QUANTITATIVE SEPARATION OF WC FROM W_2C AND TUNGSTEN, AND THE CONDITIONS OF FORMATION OF THE TWO CARBIDES.

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Introduction.

Three different carbides, WC (C = 6.12%), W_2C (C = 3.16%), W_3C (C = 2.12%), have been described of tungsten. H. Moissan and M. P. Williams[1][2] got W_2C by heating WO_3 or W with carbon in an electric furnace above 2000°C., WC was formed, in this case, only when excess of iron was added. This result has been written in many books and seems to be still generally believed. W. Hempel and P. Rucktäschel[3] heated the compressed mixture of metallic powders of W with carbon black at high temperatures, but they did not find a carbide containing more carbon than 3.3 per cent. J. N. Pring and W. Fielling[4] got W_2C by heating a carbon rod in WCl_6 gas above 1500°C. O. Ruff and R. Wunsch[5] melted the mixed powders of tungsten and carbon in an electric furnace at above 2750°C. in vacuum or in the atmosphere of hydrogen. They could not get a higher carbide than WC. On quenching the molten mass containing both WC and W_2C in ice-water remained WC undecomposed. But when the quenching was done a little slowly some WC decomposed into W_2C and free carbon. They believed, besides, the existence of W_3C. M. R. Andrews[6] heated

(1) Moissan, *Ann. chim. phys.*, **7** (1896), 8,570; *Compt. rend.*, **116** (1893), 1225; ibid. **123** (1896), 13.
(2) Williams, *Compt. rend.*, **126** (1898), 1722; ibid. **127** (1898), 410.
(3) Hempel and Rucktäschel, Z. *angew. Chem.* **17** (1904), 296, 321.
(4) Pring and Fielling, *J. Chem. Soc.*, **95** (1909), 1497.
(5) Ruff and Wunsch, *Z. anorg. Chem.*, **85** (1914), 292.
(6) Andrew, *J. Phys. Chem.*, **27** (1923), 270.

tungsten filament in the atmosphere of naphthalene etc. at above 1600°K. Free carbon deposited upon the filament and diffused into it. The electric resistance-composition curve proved clearly the existence of WC and W_2C but denied any higher carbides and W_3C. C. A. Matignon[1] got W_2C from WO_3 and carbon at 2130°C. A. Westgren and G. Phragmen[2] observed that WC decomposes into W_2C and carbon on strong heating in a closed vessel. From these literatures we can conclude as following :

(a) There is no carbide richer on carbon than WC.

(b) Two carbides, WC and W_2C, were proved really to exist.

(c) WC is formed only at very high temperatures or in presence of excess of iron. It decomposes into W_2C and carbon on cooling.

(d) W_2C is most easily obtainable.

(e) Ruff and Wunsch believed the existence of W_3C, but from insufficient evidence. Andrews showed, on the contrary, exactly that it does not exist. Other authors did not describe on it. So that it may be quite natural to deny its existence.

The samples prepared by previous investigators were all mixtures of W, WC, W_2C and C. They found total carbon, tungsten and free carbon by analysis and calculated the combined carbon. But they could not know the percentages of W, WC and W_2C. Their conclusions were, therefore, very ambiguous. In this paper a new analytical method to find directly the percentage of WC in the mixture was developed, and hence those of W and W_2C were also calculated. And the conditions of formation of the two tungsten carbides were found.

Experimental.

Preparation of Pure WC. The most reliable method ever known to get WC is to melt WO_3 or W with carbon in presence of excess of iron. The samples used in the experiments were prepared by the following two ways.

(a) Powder of ferro-tungsten containing 80% of W was mixed with 2% of carbon black and melted in a carbon crucible. After cooling it was powdered and analysed.

Total carbon = 4.38 ; Free carbon = 0 % .

(Total carbon was determined in an ordinary way by combustion on adding CuO powder. A sample was taken in a platinum dish and the mixture of moderate HNO_3 and conc. HF was added. After the reaction was

(1) Matignon, *Compt. rend.*, **177** (1923), 1290.
(2) Westgren and Phragmen, *Nature*, **113** (1924), 122.

completed, the acids were removed by evaporation. The excess of ammonia was then added and the solution filtered through asbestos wool. Free carbon caught by asbestos was dried and analysed by combustion with oxygen.)

The sample was ground very finely in an agate mortar and the greater part of iron in it was extracted by warm hydrochloric acid (2 normal) on a water bath for 4 days. After the residue was washed with water and dried, it was subjected to magnetic separation. The residual sample containing about 10 per cent. of iron was heated at about 580°C. in the atmosphere of chlorine gas; it lost about 11 per cent. of its weight in this refining process. After washing with dilute ammonia and water it was dried and analysed.

Total carbon = 6.12; Free carbon = Trace; Fe = 0.16%.

(b) Tungsten powder mixed with 7 per cent. of carbon black was heated in a carbon crucible at about 1800°C. The product was powdered and treated three times in the same way. The analysis of the final product was as follows.

Total carbon = 5.98; Free carbon = 0%.

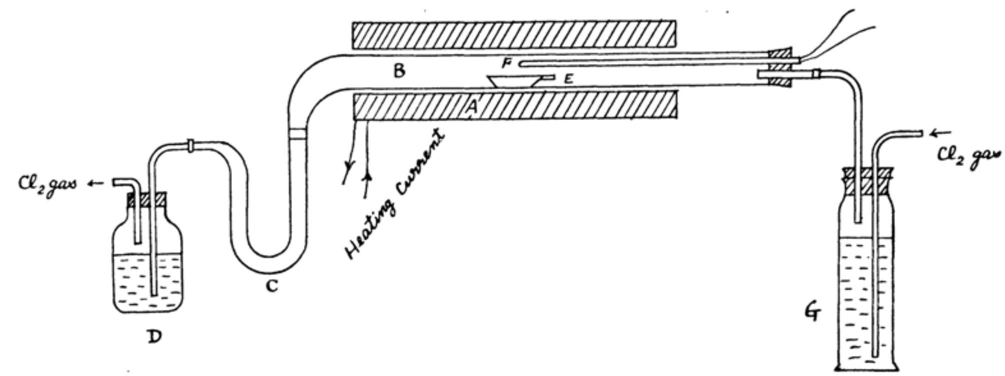
It was then ground very finely and heated at 580°C. in an atmosphere of chlorine gas, it lost 5.6 per cent. of its weight. It was washed by dilute ammonia and water and analysed after drying.

Total carbon = 6.10; Free carbon = 0.12%; Fe = nil.

Considering from the results of the previous investigators and from the above analyses, it is certain that the samples prepared by the both processes (a) and (b) are pure WC.

A New Analytical Method to Separate WC Quantitatively from W_2C and W. *Principle:* Tungsten and W_2C react with chlorine gas and sublime at relatively low temperatures, but WC does not react until higher temperatures. This difference of reacting temperatures (or reaction velocities) was studied accurately and applied for the quantitative separation of WC from the others.

Experiment: The apparatus is shown in Fig. 1. Chlorine gas from a bomb was dried by passing through conc. sulphuric acid and introduced into the reaction tube. Care was taken each time to place the hot junction of the thermocouple, sealed in a thin porcelain tube, just above the center of the boat. When the required temperature was reached, the boat which had been kept at a cold part of the reaction tube was placed under the hot junction of the thermocouple. After a definite time (30 minutes) the heating current was cut off and the furnace was allowed to cool, still passing chlorine



A ··· Electric resistance furnace
B ··· Reaction tube
C ··· U-tube to collect the sublimed product
D ··· Bottle containing dilute alkali
E ··· Boat for sample
F ··· Hot junction of thermocouple
G ··· Bottle containing conc. H_2SO_4

Fig. 1.

gas. The weight decrease of the sample was determined by weighing the boat before and after the experiment. The sublimed product was collected at C and D and analysed occasionally to check the result.

The Reaction of WC: Two samples (a) and (b) previously described were tested. The results are shown in Fig. 2. The decreases of weight expressed in percentage of the initial weight are taken as ordinates, while the temperatures as abscissae. The tungsten which was sublimed at 800°C. and collected together was 0.440 gr. This amount well coincides with 0.439 gr. of the weight decrease.

The Reaction of Tungsten: Two samples were tested. (a). Tungsten powder from E. Merck in Germany was reduced by hydrogen at 1000°C. (b). Powder of tungstic acid (WO_3) from E. Merck was reduced by hydrogen at 1000°C. The results are shown in Fig. 2.

The Reaction of W_2C: W_2C is most easily obtainable among tungsten carbides. Two kinds of samples were prepared. (a). Tungsten powder was mixed with 3.3 per cent. of carbon black and heated in a carbon crucible at about 1600°C. for

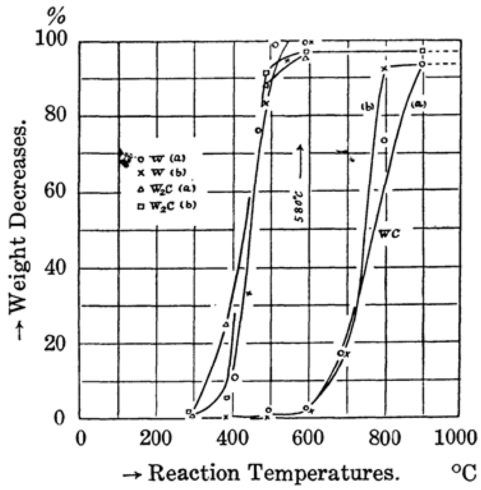


Fig. 2.

one hour. The greyish outer zone of the obtained mass was removed after cooling and the central part of yellowish brown was ground in an agate mortar. The elutriated and dried powder was reduced by hydrogen at 1000°C. (b). The second product had also greyish outer zone but its central part was coloured from green to blue. The blue part was collected and treated as (a). The results of analyses were as following.

(a) Total carbon = 2.41; Free carbon = 0 %.

(b) Total carbon = 2.61; Free carbon = 0 %.

These samples consist, no doubt, mainly of W_2C, but some WC and tungsten may also be contained. The results of experiments are shown in Fig. 2.

The Reaction of Carbon: The reaction residue of W_2C (in Fig. 2) at 900°C. was weighed as 2.61 per cent. of the initial weight and was found by analysis to contain 96.0 per cent. of carbon. It may be concluded, therefore, that both free and combined carbon are not lost when heated at such high temperatures in chlorine gas. In separate experiments carbon was also observed not to decrease its weight by heating up to 800°C. in chlorine gas. From the curves of Fig. 2 the following conclusions may be drawn.

1. WC does not react with chlorine under 600°C. The reaction begins at 600°C. and completes at about 800°C.

2. Tungsten reacts fairly at 400°C., vigorously at 500°C. and the reaction completes under 550°C.

3. W_2C seems to react at a little lower temperature than tungsten and the reaction completes under 550°C.

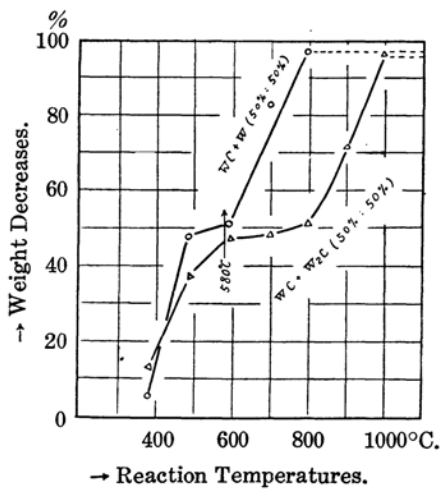


Fig. 3.

WC must, hence, quantitatively be separated from W_2C and tungsten on heating the mixture in chlorine gas at about 580°C. Some examples of analyses will be given in the next lines.

Example 1. WC+W (50% : 50%)

Equal parts of samples of WC (b) and W (a) were mixed and ground in an agate mortar and heated in chlorine gas at various temperatures for 30 minutes. The results are given in Fig. 3. The decrease of weight at 580°C. is 51 per cent. This shows that the powder contains 49 per cent. of WC.

Example 2. WC+W (W = 92.6%)

		Exp. 1	Exp. 2	Mean
595°C., 15 minutes.	Decrease of weight, %	92.5	92.6	92.55

Example 3. WC+W (W = 5.20%)

		Exp. 1	Exp. 2	Mean
595°C., 15 minutes.	Decrease of weight, %	6.3	6.5	6.4

Example 4. WC+W_2C (50% : 50%)

The results are plotted in Fig. 3. The decrease of weight at 580°C. is 47 per cent. This shows that the powder contains 53 per cent. of WC.

Thus, it was confirmed that the new method is fairly reliable for the application on the quantitative separation of WC from the mixtures of tungsten carbides and tungsten. The percentages of W_2C and W may accordingly be calculated.

Conditions of Formation of the Two Tungsten Carbides (WC and W_2C). The mixed substances prepared under various conditions were analysed by the above analytical method and the conditions of formation of the two carbides were studied. The results are summarized in the next table. The last two samples were made by the following way. Tungsten powder mixed with 4 per cent. of carbon black was heated in a carbon crucible at various temperatures for one hour. The product was cooled very slowly, and its central part was ground in an agate mortar, elutriated and reduced by hydrogen at 1000°C.

Temperature	Total carbon	Free carbon	Note	WC	W_2C	W
1600°C.	2.41 %	0 %	Sample (a) assumed as W_2C	3.8 %	68.9 %	27.3 %
1600°C.	2.61 ,,	0 ,,	Sample (b) assumed as W_2C	2.5 ,,	79.0 ,,	18.5 ,,
2000°C.	2.64 ,,	0 ,,	—	21.6 ,,	42.0 ,,	36.4 ,,
2500°C.	4.40 ,,	0 ,,	—	42.3 ,,	57.2 ,,	0.5 ,,

The following conditions may be concluded from this table concerning the formation of carbides.

1. At low temperatures the one chiefly formed is hemicarbide (W_2C), monocarbide (WC) is formed only slightly and a considerable quantity of tungsten remains uncombined.

2. With rise in temperature the content of WC increases rapidly and that of uncombined tungsten decreases proportionally.

3. WC formed at high temperatures remains, for the greater part, undecomposed even after very slow cooling.

4. WC can be formed even when excess of iron is not present.

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