CLXXI.—The Preparation at High Temperatures of some Refractory Metals from their Chlorides.

By JOHN NORMAN PRING and WILLIAM FIELDING.

VERV little has been published on the nature of the reactions whereby the metals tungsten, molybdenum, chromium, tantalum, and the non-metals, silicon and boron, may be obtained in the pure state by the dissociation of their chlorides or by decomposition of these by hydrogen at high temperatures. These reactions are made use of on a large scale in lamp manufacture for the preparation of filaments of refractory metals, and endeavours have been made to apply the method to the coating or "flashing" of carbon lamp filaments with elements which give a more favourable selective radiation than carbon.

The process devised by Just and Hanaman (*Electrical Review*, 1908, **63**, 1070; *Electrochem. and Metall. Ind.*, 1909, **7**, 24) for the preparation of tungsten filaments consists in exposing ordinary carbon filaments heated to bright redness by an electric current to an atmosphere of a volatile tungsten compound, such as a chloride or oxychloride. A uniform layer of tungsten is thereby

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deposited on the filament. This is then converted into carbide by raising the temperature, and is then decomposed and all the carbon removed by heating in an atmosphere of hydrogen containing a small percentage of water vapour. In this way a sintered filament of pure tungsten is left in tubular form.

The object of this investigation was to ascertain the conditions necessary for causing the separation of tungsten, molybdenum, chromium, silicon, and boron from the chlorides, by means of a heated carbon rod, to study the extent to which they react with



the carbon at different temperatures, and to examine briefly the photometric properties of the rods coated with these deposits.

The apparatus used consisted of a tubular glass flask of about 2 litres capacity, which contained a carbon rod usually of 5 mm. diameter and about 9 cm. long (Fig. 1). To allow of electrical heating, this rod was, at each end, mounted in water-cooled brass tubes, fitted with graphite end pieces, which were fixed by electrocoppering the ends and soldering them into the brass plugs which closed the water-cooled tubes. No difficulty was in this way experienced in ensuring good electrical contact between the carbon and the graphite; arcing was quite avoided even with high-current densities, and the rod could afterwards be removed without any loss. The water-cooled brass tubes were fixed in the side-tubes of the flask by means of wax, which proved to be quite air-tight even during the heating of the rod.

With a rod 7 cm. long and 0.5 cm. diameter in an atmosphere of hydrogen, and using a current of 160 amperes (direct current) at 18 volts, a temperature of 2200° could quite safely be attained in this apparatus, and the flask could be evacuated with the rod at 2100°. The experiments carried out with this apparatus consisted in heating the rod to various known temperatures, exposing it to the vapours of the various chlorides, either alone or in presence of hydrogen, and examining the deposits obtained.

In studying the reaction between volatile chlorides and hydrogen, the latter, before passing into the flask, was led over the surface of the chloride contained in a bulb which was kept in a water-bath to control the temperature, and hence the amount vaporised.

In cases where the chlorides were used alone, these were admitted intermittently into the vacuous flask, which was again exhausted to remove the products of decomposition. In experiments with the solid chlorides, such as tungsten and molybdenum, the substance was placed in a graphite crucible arranged 1 to 3 cm. underneath the rod, and thus vaporised by the radiant heat. Inthis case, pumping was continued throughout the process to maintain a diminished pressure and remove the gaseous products of decom-Temperature readings were taken by means of the position. Wanner optical pyrometer, sighted on to the carbon rod. The deviation from "black body" radiation with these heated rods was measured by checking the pyrometer readings against those given by a thermo-junction arranged in the interior of a hollow rod. The difference at 1250° was found to be not above 15° (Greenwood, Trans., 1908, 93, 1486).

In the course of an experiment, the apparatus was first completely exhausted by means of a Töpler pump, and then, while the glass was quite clear, a series of readings was taken, in each case, of the temperatures corresponding with the number of watts expended in the rod. Throughout each run the watts were kept as constant as possible in order to secure a uniform temperature.*

The first indications of the deposition of metal were usually given by a fall in the resistance of the rod, which continued as the thickness of this coating increased, and also in some cases,

^{*} In cases where a large change in the resistance of the rod took place during the deposition, a certain error in the temperature estimates would arise through the unknown contact resistance between the carbon rod and the graphite supporting plugs. When the rod is carefully fitted, however, there is evidence to show that this contact resistance is low. An idea of the current consumption needed for

especially with tungsten and molybdenum, by a marked increase in the luminosity of the rod.

Boron.

The decomposition of boron trichloride was brought about by mixing with an excess of hydrogen and allowing to circulate through the apparatus at atmospheric pressure. At 1500° a slight deposit of free boron occurred, which fell off on cooling. At 1750° the rod began to be coated with a smooth shell deposit of boron carbide, which could afterwards be peeled off, and was identified by its characteristic hardness, enabling it to scratch a carborundum crystal. Very little change in resistance took place during this deposition.

At 1950° the deposit of carbide took place more readily, was more adherent, and assumed a nodular form, whilst at 2150° the deposit began at several centres and expanded into large, crystalline masses, which grew outwards until they met and formed an outside casing in a zone of lower temperature.

In this case, the crystals were very loosely attached to the rod, only adhering at a few small points.

At 2200° it was no longer possible to obtain a complete deposit of carbide on the rod, but a sooty formation of this substance, together with free boron, took place on the water-cooled brass holders. This dispersion of the boron carbide under these conditions is probably not due to simple volatilisation, as the melting point of this compound has been found, in the course of some unpublished work, to be as high as 2350°, and the substance does not undergo any considerable decomposition or volatilisation below 2800°.

At temperatures above 2000° the boron appears to exert a catalytic effect in converting the carbon into graphite, as, in these cases, a layer of very soft graphite was formed underneath the deposit and extended about half way through the rod, while a thin core in the centre apparently remained as unchanged carbon. The experiments made with boron trichloride are tabulated below. In each case the carbon rod used was of 5 mm. diameter, 7 to 9 cm. long, and 5 to 8 grams of boron chloride were used.

these experiments is shown in the following table, where a rod 0.49 cm. diameter and 5.5 cm. long was calibrated for temperatures up to 1760°.

Amps.	Volts.	Watts.	Temp.	
50	7.7	385	1220°	
60	8.7	522	1355	
70	9.6	672	1470	
80	10.2	840	1590	
90	11.3	1017	1690	
96	11.6	1113	1760	

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I.—Boron trichloride used with excess of hydrogen at atmospheric pressure.

Temp.	Length of rod, cm.	Duration of run, mins.	Thickness of f layer of B_6C formed, mm.	Nature of deposit.
1800°	9	45	0.2	Smooth skin deposit.
1950	7.5	35	0.6	Nodular adherent deposit.
2200	7.0	23		Sooty deposit of $B_6 \hat{C}$ and boron on tubes. Few crystals on rod adhering by points.
1900	8.6	25	0.2	Shell deposit studded with crystals.

II.—Boron trichloride, with small quantity of hydrogen, at about half an atmosphere pressure.

	Duration of	Boron trichloride	
Temp.	run, mins.	used, grams.	Nature and weight of deposit.
1780°	80	13.05	Hard adherent shell deposit with corrugated surface.
1900	50	6.21	Weight 0.493 gram of B_6C . Small, hard crystals of B_6C , weight 0.148 gram.

Silicon.

Reactions were conducted with silicon tetrachloride in a manner similar to the above. The silicon chloride was, in some cases, admitted alone after evacuation of the globe, in others was mixed with hydrogen, and in some with hydrogen and benzene vapour (compare "Helion" filament, *Electrician*, 1907, **58**, 567; *Trans. Electrochem. Soc.*, 1907, **11**, 375).

Using silicon tetrachloride alone, no considerable deposit was obtained. With an excess of hydrogen, the silicon began to deposit at 1700° , forming a thin shell layer of silicon carbide, and above this, hard crystals of free silicon, although silicon is known to combine with carbon at 1300° (Pring, Trans., 1908, **93**, 2104).

At 1925° the whole of the deposit was in the form of carbide.

When the reaction was conducted in presence of benzene vapour, the deposit obtained was found to consist of silicon carbide (SiC), together with a varying excess of carbon. The method adopted, in most cases, for examining the nature of the deposits consisted in treating the substance with hot potassium hydroxide solution, whereby free silicon is dissolved. Free carbon was next removed by igniting in air, and the silicon carbide left unchanged. Analysis of this was in some cases effected by igniting in chlorine, ascertaining the loss in weight, then igniting in oxygen, and absorbing the carbon dioxide formed in a weighed potash bulb. The results of the experiments are given in the following table. The dimensions of the rod used were, in each case, 9 cm. in length and 0.5 cm. in diameter. No considerable change in the resistance of the rod took place during the deposition.

Mixture	Length	Tempera-	
admitted.	of run.	ture.	Nature and weight of deposit.
$\rm{SiCl}_4 + \rm{H}_2$	60 mins.	1700°	Shell layer of Si, studded with very small, hard crystals 0.05 mm. thick.
$\mathrm{SiCl}_4 + \mathrm{H}_2$	75 ,,	1830	Shell layers studded with very hard crystals of Si. Total weight de- posited 0.248 gram.
$\rm{SiCl}_4 + \rm{H}_2$	60 ,,	1925	Large, crystalline masses of SiC de- posited. Weight, 0.876 gram; graphite core, 0.485 cm. left.
$\mathbf{SiCl}_4 \!+\! \mathbf{H}_2$	35 ,,	2000	Loosely attached crystals of SiC; weight, 0.816 gram.
SiCl ₄ alone	75 ,,	1700	No deposit.
SiHCl ₃ alone	35 ,,	1830	No deposit. Rod evolved some gas on treating with hot potash solu- tion.
$\mathrm{SiHCl}_3 + \mathrm{SiCl}_4$	40 ,,	2030	Considerable gas evolution on treat- ing rod with hot potash solution.
$\mathbf{C_6H_6} + \mathbf{H_2} + \mathbf{SiCl_4}$	40 ,,	1850	Very smooth shell deposit of SiC. 0.02 gram.
$\mathrm{C_6H_6+H_3+SiCl_4}$	40 ,,	2000	Large masses of loosely adhering crystals of SiC, 0.15 cm. thick. (These, on analysis, were found to consist of SiC with excess of car- bon, namely, $Si=60^{\circ}2$ and $C=$ $36^{\circ}1$ per cent.)
$\mathrm{C_6H_6}\!+\mathrm{H_2}\!+\!\mathrm{SiCl_4}$	60 ,,	2000	Crystals containing Si=63.2 per cent.
$\mathrm{C_6H_6} + \mathrm{H_2} + \mathrm{SiCl_4}$	2 hrs.	1870	Deposit of 1.76 grams. No free Si. Combined Si in deposit = 64.4 per cent.
$\mathrm{C_6H_6} + \mathrm{H_2} + \mathrm{SiCl_4}$	$1\frac{1}{2}$,,	1750	Bright crystalline deposit of 1.59 grams. Combined Si=65.5 per cent.
$\mathbf{C_6H_6} + \mathbf{SiCl_4}$	$1\frac{1}{2}$,,	1700	Dull black, crystalline deposit, 1.35 grams.

The deposits obtained when silicon tetrachloride is decomposed in conjunction with hydrocarbons appear to consist of silicon carbide, SiC (which contains 70.3 per cent. of silicon), with an excess of carbon.

Tungsten.

Tungsten hexachloride was obtained as purple crystals contaminated with traces of the red oxychloride by passing dry chlorine over metallic tungsten, heated in a Jena glass tube. This was luted into a wider glass tube, to serve as condenser for the sublimed chloride. Great care was taken to keep everything dry and exclude moisture. The chloride, which volatilises at 346°, was placed in a graphite crucible of 3.6 cm. height, 2 cm. internal depth, 2.6 cm. internal diameter, and 3.2 cm. external diameter. The crucible was fixed on to the end of an iron rod, as shown in Fig. 2. This and a second rod passed through two holes in the stopper at the neck of the flask, and permitted an adjustment of the distance from the heated carbon rod.

In some experiments, to facilitate further the heating of the crucible, a spiral of platinum wire was wound round, the ends being joined on to the two iron rods. A sheet of mica was placed around the crucible for insulation. The flask was then exhausted by means of a Töpler pump, and the rod heated. In some cases, hydrogen was introduced, but this was not found to assist the reaction. Probably owing to difficulties in causing volatilisation, there was usually no deposition when the pressure of gas inside the flask exceeded 2 cm.

A coating of metal on the rod began to take place at 1000° under a pressure of 1 cm. When the deposition began, an immediate fall in the resistance of the rod occurred, in many cases amounting to more than half the original value. The current was adjusted throughout each run so as to keep the watts as constant as possible. The deposits were, in all cases, of a silver-white colour, adherent and smooth, and their nature was ascertained by their hardness, the pure metal being comparatively soft and unable to mark glass, whilst the carbide is very hard and scratches glass readily (compare Moissan, "The Electric Furnace," London, 1904, p. 160).

In the experiments tabulated below, the crucible was placed at a distance of about 1 to 1.5 cm. from the rod.

	TIT 11	Resistance	Duration of experiment.	Nature and weight of deposit.	
Temp.	consumed.	after (ohm.)			grams.
2050°	2170	$\left. \begin{array}{c} 0.112\\ 0.122 \end{array} \right\}$	60 mins.	W_6C	0.32
1530	800	0.260 0.141	90 ,,	w	0.69
1770	1100	$0.149) \\ 0.104$	60 ,,	W_6C	0.18
1550	610	$\left[\begin{array}{c} 0.105 \\ 0.076 \end{array} \right]$	60 ,,	W_6C	0.86
1580	650	0.163 0.147	$2\frac{1}{2}$ hrs.	w	0.1
1500	580	$\left\{ \begin{array}{c} 0.260\\ 0.122 \end{array} \right\}$	90 mins.	$W + W_6 C$	
1400	420	$\left. \begin{array}{c} 0.23\\ 0.10 \end{array} \right\}$	60 ,,	W	1.13
1200	250	$0.252 \\ 0.089 $	90 ,,	W	1.1

From this it is seen that metallic tungsten is deposited from the chloride at temperatures between 1000° and 1500°, and that tungsten carbide is formed above this temperature. 1504 PRING AND FIELDING: THE PREPARATION OF

Molybdenum.

Reactions with molybdenum tetrachloride and pentachloride, prepared by passing dry chlorine over the heated metal, were carried out as with tungsten hexachloride. The graphite crucible was placed at a distance of 1.5 cm. from the heated rod, and the following results were obtained.

Femp.	Watts consumed.	Resistance (ohm) before and after.	Duration of experiment.	Deposit.
1600°	750	$\left. \begin{array}{c} 0.200\\ 0.145 \end{array} \right\}$	60 mins.	{Crystalline deposit of Mo ₂ C (white).
1480	520	$\left. \begin{array}{c} 0.140\\ 0.139 \end{array} \right\}$	60 ,,	{Hard, smooth deposit of Mo ₂ C (white).
1330	380	$\left. \begin{array}{c} 0.198 \\ 0.100 \end{array} \right\}$	45 ,,	Metal with carbide in places, 0.3 gram.
1280	308	$\left. \begin{array}{c} 0.158\\ 0.098 \end{array} \right\}$	80 ,,	Bright smooth metallic deposit, free from car- bide.

Metallic molybdenum is thus separated from the chloride at temperatures below 1330°, the carbide being formed above this temperature.

Chromium.

An endeavour was made to obtain deposits of chromium, using the volatile oxychloride, CrO_2Cl_2 . The temperature of the rod was slowly raised up to 2000°, and the pressure of oxychloride vapour varied, but no visible deposit of metal took place.

On admitting hydrogen, the mixture detonated, and chromium chloride was deposited on the sides of the flask.

The carbon rod became considerably pitted during the experiment, and on treating with aqua regia was found to have taken up traces of chromium, but no distinct coating of metal or carbide could be obtained by this reaction.

Removal of Carbon from the Carbides of Tungsten and Molybdenum.

The above experiments show that it is possible to prepare the metals tungsten and molybdenum by the dissociation of their chlorides at high temperatures. Any desired thickness of metal can, in this way, be obtained as a deposit on the carbon heaters. Endeavours were made to remove the metal deposits from the carbon rods and obtain them in the form of tubes, and, at the same time, to remove any trace of combined carbon from the metal. The authors were not successful in preparing tubes of these metals, but it was found that if the deposition of tungsten and molybdenum from the chlorides was allowed to take place on carbon rods in

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presence of 1 to 2 c.c. of water vapour, the flask being otherwise vacuous, that the metal deposited at all temperatures was free from carbon, although less adherent than that prepared in absence of water vapour (compare Just and Hanaman's process, *loc. cit.*).

Photometric Measurements.

Some approximate measurements were made on the relative efficiencies of these metal-coated rods as sources of light at different temperatures.

The nature of the light radiated from heated filaments and the emissive properties of tungsten and other refractory metals have been extensively investigated by W. W. Coblentz [Bull. of the Bureau of Standards (Washington), 5, No. 3, p. 339].

The apparatus used in the present measurements was of the same type as that described above. The rods were mounted in the well-cleaned glass globe in which they had been prepared. An air-tight connexion between the water-cooled holders and the sidetubes of the globe was made with soft wax, and the apparatus evacuated to a pressure of 4 mm. of mercury.

A current was then passed through the rod and adjusted so that a known number of watts was expended, and the light radiated was compared photometrically with that from a standardised carbon filament lamp. A scale of "black body" temperatures corresponding with the number of watts consumed by the rod was derived optically from a carbon rod of the same size and heated under similar conditions.

In each experiment with the coated rods, readings were taken at two different temperatures, namely, 1600° and 1775° . The chief sources of inaccuracy in this work were probably the variation in the end contact resistance of the carbon, and also the fact that small, thin rods had to be employed to avoid using a current greater than 100 amperes, hence any variation in the thickness of the deposits would alter sensibly the amount of radiating surface. The carbon rods were 5.5 cm. long and 4.0 mm. in diameter, and deposits 0.25 mm. thick were generally obtained, although in the case of silicon this amounted to 0.75 mm.

During the heating, a small, steady evolution of gas took place. This effect has been observed before in experiments in which carbon rods alone were used, and is due either to occlusion of gas by the carbon, or else to the reaction of the carbon with water vapour condensed on the surface of the glass. By pumping at intervals, the pressure could be kept at 4 to 5 mm.

The photometer used was of the Lummer-Brodheim type, and the

following comparative results were obtained, the values being expressed in terms of the standardised lamp.

	Carbon rod.	Tungsten deposit.	Molyb- denum deposit.	Boron deposit.
Luminous intensity with 332 watts, temp. 1600°	1.01	3.00	2.97	-
Luminous intensity with 465 watts, temp. 1775°	3.40	6.06	6.27	1.16

In the case of the rod coated with silicon carbide, the value obtained was as low as 0.91. This is perhaps largely accounted for by the greater diameter of the coated rod (5.5 mm.), although the result is in great disagreement with the supposed high efficiencies of silicon-coated filaments.

With the boron and silicon deposits, the luminosity was not sufficiently high for measurement with the lower amount of power, so that results could only be obtained at the one temperature.

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