—agrees much more closely with the complex formula than with the simple one, and the other values can be accounted for as mentioned above. His chloride is therefore without doubt the exact analogue of the bromotantalum bromide, and should be called "chlorotantalum chloride."

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METALLIC TITANIUM.

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All the earliest attempts at the preparation of metallic titanium resulted for the most part in the production of the various nitrides which from their metallic appearance were always mistaken for the metal. Thus Wollaston[1] mistook the cyanonitride which is frequently found in the slag and metal from the blast furnace for the metal. Again Berzelius[2] reduced potassium titanifluoride with potassium and obtained a black powder which on polishing showed a metallic streak. This substance was insoluble in hydrofluoric but easily soluble in a mixture of hydrofluoric and hydrochloric acids and whatever it may have been it certainly was not metallic titanium, for titanium is immediately soluble in hydrofluoric acid. Rose[3] produced a dark blue or a black powder insoluble in hydrochloric acid from the compound $TiCl_4.4NH_3$ by heating alone or by reduction with metallic sodium. This material, which he considered to be metallic titanium, is now known to be Ti_3N_4.

Wöhler[4] and Wöhler and Deville[5] in their attempts at producing the metal succeeded in all cases in obtaining the nitrides. Up to this time no analysis of the material produced by the experimenters above mentioned appears to have been made. The confusion which existed in the earlier literature with regard to the pure metal titanium and its nitrides is therefore easily explained.

Nilson and Petersson[6] attempted to prepare metallic titanium by reducing $TiCl_4$ with sodium in an air-tight cylinder of solid steel. The metal was obtained in yellow scales (with frequently a bluish surface color) containing about 95 per cent. of titanium, the chief impurity being the monoxide of titanium.

Then Moissan[7] by reducing titanium dioxide at the extreme temperatures of his electric furnace produced a material containing 5 per cent. of carbon. On reheating this material with titanium dioxide, the amount of

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[1] *Phil. Trans.*, 17, 1823.

[2] *Pogg. Ann.*, 4, 3 (1825).

[3] *Ibid.*, 16, 57.

[4] *Compt. rend.*, 29, 505 (1849).

[5] *Ibid.*, 45, 480 (1857).

[6] *Z. physik. Chem.*, 1, 25 (1887).

[7] *Compt. rend.*, 120, 290 (1895).

carbon was reduced to 2 per cent. and the resulting product was free from nitrogen. This appears to be the nearest approach to metallic titanium which has yet been obtained.

In the following pages each of these methods of preparation is taken up in succession and the results of many attempts to obtain the pure metal from the various compounds of titanium are set out in detail.

Reduction of the Titanifluorides by the Alkali Metals.

In searching in the first instance for materials with which to work it was evident that those substances which were most soluble in water would best suit the purpose: for these materials can be most readily removed on subsequent lixiviation. Among the double fluorides sodium titanifluoride is given by Comey as the most soluble salt and among the simple fluorides of the alkali metals potassium fluoride is deliquescent. The combination of sodium titanifluoride and metallic potassium appeared then the best to use; though, as will be shown, both potassium titanifluoride and barium titanifluoride have been used as a starting material. The sodium titanifluoride was prepared in the following way: Titanium dioxide free from iron was dissolved in hydrofluoric acid. While the liquid was still hot it was filtered from the undissolved residue and almost neutralized by a hot concentrated solution of sodium hydroxide. Sodium titanifluoride was immediately thrown out as a crystalline precipitate, which was easily filtered, then washed with water containing hydrofluoric acid and on drying and bolting was ready for reduction. A sample of K_2TiF_6 prepared in this way was analyzed and found to contain 20.4 per cent. Ti instead of the theoretical 20 per cent. The discrepancy may be due to the presence of some excess of TiF_4 in the double fluoride.

The sodium double fluoride with the potassium necessary for reduction was then placed in an iron cylinder fitted with a lid loosely screwed on. This cylinder was wound with nickel wire which served as a means of heating the cylinder, and was inserted inside a second cylinder of copper which was made perfectly air-tight.

The copper cylinder was evacuated and a current was passed through the nickel wire until the reduction had taken place. This was observed by a slight shift in a manometer attached to the apparatus. When the iron cylinder had cooled it was opened, the excess of potassium was removed by dry alcohol and the whole was then thrown into a large quantity of water. The black powder remaining after several washings was collected on a filter, washed, dried and analyzed. The first material prepared after completely drying in a vacuum caught fire within 30 seconds after being exposed to air. A second material proved to be not pyrophoric in the least degree and could be easily handled in air. An analysis gave from 0.1034 gram on oxidation, 0.1040 gram TiO_2 corresponding to 60.4 per cent. of titanium. A third reduction of Na_2TiF_6 with K on treatment with alcohol and warming with successive small quantities of water gave a material which contained 68.0 per cent. Ti. A fourth experiment carried out *in vacuo* when the conditions for reduction were well ascertained gave a material which contained 73.2 per cent. of titanium.

This represents the best material yet obtained by this method. Three reductions were made on potassium titanifluoride with potassium. The resulting materials contained 60.1, 56.0, 56.1 per cent. of titanium. Barium titanifluoride reduced with potassium gave only 49.5 per cent. of the metal.

It seems to me quite certain that the double fluorides are reduced by the alkalis *in vacuo*, but that in the subsequent removal of the alkaline fluorides, the finely divided metallic titanium is attacked by the water with the ultimate formation of the oxides TiO and TiO_2. In view of the success of a subsequent method of preparing the metal the means for the prevention of this oxidation will not be further discussed.

It remains only to be said that by the methods used by Berzelius, Wöhler and Deville I could not produce a material containing more than 73 per cent. of titanium.

Reduction of Titanium Dioxide by Carbon.

The reduction of titanium dioxide by carbon was next tried as a means of obtaining titanium. To this end the purest lampblack obtainable was taken and fired at a red heat in a gas furnace to remove hydrocarbons and this carbon was then used for the reduction. An intimate mixture of the oxide and carbon was made by grinding and bolting the materials together till the whole appeared a blue homogeneous mass.

The reductions were carried out in an Arsem vacuum furnace, the heat being continued in each experiment until the charge ceased to give off gas. The analyses show the amounts of titanium oxygen and carbon in the resulting product.

EXPERIMENT I, $TiO_2 + 2C$.

Reduction carried out at 5 kw. (1800° C.) in a carbon crucible.
Analysis of product (wt. taken 0.4615 gram):

Ti	0.3656
O	0.0320
C	0.0639

Now since oxygen remains in the mixture it may be safely assumed that the carbon remaining is not in its original free condition but exists in combination with Ti and is not available for reduction. If we assume that it exists as carbide we find:

Ti combined as TiC	0.2556
Ti free or combined with O	0.1100

The ratio of Ti and O considered in atomic proportions is Ti/O = 1.14. The complete analysis of the material is then:

	Per cent.
TiC	69.2
TiO	30.8

The results are tabulated below.

Crucible.	Temp. Degrees.	Per cent. C.	Ratio. Ti/O.	Per cent. TiC.	Per cent. TiO.
Al_2O_3	1700	10.9	....	54.5	45.5
Carbon	1800	13.8	1.14	69.2	30.8
Carbon	1800	12.7	0.97	63.1	36.9
Carbon	2400	8.7	1.00	43.5	56.5
Carbon	2400	6.6	1.28	26.6	73.4
Tungsten	2100	4.7	....	23.6	76.4
Tungsten	2400	4.6	1.09	24.7	75.3

In general the presence of a crucible made of a substance other than carbon reduces the amount of carbon in the material but the results are largely influenced by difference of temperature during the reduction. The best results were obtained in a tungsten crucible at 2400° where the percentage of carbon remaining in the material sank as low as 4.6 per cent.

But it seems doubtful whether we can prepare metallic titanium by this method. All experiments up to this point have succeeded in giving us only a bluish purple material which contains varying quantities of TiC and TiO.

The Reduction of Titanium Tetrachloride with Sodium.

The best material which Nilson and Petersson[1] prepared by this method contained about 94.73 per cent. of titanium. The material was obtained in yellow scales (frequently with bluish surface color), the chief impurity being considered as oxygen in combination. It is quite probable that the oxygen is combined as TiO in which case the material produced would contain only 78.92 per cent. of metallic titanium.

In repeating the experiment extraordinary care was exercised during and after the reduction of the chloride by sodium to exclude air from the apparatus.

The preparation of titanium chloride was carried out on an extensive scale by the chlorination of approximately pure titanium carbide. The chloride was refluxed in a current of nitrogen to remove chlorine and then repeatedly distilled, the end fractions being continually rejected. The fraction boiling between 136° and 137° was taken and shaken repeatedly with mercury and sodium amalgam. On redistillation a perfectly water white $TiCl_4$ was obtained boiling at constant temperature (136.5° uncorrected).

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[1] *Loc. cit.*

The first bomb used for the reduction was of 100 cc. capacity accommodating 50 grams of titanium tetrachloride and 25 grams of sodium needed for its reduction. On heating the bomb to a low red heat the reaction took place and on opening it, the titanium was found for the most part as a gray powder, some of it, however, being melted by the heat of the reaction to small metallic beads. By this means however, only 12 grams of metal were obtained in each experiment.

When the progress of the reaction was understood from this experiment on a small scale a larger bomb was constructed of ten times the capacity of the preceding one. In this bomb 500 grams of titanium chloride were successfully reduced by 245 grams of sodium, giving as a theoretical yield 126 grams of titanium. The bomb was constructed of machine steel and was capable of withstanding a total internal pressure of 80,000 pounds. The lid was screwed to the body of the bomb by six stout braces (one inch thick) screwed tightly down with an intervening gasket of soft, annealed copper.

The reaction inside the bomb must be almost instantaneous. The lid is raised a little by the force of the explosion, a slight puff of vapor escapes but the main force of the explosion is already spent and the lid closes air-tight again.

On cooling the bomb and leaching the contents with water, titanium alone remains. Thus in one experiment the weight of $TiCl_4$ used was 470 grams, the titanium content of which is 119 grams. The resultant product contained:

	Grams.
Melted metal	71
Coarse and semimolten powder	31.5
Fine powder	4.5
Total	107

The actual yield was then 90 per cent. The reaction heat had been so great that the greater part of the metal had been more or less perfectly melted during the reaction. The loss of material, amounting to 10 per cent., is accounted for by the fact that some of the titanium is oxidized during the reaction from the presence of oxygen in the sodium used. This introduction of oxygen could not be avoided even when the sodium was carefully peeled before being introduced into the reaction bomb. Again some of the finely divided metal is oxidized by the water during the washing. A flocculent blue ppt. of meta-titanic acid, which rapidly turns white in air, is formed but may be easily removed by decantation from the heavier metal beneath. The slag from the reaction, which should be pure white, is always colored blue or green from the presence of lower titanates of sodium.

This method then is an admirable one for producing titanium in moderately large quantities in a state of purity which has hitherto not been attained.

Analysis of the Material.

A bead of metallic titanium was taken, broken up in three portions and analyzed in the following ways:

1. Dissolved by long boiling in moderately concentrated hydrochloric acid—oxidized with a drop of nitric acid and the titanium precipitated with a slight excess of ammonium hydroxide.

0.1581 gram gave 0.2361 gram TiO_2 equivalent to 0.1579 gram Ti.
Per cent. titanium = 99.9.

2. Dissolved in hydrofluoric acid—neutralized and precipitated with ammonium hydroxide.

0.4365 gram gave 0.7085 gram TiO_2 equivalent to 0.4251 gram Ti.
Per cent. Ti = 97.4.

3. Dissolved in hydrofluoric acid, sulphuric acid added and the solution evaporated to the fuming point, taken up with water and precipitated with ammonium hydroxide.

0.4955 gram gave 0.7954 gram TiO_2 equivalent to 0.4773 gram Ti.
Per cent. Ti = 96.3.

The solution of the metal in hydrofluoric acid always brings about a loss of material due perhaps to the evaporation of titanium fluoride.

4. A fourth method of analysis by the solution of the metal in acid potassium sulphate and subsequent precipitation by boiling the solution gave in the hands of Prof. Mixter[1] 100.2 per cent. of titanium.

No trace of iron or of sodium could be found in the beads of titanium which were melted during the reduction and since two reliable methods of analysis yield results so closely approximating to 100 per cent. There is strong reason to believe that the material thus obtained is pure metallic titanium.

Properties of the Metal.

The metal does not differ in outward appearance from polished steel. It is, however, hard and brittle in the cold. If it be raised to a low red heat it may be readily forged like red hot iron. By this means some of the beads of from 10 to 12 grams in weight have been forged into rods about six inches long.

Unsuccessful attempts have been made to draw the material through a heated draw plate in order to produce wire from it.

The pure metal can be melted only with difficulty. A rod of metal 12 cm. long and 1.8 mm. in diameter burned in air at a temp. of 1200° when a current of 50 amps. was sent through it. The heat of oxidation was sufficient to melt the oxide thus produced. The metal was melted in a lime crucible placed in a vertical carbon tube furnace through which

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[1] *Am. J. Sci.*, 27, 393 (1909).

a rapid stream of hydrogen was passed to prevent access of carbon monoxide to the metal. The resulting bead swelled up and became porous in texture resembling titanium carbide. In the Arsem furnace the resulting material was always porous and contained titanium carbide.

A rough determination of the melting point of the material was carried out as follows: The filament of a Gem incandescent lamp was superimposed on a rod of titanium maintained in as perfect a vacuum as could be obtained by a hammering Boltwood pump.

An increasing current was sent through the titanium rod and the temp. of the Gem filament was gradually raised to an equal intensity. It was found that the titanium rod slowly melted and finally broke when the Gem lamp was burning at an efficiency of 3.55 watts per c. p. The melting temperature is therefore between 1800 and 1850° and is certainly not greater than this latter value. Observations, confirming this result, were also made with a Wanner pyrometer.

The specific gravity of the metal is 4.50. It is therefore appreciably lighter than the metal obtained by Moissan (sp. gr. 4.87).

In conclusion it may be said that the metal titanium is not by any means as refractory a substance as former experimenters have been led to believe. Its melting point is comparatively low—being within one hundred degrees of platinum. Further, though brittle in large pieces in the cold yet at a low red heat it shows a remarkable malleability, and very small beads even in the cold may be flattened out with ease without disruption. A method is here given by means of which moderately large quantities of pure titanium may be produced with ease, so that the air of mystery which has so long enshrouded this refractory element will soon be dispelled.

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NOTE.

The Preparation of Platinum Black.—Of the various methods which have been proposed for the preparation of the finely divided form of platinum known as "platinum black," but two are ordinarily employed, *viz.*, (1) the reduction of a solution of chloroplatinic acid by zinc, and (2) the method of Loew[1] depending on the precipitation of the platinum by means of sodium hydroxide and formaldehyde. In their study of the reducing action of platinum black on nitrates in the presence of formal-

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[1] Loew, *Ber.*, 23, 289 (1890).