XXXI.—*The Reducibility of Magnesium Oxide by Carbon.*

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THE investigation already described in a preliminary note (Proc., 1907, **23**, 152) has been continued and extended, and, since the results now appear to be conclusive, it is thought advisable to publish a complete account of the work.

Considerable interest attaches to the reaction between magnesia and carbon, since, of all the metallic oxides, magnesia has longest withstood attempts to effect its direct reduction. Moissan (*The Electric Furnace*, p. 224) states that "Magnesia may be fused and kept liquid in a carbon crucible without being reduced."

In some electric furnace work in which it was necessary to brasque carbon crucibles with magnesia, it was observed that the walls of the crucible were considerably corroded in those places where they had been in contact with the strongly heated magnesia. This led to the investigation of the cause of the attack.

On consideration, it became clear that any reduction products formed under these conditions might escape notice on account of the ready volatility of magnesium and the ease with which it reacts with carbon monoxide and other gases with which it would come in contact.

During the progress of this work, Lebeau has published a paper on the subject (*Compt. rend.*, 1907, **144**, 799), but he considers that the reaction only occurs between the vapours of carbon and magnesia at the high temperature of the electric arc. By the use of a more suitable form of electric furnace, in which the heating is under better control, it is easy to prove that reduction occurs at far lower temperatures.

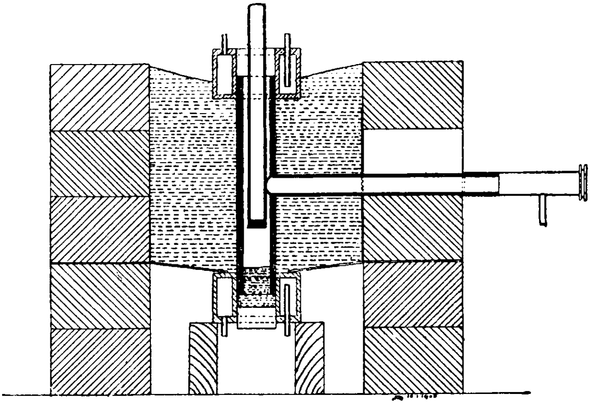
EXPERIMENTAL.

Series I.—A small piece of magnesia placed on a carbon plate was heated for some minutes in a horizontal carbon-tube resistance furnace to a temperature above the fusing point of magnesia; the magnesia was found to have penetrated through the carbon plate.

With the object of collecting any magnesium which might be set free by this reaction, it was decided to employ molten copper in conjunction with the mixture of magnesia and carbon. The copper served as a solvent and condenser of the metal vapour, the method being similar to that employed for aluminium by Hutton and Petavel (*Phil. Trans.*, 1908, *A*, **207**, 446). Alloys containing up to 2 per cent. of magnesium were prepared in this way, but the method is not suitable for condensing larger quantities of the reduced metal, apparently on account of the relatively low temperature at which the magnesium volatilises. The objection to this method, that the copper itself may exert some chemical affinity for the metal it absorbs, appears to be disproved by the absence of any considerable heat change when molten copper free from oxide is alloyed with magnesium.

The experiments were carried out in a vertical carbon-tube resistance furnace fitted with a side-tube for observing the temperature with a Wanner optical pyrometer, the side-tube being kept free from fumes, which would absorb some of the light, by means of a current of hydrogen passing through it towards the inside of the furnace. The containing vessel consisted of a smaller carbon tube, one end of which was closed with a graphite plug (see Fig. 1).

FIG. 1.



Vertical carbon-tube furnace.

Scale 1/9th.

With this type of furnace, a more efficient condensation of the reduced magnesium was effected by constant additions of reduced copper in the form of fine powder, which, fusing and falling through the strongly heated layers of the charge, collected and removed the magnesium. In all experiments above 1700°, an alloy containing magnesium was obtained. In one case, at 1883°, for example, the amount of magnesium in the alloy was 1·6 per cent.

That this magnesium was not dissolved in the copper in the form of magnesia was shown by heating magnesia and copper to above the melting point of the latter in a wind furnace for half an hour, keeping the mixture constantly stirred. The copper proved on analysis to have taken up no magnesium.

Series II.—A mixture of magnesia and carbon, the magnesia being in excess, was placed in a graphite boat in a horizontal carbon-tube resistance furnace. A rapid stream of nitrogen was passed through the tube during the heating, which was continued for twenty minutes at about 1900°. The exact temperature could not be determined, owing to the formation of an opaque film across the cool end of the tube. On examining the boat, it was found to contain unfused magnesia, quite white and free from carbon. A quantity of carbon insufficient to reduce all the magnesia having been present, all the carbon was used up, leaving an excess of magnesia in the boat. This shows that the reduction takes place below the fusion point of magnesia.

In another experiment, a mixture of carbon and magnesia was placed in a graphite boat in a furnace similar to that used in the last experiment. A rapid stream of hydrogen was passed through the furnace while the temperature was slowly raised, readings of the temperature being taken with the Wanner optical pyrometer; at about 1670°, it was noticed that the tube became filled with fumes which settled, forming a grey film; this was found to contain traces of magnesium carbide. The temperature of reduction of magnesia by carbon thus probably begins a little below 1700°.

Series III.—In these experiments, a mixture of magnesia and carbon was placed in a graphite boat, which was heated in a vacuum by the resistance which it offered to the passage of an electric current.

In order more carefully to examine the products of the reaction and to keep a close observation on the process, an electrically heated device was mounted in a glass apparatus similar to that used by Pring and Hutton in the synthesis of acetylene (Trans., 1906, **89**, 1593). A carbon rod held in graphite end-pieces, which were mounted in water-cooled brass tubes, served as the heater, the rod being grooved out into the form of a boat to support the mixture of magnesia and carbon. The apparatus was exhausted and the experiments made in a vacuum, the gas generated being pumped out and subsequently analysed.

These experiments proved most successful, the magnesia being reduced and the inner surface of the glass globe above the heated rod being coated with a bright mirror of magnesium.

In one experiment, a carbon rod 10 cm. long and 0·7 cm. in diameter was used, and the following are particulars of the experiment:

Time in minutes.	Amperes.	Volts.	Pressure in mm.	Remarks.
0	60	12·7	2·7	—
1	100	16·8	45	—
2	115	16·2	—	—
4	—	—	80	—
5	—	—	—	35 c.c. pumped out
6	—	—	—	58 ,, ,,
7	120	16·2	42	—
14	120	16·0	44	—
15	(current stopped)			
85	—	—	24	52 c.c. pumped out
90	—	—	7·5	—

The temperature was approximately 1900° as determined with the Wanner optical pyrometer. The gases pumped out were subsequently analysed.

The inside of the globe was coated with a bright silver-like mirror. This metallic-looking deposit dissolved readily with effervescence in dilute hydrochloric acid, and oxidised to a white oxide when heated in air. Further proof of the reduction of the magnesia having been effected is given by the gas analysis. The last sample of gas taken gave on analysis $CO = 57·4$, $H = 38·1$, $N = 4·4$ per cent. After allowing for the carbon monoxide produced by the reaction of the small amount of residual water, this leaves a considerable excess of carbon monoxide produced by actual reduction of the magnesia. Blank experiments in which carbon rods were similarly heated in the absence of magnesia served to confirm this conclusion.

Series IV.—A vacuum having been successfully employed in removing the carbon monoxide from the magnesium before the reverse reaction $CO + Mg = C + MgO$ was complete, other methods were attempted for removing this carbon monoxide and facilitating the condensation of the magnesium.

A mixture of magnesia and carbon was heated to about 1900° in a rapid stream of hydrogen, which then passed through a water-cooled copper tube serving as a condenser.

The apparatus used is shown in Fig. 2. It consists of a retort made up of two carbon crucibles, one inverted over the other—the two being held together by graphite supports. Into a hole in the top of this retort a carbon tube is ground, which serves as an inlet for the hydrogen. In the side near the top, an outlet hole is bored and ground to fit the water-cooled copper tube.

The retort was charged with a mixture of 40 grams of magnesia and 12 grams of carbon (petroleum coke), and then embedded in a granular carbon resistance furnace.

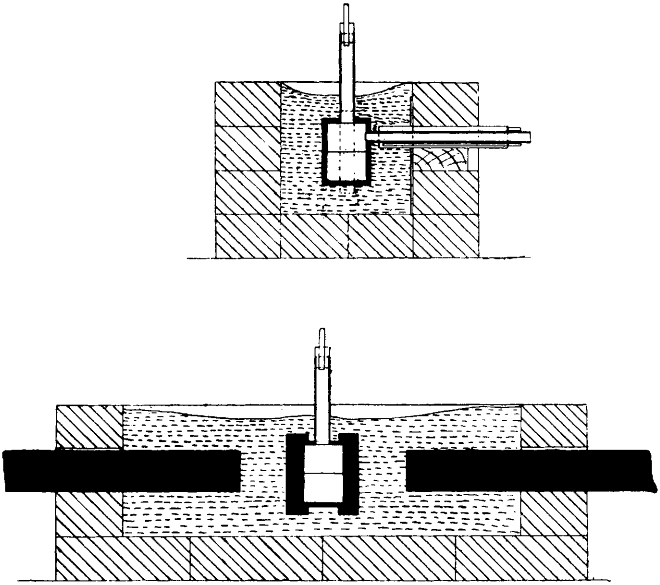
The following are particulars of the power used :

Time in minutes.	Amperes.	Volts.
0	50	70
5	100	—
7	140	58
18	450	26
30	450	23
65	450	21
90	450	20

The temperature of the retort was probably 1800° to 1900°; it was certainly below the fusion point of magnesia.*

In the condenser tube were found about 2 grams of a grey powder. This, on exposure to the atmosphere, gave off a little ammonia, which was recognised by its odour and by its action on litmus paper. The powder was treated with dilute hydrochloric acid, when 70 c.c. of gas were evolved, which, on analysis, gave $H_2S = 49{\cdot}94$, $C_2H_2 = 7{\cdot}82$, $H = 42{\cdot}13$ per cent. A residue of carbon was left undissolved, and the solution was tested and found to contain only magnesium; it was quite free from calcium. The powder must therefore have consisted of a mixture of magnesium together with its nitride, sulphide, carbide, and oxide, and some carbon.

FIG. 2.



Granular carbon resistance furnace and retort.

Scale 1/12th.

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* About 1920°, according to H. M. Goodwin and R. D. Mailey, *Trans. Amer. Electrochem. Soc.*, 1906.

The nitride would be formed from the heated magnesium on its coming into contact with nitrogen, the sulphide from its coming into contact with hydrogen sulphide, the sulphur being derived from the carbon; it is a well-known fact that the sulphur always present in commercial carbon can be partly converted into hydrogen sulphide by heating to 2000° in a stream of hydrogen. The carbon and magnesia probably resulted from the interaction of heated magnesium and carbon monoxide.

In another experiment, a similar apparatus was used, except that in place of the water-cooled copper condensing tube a carbon tube was used, and a piece of aluminium weighing 60 grams was placed in the retort along with the charge of magnesia and carbon. A swift stream of hydrogen was passed as before. It was hoped that the aluminium would remove the carbon monoxide by reacting with it, forming a mixture of alumina and aluminium carbide, thus: $6Al + 3CO = Al_4C_3 + Al_2O_3$.

This seems to have taken place, for the aluminium was found to have been largely converted into carbide, and in the condenser tube were found 2 grams of magnesium as powder and a further quantity of 2 grams which had been melted in the hot tube and had run down to the bottom, where it solidified. This metal gave on analysis Mg = 99·45, Al = 0·47 per cent. If the addition of the aluminium was omitted, it was found that in place of the fused metal there was a mixture of magnesia and carbon, formed doubtless by the action of carbon monoxide on the molten metal. Some powder found in the tube, however, was shown to consist largely of metal, for it gave a mixture of hydrogen, acetylene, and hydrogen sulphide on treatment with dilute acid.

When the carbon monoxide was absorbed by aluminium, it was possible for the magnesium formed to run together; without the aluminium, however, this metal was oxidised by the carbon monoxide.

Conclusion.

The work here recorded seems to prove satisfactorily that magnesia is reduced by carbon, not only at the high temperature of the electric arc, but as low as 1700°.

Watts (*Trans. Amer. Electrochem. Soc.*, 1907, **11**, 279) mentions the fact that carbon can be volatilised from a bed of magnesia, and he obtained sublimates consisting of intimate mixtures of magnesium oxide and carbon; his explanation of the reaction is similar to that put forward here, although he was unable to produce evidence of the existence of free metal.

The present work, however, shows clearly that the metal can be isolated, although under ordinary conditions re-oxidation of the magnesium is effected by the carbon monoxide, for if some device is used for removing this gas, for instance, by working in a vacuum, by absorption of aluminium, or by a rapid stream of hydrogen, then metallic magnesium is obtained. The condensed magnesium is always associated with small quantities of a carbide, which, on treatment with water or dilute acid, gives off acetylene. Small quantities of this carbide are also found together with the mixture of magnesia and carbon in the condensate obtained when magnesia and carbon are heated together in an open furnace. All attempts to prepare this carbide from magnesium and carbon in anything like a pure state failed, but it was shown only to give off acetylene on treatment with dilute acid. It is therefore probably identical with Berthelot's carbide, prepared by heating magnesium to a red heat in a stream of acetylene. In this case, it must be formed by the cooling magnesium coming into contact with acetylene, which is always present in traces where carbon and hydrogen come together at temperatures of 1700° and upwards (Pring and Hutton, Trans., 1906, **89**, 1600).

In all furnaces, unless very exceptional precautions be taken, there is a considerable amount of hydrogen present due to the decomposition of moisture. In no case was any carbide found in the hot parts of the furnace. This confirms the suggestion that it is identical with Berthelot's carbide, for Moissan showed that the latter was decomposed at high temperatures.

Finally, I wish to thank Dr. R. S. Hutton for many valuable suggestions, and for the interest he has taken in the work.

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