1879

Thesis for D.Sc. Exam-
1879.

"On the
preparation and properties of
Pure Graphitoid and Adamantine Boron."

by-

R. Sydney Marsden.

B.Sc. (Edin)

- On the Preparation and Properties of
Pure Graphitoid & Adamantine Boron -

For some years, two substances have been known under the names of Graphitoid and Adamantine Boron - They were both originally prepared by Wöhler and Deville and were thought to be pure allotropic forms of boron - The first may be prepared in several ways - 1st By passing gaseous Chloride of Boron for sometime over Aluminium in a state of fusion, when the metal takes up a small quantity of boron, which on breaking it, is found on the fractured surface in copper-coloured, crystalline laminae, like Graphite in cast-iron; which may be separated by dissolving the aluminium with Hydrochloric Acid - And secondly by fusing Aluminium with Amorphous Boron or Boric Anhydride and letting it crystallize out on cooling -

A large excess of Aluminium however is required to obtain but a small quantity of Boron - This substance has a semi-

semi-metallic lustre, like graphite -
But with a distinct tinge of coppered -
When well crystallized, it forms thin
six-sided tablets belonging to the hex-
agonal system - but is more generally
obtained as a reddish-gray micaceous
powder composed of fine crystalline laminae -

It has however been shown more recently
by Wöhler and Deville to consist of
Aluminium Boride AlB_3 containing
55.46% of Aluminium and 44.54 per cent
of Boron -

The 2nd so-called Adamantine Form
again is obtained in a similar manner -
by heating Aluminium in lumps and
Amorphous Boron or Boric Anhydride to
a temperature at which Nickel fuses
readily - The mixture is introduced into a
crucible of compact Charcoal fitted with
a charcoal lid and placed within an
hessian crucible the intermediate space
being filled with Charcoal - The crucible
is then heated for about five hours and
afterwards allowed to cool - The Adamantine
Boron is found crystallized inside the

the Aluminium and is obtained mixed with proportionately large quantities of the graphitoid form by dissolving the Aluminium in Hydrochloric Acid - It forms quadratic Octahedra the colour of which varies from light-red to black - It has a specific gravity of 2.63 - This substance also however has been shown by Tröhler and Duville to be not a pure form of Boron, it always contains Carbon and generally Aluminium -

After preparing specimens of the these substances, in the manner above described, and finding that I had got but very poor yield for the amount of Aluminium used - I made an experiment, in which I substituted wrought-iron in place of the Aluminium, but found that here also the iron united with the boron to form a hard compound somewhat resembling steel in its physical properties - Having noticed that Carbon united with most of the metals of the Iron group to form steel-like compounds, the idea occurred to me of substituting some other metal quite

quite distinct from the iron group, in place of the Aluminium - and Silver, Gold or Platinum appeared as if they would serve any purpose best owing to their high boiling points if only they would dissolve the Boron - Again this might effect a very considerable saving in the expense - because in the case of Aluminium the byproducts are useless, whereas in the case of Silver, Gold or Platinum the Byproducts are easily reconverted into the metallic state.

On making an experiment conjointly with Doctor Morrison in which we substituted Silver in place of the Aluminium, we found that it did dissolve Boron, and that on dissolving the Silver away with Nitric Acid a steel grey powder was left behind - This powder on being examined after purification, was found to be Boron, and to contain nothing but Boron; under the Microscope, it presented a complex composition, some being transparent and some opaque - The opaque portions consisting of Hexagonal

hexagonal prisms has a semi-metallic lustre like graphite or crystalline ferric oxide - the transparent portion being composed of plates and a few small tetrahedra - the colour of the transparent portion also varying from pure white to deep red the latter colour being most probably due to dissolved amorphous boron - The quantity obtained was but small so we repeated our experiment several times at last obtaining sufficient to examine the properties of these crystals - The yield of each experiment varied considerably, owing to variations in the manner in which each experiment was conducted - This point I will consider after discussing the method of preparation -

The method which we employed in conducting these experiments is as follows:-

The Silver in small lumps and the Amorphous Boron were placed in alternate layers in a porcelain crucible, which was fitted with a double lid to keep it perfectly airtight - the one fitting

fitting inside the crucible and the other outside - The intermediate space being filled with Amorphous boron to prevent oxidation of the boron to be dissolved.

Care was taken that the Silver did not touch the sides of the crucible and that the mass was well packed to prevent subsidence - This crucible was then placed inside a plumbago crucible, and the intermediate space was filled with pure sugar Charcoal to burn any air which might be forced in by the blast. - The whole was then introduced into a gas furnace and heated to the temperature of boiling Silver, and this temperature was kept up for five hours - During this time the Silver melts and becomes quite saturated with the boron, which crystallizes out on cooling - Special precautions were taken to allow of very gradual cooling and by means of another furnace, heated to a bright red heat, & which fitted exactly round the gas furnace,

furnace, we found it possible to prolong the process of cooling over some six or seven hours, this giving every facility for the formation of crystals -

We varied the temperature in several of the experiments sometimes leaving it considerably under the temperature of boiling silver, but generally the experiments were done fully at that temperature as we found that this gave us the best results - The time for which we kept it at this degree of heat varied from three hours to eight days (of twenty four hours) continuous heating - but we found the best results to come from those experiments as described above, in which it was kept at the temperature of boiling silver for five hours, we did not find that heating it for a longer time than this gave a larger quantity of the Graphitoid and Adamantine forms, but we found that when heated for a less time than this our yield was not so good -

If however we replace silver by some other metal the time varies according to the metal used - the more easily fusible metals taking

taking less time to become saturated than the more difficultly fusible ones -

On opening the Plumbago Crucible after the operation, care was taken not to break the porcelain crucible inside - which was first well cleaned and then itself broken open - We were particularly careful not to get any of the crucible mixed up with the contents inside - These contents were found to be 1st a lump of metallic silver and secondly a bluish grey powder -

The silver was well cleaned and dissolved in moderately strong Nitric Acid, and yielded from its interior a quantity of a steel-grey crystalline powder -

This powder was then examined in order to ascertain its composition and properties.

First from its mode of preparation the only substances which could be present are Boron & silver, and (though improbable owing to the precautions taken) Silica and Alumina from the crucible -

Second, A portion was oxidized by means of fused nitre, and the mass dissolved

9

dissolved in acid and tested for silver, but not even a trace was found.

In a similar manner we have also proved silica and alumina to be absent. Nor were we able to detect anything except boron. These crystals, therefore, must must be pure boron, partly graphitic and partly Adamantine.

Thus Boron is found to have three forms, viz: Amorphous, Graphitoid and Adamantine; although the so-called graphitic boron of Wöhler and Drville has been found to be a boride of Aluminium, and the Adamantine of the same two chemists to contain Carbon and Aluminium.

The properties of this powder are as follows, viz -

- 1st It is infusible at a white heat.
- 2nd It is not oxidized by air at a white-heat even superficially.
- 3rd It is completely oxidized, though slowly by fused Nitrate of Potash.
- 4th It is completely oxidized, ~~thereby~~ slowly by fused Nitrate of Potash.

4th continued - oxidized by Nitric Acid when treated with it for twenty four hours at a temperature of 90° - 100° C.

5th It is completely volatilized when heated with a mixture of Hydrofluoric and Sulphuric Acids -

6th It does not alloy with platinum at a white heat -

7th As a powder it is a non-conductor of Electricity -

We have not yet had the opportunity of taking its specific heat -

We have not yet had the opportunity of using gold or platinum in place of the silver, but have made a number of experiments with the following metals.

viz. Lead, Tin, Copper, Antimony, Bismuth, Iron, Magnesium and Zinc and have obtained some very interesting results. This part of the research is not yet quite finished but the following are some of the principal results -

1st Lead has no action on Boron the properties of the metal remain unchanged and no Boron is dissolved -

2nd Zinc dissolves a large quantity of Boron which crystallizes out from it again on cooling in fine and very beautifully formed crystals -

3rd Copper unites with boron to form a bronze which is excessively hard & tough & which when broken presents a beautiful fracture of a rich bronze-colour -

4th Antimony yields but a small quantity of graphitoid boron and this not in very well-formed crystals -

5th Bismuth also yields but a small quantity of the graphitoid form but these crystals have a very beautiful appearance and well marked character -

6th Iron as before said unites with the Boron to form a steel-like compound of very considerable degree of hardness & tenacity -

7th Magnesium unites with the Boron to form a greyish compound of the two elements -

(This substance it is said when treated with acid yields the long missing Borated Hydrogen BH_3)

8th Zinc dissolves but a very small quantity of Boron and yields almost none of the graphitoid

Graphitoid form insoluble in acid -

In all cases the metals on opening the crucible are found surrounded with a powder which varies in colour from light grey to nearly black according to the metal ~~which~~ has been used - This powder is a compound of Boron with the metal and perhaps represents an intermediate stage through which the whole of the boron has to ~~pass~~ go, in passing from the Amorphous to the graphitoid and Adamantine conditions -

The results as here stated seem but very few for the amount of time and money spent over them but trust that in the application of the information obtained from the experiments to arrive at even more valuable and interesting discoveries - In all we performed some nine-and-twenty experiments varying in length from three hours to eight days and under at least fifteen different temperatures - We have also tried experiments with Carbon ^{with interesting results} but as these belong to a separate research I will not say more about them here -

R. S. Mansden

University of Edinburgh.

February 26th 1879 -