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# CLI.—The Reduction of Metallic Oxides by Aluminium Carbide.

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## Introduction.

THE behaviour of aluminium carbide when heated in contact with metals and metallic oxides is of considerable importance to the metallurgy of aluminium. Although it is possible to prepare alloys of aluminium by reduction of the oxide by carbon in presence of such metals as copper and iron, when it is attempted to obtain the pure metal by direct reduction, the product is almost exclusively aluminium carbide. It was therefore hoped to get a clearer idea of the metallurgical process by a more detailed study of the reactions of aluminium carbide.

Moissan (*The Electric Furnace*, p. 235), who first isolated this interesting compound, studied its behaviour when heated with metallic oxides, but seems only to have carried out a few experiments in this direction.

Recent investigations at the Manchester University on the reduction of alumina by carbon indicated the importance of a closer study of this branch of the subject, and it is hoped that the results here recorded may help towards the solution of the main problem.

## I. Preparation of Aluminium Carbide.

For the preparation of small quantities of the carbide the most suitable method was found to be that described by Moissan, which consists in heating aluminium contained in a carbon crucible in his ordinary arc type of furnace.

The following observations, which are of importance as throwing

more light on this preparation, and the power consumption, taken in conjunction with a furnace of the dimensions given in the sketch (Fig. 1), may prove of some general interest.

(1) Two kilowatt-hours were required on an average to raise the aluminium (300-400 grams) to the boiling point. The furnace worked very steadily with a current of 250-300 amperes at 35-45 volts.

(2) To obtain good yields it was necessary that the aluminium used should be in the form of small pieces about the size of a walnut.



(3) If the heating was effected too rapidly, a poor yield resulted. The boiling point of the metal should not be reached for at least nine minutes. For the best results it was found necessary to continue heating for about six minutes after the boiling of the metal had commenced. When the aluminium started to boil, as a result of the increased conductivity of the vapour surrounding the arc, the voltage fell considerably, with a corresponding rise of current. This condition was maintained for some minutes and served as an indication of the progress of the carburisation; for, when a large part of the free aluminium was fixed, the current usually returned to nearly its normal condition. Further heating only resulted in decomposition of the carbide.

(4) It was found quite unnecessary to add carbon to the aluminium before heating. Any thus added remained uncombined.

(5) During the formation of carbide, the ingots of aluminium retain their shape even when the temperature is considerably above the melting point of the metal, owing to the formation of a very tenacious skin of alumina which binds the metal. This skin probably remains intact until the boiling point of the metal or melting point of alumina is reached. In most cases where a good yield was obtained, the carbide at the bottom of the crucible perfectly retained the shape of the original metallic ingots.

(6) In all successful carbide preparations, during the cooling, a large amount of metallic aluminium was forced out from the surface. The 380—400 grams of aluminium taken at the beginning gave from 30 to 80 grams of exuded metal, which, when allowed to cool in the furnace in the presence of carbon monoxide, contained a few crystals of carbide. When cooled away from furnace gases, however, it consisted of pure metal. Analysis of samples, cooled while being protected as much as possible from the air by covering the crucible, showed a composition of 99.9 per cent. of aluminium, and on decomposition with hydrochloric acid gave no noticeable amount of methane. It appears from this that aluminium carbide is insoluble in aluminium.

(7) The change in weight of the crucible and contents seems to point to a taking up of carbon from an outside source. In all the methods of preparation employed, it was found that the maintenance of an atmosphere of hydrogen greatly diminished the yield of carbide, and apparently in proportion to the amount of hydrogen present. A large amount of alumina always occurred together with the carbide in the product. The relative amount of these two substances approximated in most cases to that demanded by the equation

$$3\mathrm{CO} + 6\mathrm{Al} = \mathrm{Al}_2\mathrm{O}_3 + \mathrm{Al}_4\mathrm{C}_3.$$

With the Moissan furnace, carbon dioxide was continually given off by the limestone blocks, and was of course transformed into carbon monoxide in contact with the electrodes. This then interacts with aluminium according to the above equation. It appears that the aluminium carbide formed in these experiments results chiefly, and probably entirely, from the action of carbon monoxide on aluminium.

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#### Extraction of Crude Product.

The composition of the products obtained in these experiments consisted on an average of

On breaking up and sieving, a fine powder was separated containing 55-65 per cent. of carbide and 7-10 per cent. of aluminium.

The method used by Moissan for obtaining the carbide from the crude product consisted in treating small lumps of the material with concentrated hydrochloric acid, well cooled in ice. Except for extracting small quantities of material, this method was found to be unsatisfactory owing to the large amount of heat evolved and the consequent violent reaction which sets in. The low solubility of aluminium chloride in concentrated hydrochloric acid is also a disadvantage.

The most satisfactory method of treating large quantities of material was found to consist in the use of strong caustic soda solution. This acts very rapidly on the aluminium, and the temperature can easily be kept below 13° by submerging in the reaction vessel a lead spiral, through which a stream of cold water is passed. The carbide crystals sink to the bottom, are washed by decantation, filtered, washed with alcohol and ether, and then dried. During the extraction, the free carbon present came to the surface, and could thus be readily removed. The carbide left from this process still contained about 2 per cent. of free aluminium. Further extraction of aluminium could only be carried out at great sacrifice of carbide. Hence, the above amount was usually left in, and allowance made for it in the subsequent experiments. It was not possible to obtain the carbide free from alumina, as the latter occurred in a very stable and insoluble form.

## II. Reactions with Oxides up to about 1200° without a Flux.

Aluminium carbide interacts very slowly with the oxides of copper and lead at a dull red heat, giving off carbon dioxide and forming alumina. If the temperature is raised a little higher, a sudden reaction occurs, the whole mass being raised to incandescence. The reaction is, however, never so rapid as is that of aluminium on oxides.

The gas evolved was found to consist of carbon dioxide together with from 2 to 4 per cent. of carbon monoxide. In these reactions, in which a high temperature was reached, the product formed a net-like structure, which, except in the case of lead, could not be made to run together to an ingot owing to contamination with slag. PRING: THE REDUCTION OF

Quantitative Examination.—Reactions between aluminium carbide in excess and the oxides of copper and lead were brought about in a porcelain tube, and the evolved gases measured and analysed. From this and the decrease in weight of the reacting substances, it was estimated that the amounts of oxygen which went to the aluminium and to the carbon were such as to satisfy the equation

 $Al_4C_3 + 12MO = 2Al_2O_3 + 3CO_2 + 12M.$ 

Analysis of the product showed that the excess of carbide used remained undecomposed.

# III. Reactions with Oxides up to about 1200° in presence of a Flux.

Great difficulty was found in the selection of a flux which would withstand the action of aluminium at temperatures produced by the reaction between aluminium carbide and oxides, and yet be sufficiently mobile in the wind-furnace to allow the metallic product to run together.

Cryolite, which becomes very mobile and as transparent as water at a bright red heat, was found to be the most suitable flux for this purpose. At a certain temperature, however, cryolite appears to be attacked by aluminium, as is shown by flashes of light issuing from the surface, which have an appearance of burning sodium. Carbon crucibles were employed to contain the fused cryolite. These were placed inside clay crucibles with the intervening space packed with carbon and were heated in a wind-furnace.

In these experiments, the flux was heated until in a mobile condition, and then the mixture of aluminium carbide and metallic oxide was added in small quantities. Reaction usually took place with incandescence, and sometimes a boiling up of the flux occurred. The reduced metal sank to the bottom of the crucible.

The experiments performed showed that the reaction between aluminium carbide and the oxides of copper, lead, and bismuth, when in the proportion of  $6MO + Al_4C_3$ , gives rise to a metallic product if interaction takes place in the mass of a flux. The best metallic yield resulted by using the proportion  $12CuO + Al_4C_3$ . An excess of carbide diminished the yield. With  $3CuO + Al_4C_3$ , the metal could not be made to run together at all. The products in the case of the oxides of lead, copper, and bismuth consisted of metal containing from 0.4 to 0.8 per cent. of aluminium, an amount which in each case was considerably less than that corresponding to the free aluminium in the carbide used.

Iron oxide and aluminium carbide could not be made to yield a metallic product by the foregoing methods.

Aluminium carbide and alumina were not found to react in cryolite flux to give aluminium, as has been stated by Blackmore (*Electrical Review*, 1904, 55, 994), but at the melting point of copper, aluminium

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carbide is slowly decomposed by cryolite. In these experiments, it is possible that, at the high local temperature produced by the reaction, any aluminium liberated from the carbide might have entered into combination with the flux.

## IV. Reactions at Higher Temperatures.

(a) In Contact with a Bath of Molten Metal.—The bath of molten metal was in these experiments used as a solvent to extract the metal liberated in the reactions and facilitate its quantitative estimation. The heating was effected electrically by means of a granular carbon resistance furnace. For this purpose, the arrangement shown in Fig. 2 was used. The current was led into the furnace by the graphite bars EE of  $5.0 \times 2.4$  cm. cross section. Powdered



FIG. 2.

Acheson graphite was tightly packed around these for a distance of 12 centimetres. A good electrical connection was thus secured between the electrodes and a resistance core which was packed between them. This core consisted of powdered retort carbon, the particles of which were obtained of uniform size by sieving and selecting the material which was arrested between the sieves having respectively 10 and 20 meshes to the inch. A carbon crucible of 4 cm. in outside diameter and 3 cm. in height was embedded in this resistance core. A carbon cylinder of the same diameter and 12 cm. in height was attached to the crucible. By clamping the cylinder, mere contact made a good joint, and the cylinder did not appreciably conduct away the heat from the crucible. The carbon cylinder was bored half way up and a brass side-tube fitted in. By this means, air could be expelled from the crucible and operations conducted in an atmosphereof hydrogen. A graphite piston, joined on to a rod of the same material, was made so as to fit loosely in the cylinder. When using a metal bath in the crucible, this arrangement enabled the slag to be pressed beneath the surface of the metal and extraction facilitated. With a copper bath, a very satisfactory method of washing out metal from the surface slag consisted in allowing a shower of finely divided copper (reduced from the oxide) to fall on to the surface.

The furnace described above was heated with direct current. At first it took 10 amperes at 80 volts. The current gradually rose, 180 amperes at 44 volts being finally reached. In subsequent experiments, the furnace showed initially a higher conductivity.

In the experiments with copper carried out in this furnace, from 40 to 50 grams of metal were first melted in the crucible to form a bath. This required eight to ten minutes and the consumption of about 0.5 kilowatt hour. The air was displaced by a current of dry hydrogen, except when using very high temperatures, when the oxygen was fixed by the carbon. The reagents were then dropped on to the metal, and by the means described above to secure intimate contact and extraction by the bath a slag was left containing practically no metal.

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Mixture added.				Estimated tem- perature of bath of copper.	Percentage of the aluminium of the carbide taken up by the copper.	Remarks.
1.	6CuO	+ Al4(		Melting point of copper.	4.2	The slag contained 38 per cent. of the original aluminium carbide.
$^{2}$			•••	Bright red heat.	8.4	
3.				White heat.	10.9	_
4.	· ,,	,,	•••	Very bright white.	51.0	Total carbon in alloy, 0.1 per cent.
5.	• ,,	,,	••••	Above melting point of alum-	76.8	·
6.	. Al <sub>4</sub> C <sub>3</sub>	alone	••••	White heat, be- low melting point of plat-	17.0	Substances heated during six minutes.
7.	• ,,	,,	•••	Above melting point of plat- inum; below melting point	83•5	Violent reaction, causing copper to vaporise. Heated during five minutes.
8.	6CuO	+ Al4(	3	Intermediate temperature; melting point of silica.	50.0	Experiment conducted in an electrically heated car- bon tube * furnace.
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Reactions in a Bath of Molten Copper.

\* Hutton and Patterson, Trans. Faraday Society, 1905, 1, 187.

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Mixture added.	Estimated tem- perature.	Percentage of aluminium of the carbide taken up by the bath.	Remarks.
1. Fe <sub>2</sub> O <sub>3</sub> + Al <sub>4</sub> C <sub>3</sub>	Melting point of alumina.	64.0	Alloy contained 3.5 per cent. of free and 0.3 per cent. of combined carbon. Visible reaction occurred, causing ejection of sparks of carbon. During the cooling, a large separation of flocculent graphite oc- curred. The metal bath separated into two alloys containing 6.2 and 17.5 per cent. of aluminium re- spectively, both of which were hard and brittle. By decomposition with acid and analysis of the gas, it was found that less than 1.2 per cent. of the alum- inium in these alloys oc- curred in combination with earbon
2. $Al_4C_3 + Fe$ (very fine)	Just above melt- ing point of	21.5	Heated for six hours in a carbon tube furnace.
3. Al <sub>4</sub> C <sub>3</sub>	Melting point of alumina.	91.3	Alloy contained less than $0.23$ per cent. of $Al_4C_3$ . Heated for fifteen minutes
4. Al <sub>4</sub> C <sub>3</sub>	Well above melt- ing point of alumina.	92.0	The hot molten bath was cooled by immersion in cold water.

Reactions in a Bath of Molten Iron.

## (b) Metallic Oxides and Aluminium Carbide interacting alone in an Empty Carbon Crucible at High Temperatures.

When a mixture of aluminium carbide and the oxides of copper or iron is dropped into a highly heated crucible, a violent reaction occurs and the metallic product runs together in the form of a button or globules.

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Mixture added.	Estimated tem- perature of crucible.	Percentage of aluminium in alloy.	Remarks.
1. $6$ CuO + Al <sub>4</sub> C <sub>3</sub>	Little below melting point	18:5	White, brittle alloy con- tained 1.1 per cent. of
2. ,, ,,	Melting point of alumina.	14.2	Violent reaction. Alum- inium lost through volatil- isation.
8. ,, ,,	Temperature low- er than above, adjusted so as to prevent ex- cessive loss of metal by vola- tilisation.	19.1	1.3 per cent. of graphite.
4. ,, ,,	Melting point of silica.	5.7	Experiment conducted in tube furnace.
5. 3CuO + Al <sub>4</sub> C <sub>3</sub>	Temperature as 3.	27 .9	1.2 per cent. of graphite.
6. $2 \text{Fe}_2 \text{O}_3 + \text{Al}_4 \text{C}_3$ .	Melting point of alumina.	34.9	4.5 ,, ,,
7. Fe <sub>2</sub> O <sub>3</sub> +Al <sub>4</sub> C <sub>3</sub>	Melting point of alumina (as above).	46.7	2.8 ,, ,,

## V. Calcium Carbide and Lead Oxide at a High Temperature.

The object of this experiment was to ascertain if temperature had any influence on the product obtained in the reduction of oxides by calcium carbide. The large amount of work which has been done in this field shows that at lower temperatures metals are produced which contain traces of calcium.

In some cases, the formation of alloys containing up to 1 per cent. calcium has been observed (Moissan, Compt. rend., 1897, 125, 839; Kugelgen, Zeit. Elektrochem., 1901, 7, 541, 557, 573).

### Lead Oxide dropped into Molten Calcium Carbide.

The lead oxide was added in very small quantities owing to the violent reaction which occurred. Some metal volatilised. When cold, a metal was left in the crucible which had an appearance of lead. This was soft, very bright, and had no appreciable action on the water.

### Analysis.

Lead.	Calcium.	Residue (by	diff, ).	
96.60	2.58	0.82		100

## VI. Action of Metallic Calcium on Aluminium Carbide.

It was thought that a study of the action of calcium on the carbide would form an interesting addition to the above work. Experiments were carried out both in the wind furnace and at higher temperatures by electric heating, as great care as possible being taken to exclude the furnace gases, although this was probably not complete at the highest temperatures.

Reaction was found to occur at all temperatures above the melting point of calcium. The aluminium carbide was transformed to the extent of 83 per cent. at the lower temperatures, but apparently less completely as the temperature of reaction rose.

The reverse reaction, that of aluminium on calcium carbide, was also investigated and found to take place, the amount of reaction seemingly increasing with the temperature and varying between 7 and 25 per cent. Thus it is probable that an equilibrium exists as indicated by the equation

 $2Al_4C_3 + 3Ca \simeq 3CaC_2 + 8Al.$ 

## Summary and General Conclusions.

The work here recorded seems satisfactorily to explain the reactions which occur between aluminium carbide and metallic oxides and metals.

Up to about 1400°, the carbide behaves as a strong reducing agent, but both aluminium and carbon are simultaneously oxidised even when the carbide is in excess. Thus, under these conditions, no separation of aluminium or of carbon can be detected. For instance, aluminium carbide interacting with copper oxide produces metallic copper and carbon dioxide, together with small quantities of carbon monoxide. A similar behaviour is noticed when the reactions are brought about in the mass of a flux so as to facilitate the agglomeration of the reduced metal. At higher temperatures, however, selective reduction begins to be apparent, the reduction being more and more brought about by the carbon of the carbide, with a result that alloys of aluminium and the reduced metal are obtained, the percentage of aluminium increasing the higher the temperature of reaction.

In the case of copper, the percentage of aluminium in the alloy seems to be limited by the volatilisation of aluminium. Copper alloys were obtained containing up to 28 per cent. of aluminium, whereas the equation

$$3$$
CuO + Al<sub>4</sub>C<sub>3</sub> = 4Al,3Cu + 3CO

demands an alloy containing 36 per cent. of aluminium.

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In the case of iron, an alloy was obtained containing 46.7 per cent. of aluminium, or subtracting the amount of free carbon, 49.6 per cent. of aluminium. This corresponds to the equation

$$\operatorname{Fe}_{2}O_{3} + \operatorname{Al}_{4}C_{3} = 2\operatorname{Fe}_{4}\operatorname{Al} + 3\operatorname{CO}_{4}$$

which demands an alloy containing 49.2 per cent. of aluminium. Any excess of oxide used in the reaction resulted in oxidation of the aluminium of the alloy. When the reaction between aluminium carbide and iron oxide was brought about in presence of a bath of molten iron at a high temperature, alloys were also obtained in which more than 90 per cent. of the aluminium of the carbide used had been set free and taken up by the iron.

Calcium carbide exhibits, in a smaller degree, a behaviour similar to that of aluminium carbide in the relative affinities of the calcium and the carbon for oxygen at high temperatures.

Reactions between lead oxide and excess of molten calcium carbide gave an alloy containing 2.6 per cent. of calcium.

These results are explained by the fact that at high temperatures alumina can be reduced by carbon, and the following equation, which at comparatively low temperatures is known to go in the direction from left to right, would, at high temperatures, apparently be reversed and occur in the opposite direction :

$$6Al + 3CO \equiv Al_4C_3 + Al_2O_3$$
.

Owing to the evolution of heat in these reactions between oxides and aluminium carbide, it was not possible to fix or estimate the temperature at which reaction actually took place.

Aluminium carbide reacts with copper at a temperature below the melting point of platinum, and with iron just above this temperature, to form an aluminium alloy with liberation of free carbon. At higher temperatures, the reaction takes place with violence and is complete.

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