMIUM CARBIDE.

	Analysis 1.	Atomic ratio.	Analysis 2.	Atomic ratio.
Iron	0.4639	0.828	0.4650	0.830
Chromium	0.4623	0.882	0.4606	0.879
Molybdenum	0.0201	0.021	0.0194	0.020
Carbon	0.0553	0.461	0.0559	0.464

No manganese, silicon, or phosphorus were present. These results give the ratio Fe : CrMo : C : : 1.79 : 1.95 : 1, or formulated $Fe_7(CrMo)_8C_4$. To this compound I give the name Wahlite, from Dr. William H. Wahl, well known for his valuable contributions to metallurgy.

Alloys II and II B.—*Ferrotungstenchromium Carbide.* In addition to the alloy (II) described in the first paper, a second alloy (II B) was made using 200 grams of iron in the melt instead of fifty. The object in doing so was to determine whether change in composition of the melt had any effect on the composition of the resultant crystals. The quantity of crystals obtained for analysis II was small. Iron, chromium, and tungsten were determined after purifying by nitric acid one gram of the original material. The residue was then analyzed and the calculations made to 100 per cent. For analysis II B abundant material was available. Considering the small quantities available for the first analysis the agreement is satisfactory. Comparing with alloy V it would appear that the ratio of chromium to iron is not the same in the two alloys. Tungsten and molybdenum probably play the same role as chromium and replace it perhaps in varying quantities. The analysis was made by decomposing the crystals as with alloy V. The solution containing tungstate and chromate was acidified with hydrochloric acid, alcohol added, and evaporated to dryness. The residue was taken up in dilute hydrochloric acid and an equal bulk of alcohol added.

The tungstic acid was filtered off, dissolved from silica by ammonia, the solution evaporated, and tungsten determined as WO_3. The filtrate containing chromium was brought to boiling and chromium hydroxide thrown down by ammonia. Alloy II, as obtained in original sample, contained iron 0.0423, chromium 0.0317, tungsten 0.0102. The analytical results gave :

TABLE IV. FERROTUNGSTENCHROMIUM CARBIDE.

	Alloy II.	Atomic ratio.	Alloy II B.	Atomic ratio.
Iron	0.4724	0.843	0.4723	0.843
Chromium	0.3542	0.676	0.3682	0.702
Tungsten	0.1139	0.060	0.1007	0.054
Carbon	0.0595	0.496	0.0599	0.494

No manganese, silicon, or phosphorus was present in II B. These results give the ratios :

Alloy II. Fe : CrW : C :: 1.69 : 1.49 : 1, or formulated $Fe_7(CrW)_6C_4$.

Alloy II B. Fe : CrW : C :: 1.73 : 1.53 : 1, or formulated $Fe_7(CrW)_6C_4$.

Carbon in both cases was determined by direct combustion of the crystals. To the compound I give the name Garrisonite, from Professor F. Lynwood Garrison, a valued contributor to the study of the microstructure of iron and to its metallurgy. Alloy II B contained, chromium 0.1070, tungsten 0.0871.

ON THE POSSIBILITY OF THE OCCURRENCE OF HYDROGEN AND METHANE IN THE ATMOSPHERE.[1]

Received September 9, 1895.

BY FRANCIS C. PHILLIPS.

WHATEVER may have been the process by which organic remains have in the course of time been caused to yield gas and petroleum, a considerable portion of the gas evolved in the early stages of decay must have escaped into the atmosphere before the burial of such remains under sedimentary deposits, and the consequent imprisonment of the more volatile products could have occurred. This would have been the case if, as in the view of the older geologists, the source of gas and oil is to be looked for in the slow decomposition, at low temperatures, of

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[1] Read at the Springfield meeting.