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ALUMINIUM AS A HEATING AND REDUCING AGENT.
BY DR. HANS GOLDSCHMIDT AND CLAUDE VAUTIN.
(See also pp. 584 and 612.)

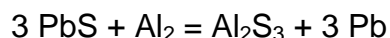
ALTHOUGH it is well known that the oxide of aluminium (Al_2O_3) is a remarkably stable body, no experimenters have hitherto taken advantage in a practical way of the enormous affinity exercised for oxygen by aluminium to effect reductions of other oxidised bodies. A few experiments on a laboratory scale, chiefly on the reduction of metallic chlorides, and fluorides, have been recorded, amongst which may be mentioned those of Wöhler, Tissier, and Deville. Wöhler attempted to produce the metals chromium and manganese by heating their chlorides with aluminium, but only partial success was obtained, as it was found impossible to obtain the metals free from aluminium. He also produced tin alloy of titanium and aluminium by heating together titanous acid, cryolite, and metallic aluminium. He states that the use of cryolite is to cause the formation of fluoride of titanium, which shows that his object was to bring into action a fluoride of the metal and not to effect direct reduction of the titanous acid. The brothers Tissier heated together aluminium with oxide of manganese, but they state that no reaction takes place. Deville produced an alloy of aluminium and silicon by heating together the metal and silica, and Beketoff produced a substance containing 33 per cent. of barium by heating baryta with aluminium and barium chloride. Lastly, Greene and Wahl separated manganese from its oxide by direct reduction.

Although these results are not very encouraging it is a remarkable fact that the value of aluminium as a deoxidiser has been so long overlooked. It is probable that the comparatively high cost of the metal and the explosive nature of the mixtures deterred some from attempting to use it on a large scale.

The fact that metallic aluminium is a powerful reducing agent may be inferred from the figure 3 representing the heats of combination of aluminium with oxygen, sulphur, &c. For example, the heat of formation of Al_2O_3 is about 360,000 calories, while that of $[\text{K}_2\text{O}]$ is 97,000. Again the heat of formation of $[\text{Al}_2\text{Cl}_6] = 321,000$ against $[\text{Fe}_2\text{Cl}_6] = 192,000$ and $[\text{Na Cl}] = 97,300$, but judging by results, even these figures failed to promote further research.

In the latter part of 1892 and early in 1893, one of the authors was engaged in investigating certain processes for the production of aluminium, and for special reasons it quantity of pure aluminium sulphide was required. Attempts were made to produce it by the usual text book methods, such as heating alumina in the vapour of carbon bisulphide, or heating together alumina, carbon, and sulphur, but these failed to produce the sulphide in sufficient quantity and of the required purity. It then occurred to the author to reduce sulphide of lead by means of metallic aluminium in imitation of the well-known reaction between galena and metallic iron. To carry out the experiment, about 5 lb. of practically pure galena were crushed and mixed with the theoretical

quantity of aluminium in coarse lumps to produce Al_2S_3 and metallic lead in accordance with the equation—



The mixture was charged into a crucible, and placed in a furnace. As soon as the contents of the crucible had attained to its full red heat, reaction took place with the evolution of enormous heat. The contents of the crucible were cast into a mould, and it was found that the reaction as I expressed above had taken place, yielding practically theoretical amounts of the products. The aluminium sulphide produced is of a greenish colour ; it decomposes water readily with the production of sulphuretted hydrogen, though it may be kept in air-tight tins or bottles for an indefinite time. It fuses at a clear red heat, and the metal can easily be obtained from the fused mass by electrolysis. The presence of sulphide of lead as an impurity is guarded against by keeping a slight excess of aluminium in the charge, which excess of metal will be found after casting the molten product as a hard, brittle, and easily detachable button on the surface of the lead. Aluminium will not alloy with lead, but it will form alloys with iron, silicon, copper, silver, gold, &c. The excess of metallic aluminium therefore performs the double function of keeping the sulphide of aluminium pure, and of removing all iron, copper, &c., from the lead, giving to the latter remarkable purity and softness. Further, by judiciously mixing the aluminium and the galena, this excess button removes any precious metals which may be contained in the sulphide of lead, much in the same manner as zinc desilverizes lead in the Parkes process. (The addition of a small percentage of aluminium to the zinc used in the Parkes process permits of a higher temperature being used ; it prevents the formation of oxide of zinc and effects better separation of the precious metals. (sic))

The concentration of the precious metals in the excess button presents only a theoretical interest, as the present price of aluminium entirely excludes its use for that purpose. This first successful experiment led to further attempts at reducing the sulphides of other metals in spite of the frequently repeated statement that aluminium sulphide could be reduced by metallic iron, zinc, copper, &c. The supposed decomposition of aluminium sulphide by metallic iron has been the basis of numerous patents for the production of aluminium. The patentees describe at length a process for producing the sulphide, after which the specification draws to a conclusion with the statement that the sulphide may be decomposed by iron, copper, or even by lead. As a matter of fact, it is the reverse action which takes place. Nearly all metallic sulphides, except those of the sodium and barium groups and magnesium, are readily decomposed by metallic aluminium with the characteristic feature of the evolution of great heat. So much so that on reducing common sulphide of iron in a small crucible, the molten iron, free from carbon, melts into one mass which can be cast into a mould, while the temperature of the furnace, in which the reaction took place, is some hundreds of degrees below the melting point of the metal. It is interesting to note that iron produced in this manner, rising in a magnesia-lined clay crucible, is obtained absolutely free from carbon, the only impurities being traces of aluminium and sulphur, and by using a small excess of the sulphide the aluminium may be eliminated. Among

the sulphides that are decomposed by aluminium may be mentioned those of cobalt, nickel, molybdenum, (sic) and zinc.

Our next experiments were carried out with metallic oxides and aluminium; here, the range of possible reductions extends to the oxides of the alkalis and the alkaline earth metals, all of which yield their oxygen, though with difficulty, to aluminium. Practically all the metallic oxides are reducible by this method, the chief exception being the oxide of magnesium. Trials have been made with the following oxides of metals, all of which are reduced by aluminium, either pure or in the form of alloys :—Chromium, manganese, iron, copper, titanium, boron, tungsten, molybdenum, nickel, cobalt, zirconium, vanadium, niobium, tantalum, cerium, thorium, barium, calcium, sodium, potassium, lead, and tin ; however, the experiments with some of these metals must not be considered to be concluded.

The failure of the brothers Tissier to effect reduction of the oxide of manganese is probably due to one of two causes ; either they failed to heat the charge sufficiently to promote reaction, which is improbable, as the temperature required is not high, or else they had not the aluminium in its form best suited for the purpose. We find that nearly everywhere the aluminium must be in a powdered or granulated condition, and intimately mixed with the finely crushed oxide or sulphide to be reduced. There are, however, a few exceptions to this rule, for example, to effect the reduction of lead salts, it is not advisable to have the aluminium in its very fine state of division, because owing to the enormous heat produced: a simultaneous reaction throughout the whole charge would cause sudden vaporisation of the lead, with the result that the whole charge would be blown out of the crucible with explosive violence.

We have found that aluminium, like lead and other metals, can be easily granulated by agitating the molten metal in a suitable vessel at the moment when on cooling it reaches [544] certain critical temperature just between the solid and liquid state.

As before mentioned, the most striking feature of all these reactions is the evolution of enormous heat. So great is the temperature produced that the most infusible metals are melted, while the slag, consisting of nothing but alumina, is sufficiently molten to allow all the reduced metal to sink through it and to collect into one fused mass. It is estimated that the temperature produced is at least 3,000°C, and by means of this heat, work can be done which hitherto required the electrical furnace for its performance. The authors have made practical use of the reducing power of aluminium in the production of chromium from its oxide on the large scale, but they soon recognised the fact that to make this process commercially successful, it would be necessary to do away with external heating of the charge, both on account of high fuel costs and on account of crucible wear.

It has been proved by experiment that it is unnecessary to heat the whole of the mixture from which the metal is to be obtained to the temperature at which reaction takes place ; that is to say, it is only necessary to start the reaction at one point of a given charge as the local heat produced is sufficient to cause the whole charge to re-act, the heat

passing gradually through the entire mass. In the reduction of chromic oxide by aluminium the temperature to which it is necessary to heat one point of the charge before the reaction takes place is about 1050°C, or a bright red heat.

At first, however, it was found very difficult to cause the mixture to ignite at one point without external beating, but this trouble was overcome by using a "fuse" of a highly inflammable nature which was capable of setting up an initial impulse which subsequently caused the combustion of the whole charge. The action of the "fuse" or "cartridge" is also based on the heat produced by oxidising aluminium. By supplying the metal with a compound rich in oxygen a highly inflammable mixture is obtained, which at the same time produces intense heat. Of the various compounds tried, peroxide of barium was found to give the best results though various other per-salts may be used. A suitable mixture of the metal with the peroxide is made up into a paste with a cementing material, which on hardening forms a cartridge, capable on ignition, of imparting the requisite initial temperature to the charge. The cartridge is supplied with a piece of magnesium ribbon whereby its ignition is readily accomplished. By this process a considerable amount of chromium has already been produced by the authors.

A few experiments illustrating the beating effects of this process will be shown, and it is probable that, using cheap impure aluminium and a cheap source of oxygen such as oxide of iron, that the process as a heat producer possesses considerable commercial value as it can be supplied in cases where it would not be convenient to use other sources of heat. For heating purposes alone, it would be necessary to add some material such as magnesia or lime to the mixture, of metal and oxide so as to prevent the running together, of the metal and slag produced; thus leaving, after firing, a brittle cindery slag which can easily be removed by tapping with a hammer.

For beating purposes, as in the production of metals, the cartridge would have to be used to start the reaction in the mixture which is to produce the heat.

As we have already pointed out, a very important use to which the process may be put is for the production of pure carbon-free metals, though future work will probably lead to other important applications; nor must it be forgotten that by this method not only pure metals but also alloys can be obtained, many of which it is exceedingly difficult to produce by any other process. For example, the authors have produced ferro-boron containing 20 to 25 per cent. boron; ferro-titanium (20 per cent. and 40 per cent. of titanium, the latter being non-magnetic); ferro-chrome; chrome-manganese, &c. But we hope to show by means of experiments that the adaptation of this method to heating purposes possesses very wide application, and it is possible that its point of utility will rival the reduction process.

It may be mentioned that the alumina slag produced possesses properties superior to ordinary rock corundum both as to hardness and texture, owing, probably to the total absence of water in its composition. The slag also possesses other interesting characteristics. Thus for example, the slag formed during the production of chromium will be found to be interspersed with red crystals which must be taken to be rubies,

chromium being the colouring matter of the natural ruby. They are, however, of no value on account of their small size.

Finally, phosphates, sulphates and nitrate are also reduced by aluminium, though the latter act feebly in comparison with the sulphates.

The authors wish to acknowledge the useful work done by Mr. Hugh K. Picard, who, as assistant to one of them, successfully carried out most of the earlier experiments.

APPENDIX.

The following experiments will serve to illustrate the paper :—

1. Burning of the cartridge, the so called " inflammable cherry.
2. Heating of an iron rivet of 1 lb. weight by means of a cemented heating mixture, which surrounds the rivet so that the gradual passing of the heat is visible.
3. White heating of a rivet of about 7 lb. weight, the heating mixture being surrounded with sand. As the heat is kept from dissipating by the sand, the whole mass can be put, as shown, into a wooden tub.
4. Application of the method for hard-soldering a flange on to a tube of 1 in. diameter; instead of putting the flange (prepared with hard solder and borax as the coppersmiths do it) into a charcoal fire, it is placed in the heating mixture. For this purpose only about 3 ½ oz. of aluminium are required. If impure or raw aluminium be used at, say, 6d. per pound, the total expense will be 1 ½d. for the heating mixture.
5. Production of wrought iron from oxide of iron and aluminium. The reaction in this case is brought about without the aid of a cartridge, but by means of a mixture of peroxide of sodium (NaO_2) and carbide of calcium (CaC_2), ignited by a drop of water. The same effect is produced by a mixture of peroxide of sodium with aluminium, magnesium, zinc, or sulphide of antimony.
6. Production of a regulus of metallic chromium of about 10-12 lb. weight in a magnesia-lined crucible. In this crucible a mixture of Cr_2O_3 and Al_2 is put, and ignited ; then a further quantity of this mixture is added till the crucible is filled up. The reaction lasts only a few minutes.
7. Production of sodium (Na) from caustic soda (NaOH) and aluminium in a paper tube. The sodium distils off with a bright flame. The initial temperature of the reaction is very low ; this experiment is therefore interesting, as aluminium, as is well known, has been made with sodium from chloride of aluminium (Al_2Cl_6).

Beketoff found in 1888 that aluminium decomposes the hydroxides of the alkalis, and he distilled potassium and rubidium in an iron tube. Deville, however, expressly mentioned that he did not succeed in decomposing the molten alkalis with aluminium.

8. Reaction between a mixture of gypsum (CaSO_4) and aluminium in a paper tube; the temperature of reaction is here very high. First the paper tube is set on fire by a match, but the temperature so produced not being high enough to start the reaction, a cartridge is applied, and then the mixture goes off like a rocket.

The following metals, alloys, &c. were exhibited:—

Metals.

1. Chromium, containing 95-97 per cent. Cr and 3-4 per cent. Fe.
2. Chromium, 99.5-99.8 per cent. Cr, containing also traces of silicon and iron.
3. Manganese, 98-99 per cent. Mn.
4. Iron, hammered, equal, to best pure steel.
5. Vanadium, chemically pure.
6. Niobium, chemically pure.

Alloys.

7. Iron, containing 40 per cent. of titanium (not magnetic).
 8. Iron, containing 20 per cent. of titanium (magnetic).
 9. Iron, containing 25 per cent. of boron.
 10. Manganese, containing 30 per cent. of chromium for making alloys with copper, manganese, and chromium (so-called chrom-manganin).
 11. Copper, containing 10 per cent. of chromium (has nearly the colour of copper).
 12. Alloys of lead and barium.
 13. A plate of iron of about half an inch in thickness in which a hole has been melted by the heating mixture.
 14. Different pieces of corundum (slag, fused Al_2O_3) some of these pieces containing crystals of rubies; also corundum crushed.
 15. A piece of bronze.
- Breaking strain in lb. per sq. in. = 27.874 tons, or 62,440 lb.
Elongation = 34 per cent.

ALUMINIUM AS A BEATING AND REDUCING AGENT (IN THE PRODUCTION OF CHROMIUM AND OTHER METALS).

BY DR. HANS GOLDSCHMIDT AND MR. CLAUDE VAUTIN.

(This Journal, 1898, 543.)

Discussion.

Dr. S. RIDEAL congratulated the author and Dr. Goldschmidt on the success of the brilliant experiments they had seen, and asked if he was right in understanding that metallic calcium was reduced by the action of aluminium on calcium sulphate. If so, he would like to know what steps were taken for ensuring the permanency of the product, as he would have expected that, if the reduction were performed in air at the temperatures that were produced, it would have rapidly re-oxidised to the condition of lime.

Dr. GOLDSCHMIDT explained that he was not able to obtain pure metallic calcium. He had obtained an alloy of iron and calcium, and was so covered up during the reaction that there was a loss of only about 1 per cent.

Mr. J. B. C. KERSHAW regarded the process as one which might have important industrial results. He need hardly remind the authors, however, that there were other methods in use for the production of metallic chromium, and that therefore the success or non-success of this particular process would depend entirely on the economical aspect of the question. In their paper they had not given any particulars as to the cost of the process generally, or of obtaining the aluminium in the powdered form; and it would be of great interest to have definite information from them upon this point of cost.

Dr. GOLDSCHMIDT, replying to Mr. Kershaw, said that the process was cheaper than any other now known. The cost of the chromium and ferrochromium was about 2 marks per kilo., say, a shilling a pound. The chromium in commercial ferrochromium contained about 10 per cent. of carbon. It had been mentioned that it was possible to reduce the slag back to aluminium, even if it were not sold for the purposes to which emery was now applied. Therefore, that would considerably reduce the cost chargeable to the production of the chromium.

Mr. B. KITTO enquired whether the author had succeeded in reducing the oxide of uranium. He believed that Moissan had succeeded in getting a carbide of the metal fairly pure; still that was not uranium. Messrs. Vantin and Pickard had, about three years ago, tried some oxides of uranium with which he had supplied them, and succeeded in getting a strong uranium alloy of about 66 per cent., the rest being aluminium. Since that he had heard that metallic uranium had been obtained by the process, and would like to know if that was correct and if it had been proved by analysis to be uranium, and not an alloy. He had himself tried the ordinary text-book process of reduction from chloride, but without success. He would also like to ask which of the oxides of uranium Dr. Goldschmidt had operated upon.

Dr. O. J. STIEINHART desired to know whether the presence of carbon in chromium acted deleteriously in the manufacture of chrome-iron or chrome-steel; for, if such was not the case, the ordinary method of working would be cheaper than that brought forward by Mr. Vautin. It was to be remembered that they had to deal with chrome-iron ore containing 40 per cent. of chromium, and costing 51. per ton, whereas chromic oxide alone cost more than that, and, in addition, they had the expense of the preparation of the alumina, &c.

Dr. GOLDSCHMIDT said that the cost of the chromium in the chrome iron-ore was very small—only about a penny, whereas the cost of reduction by the ordinary method was very great. Moreover, in making the chromium for this purpose he avoided all cost for crucibles. That was a great saving, which enabled him to compete successfully with other processes. They had no difficulty in disposing of the pure chromium as fast as it could be made. In fact, many works were already abandoning the use of nickel in favour of chromium.

Mr. W. F. REID asked if the author had tried any experiments with regard to the reduction of tungsten. He presumed not, as he did not see that metal among the specimens. With regard to the very pure chromium exhibited, he would be glad to know if the author was at liberty to state how he obtained the oxide from which it was produced.

Dr. GOLDSCHMIDT replied that it was obtained from the chrome-iron ore and chromates, and the process was performed easily and cheaply.

Mr. REID, Continuing, said he would be glad to know roughly what the process consisted in.

Dr. GOLDSCHMIDT, replying, said it was no secret ; the chromates were reduced with coal. It was not necessary to have a very highly crystallised chromate, and therefore the cost of the oxide, when made in large quantities, was very small.

Mr. W. CROWER asked if any experiments had been made with vanadium, and whether that metal also was obtained in the pure state.

Dr. GOLDSCHMIDT said that it was obtained nearly pure. It was contaminated only with a little iron, and the operation was performed as with chromium and without much difficulty. Further replying to Mr. Reid's question, he would add that they had succeeded fairly well with the reduction of tungsten, but had not got it quite pure. The work, however, was easier than with uranium. He had made alloys of tungsten with both copper and iron, but to obtain the pure metal was very difficult, and that was a matter upon which he was still experimenting.

[650] Mr. BERTRAM BLOUNT, referring to a specimen of iron exhibited, said that that was probably the greatest curiosity in the room, as he understood that it was absolutely pure metal. If so, he would suggest that it would be exceedingly interesting to add the analysis of it to the paper. It would be very valuable as a basis for experiments in the production of alloys, starting with pure material.

Dr. GOLDSCHMIDT said that the specimen of iron was not quite pure. It was made from a pure oxide which was very hard to obtain. He could not at the moment remember the exact analysis, but he thought he might say that it contained no aluminium, only a little silicon from the aluminium used in the reduction.

Mr. E. ACKERMANN enquired if the author could state whether in his reaction he obtained a temperature equal in intensity to that of the electric furnace, and whether the reduction might not possibly be more economically effected by electric methods. The reduction of certain oxides by aluminium alone might be very useful where an electric furnace was not available or the quantity of metal required was relatively small. Calcium carbide for instance, could be obtained on a small scale, both electrically and chemically. But on the large scale it could only be prepared by electrical methods, and

the same with aluminium. Using an electrically obtained product on a large scale as a substitute for electricity did not appear to afford much economical advantage. Would it not be of advantage to use some other body for the purpose of the reduction, such as barium peroxide or iron filings, and to start the reaction by means of some other substance, such as liquid oxygen ?

Mr. H. L. SLMAN felt deep interest in the paper before the meeting, as he was one of those who was fortunate enough to witness some of the first experiments made with the method. By these means he had seen considerable ingots of pure metallic molybdenum, uranium, and vanadium produced for the first time in the world's history. On a later occasion, in view of the intense heat evolved, it was proposed to measure the temperature of the reaction, and Prof. Roberts Austen attempted this with his electric thermo-couple. The crucible was prepared as usual for a chromium reduction and heated, and in a few minutes the reaction occurred. The spot of light from the reflecting galvanometer, which up to this point had moved but slowly, then rapidly traveled round the scale, and upon removing the pile for inspection it was found that the heat had been so great that the immersed portion of the thermo-pile, with its platinum-rhodium terminals, had disappeared altogether into the reaction. He believed he was correct in saying that already, in Germany, large quantities of metallic chromium were being produced by this method for the manufacture of the chrome-steel for which Messrs. Krupp and Co. were famous. It was interesting to learn that the slag produced was applicable to the same uses as corundum. Altogether he regarded the process as one of the most elegant and complete reactions he was acquainted with.

Mr. CLAUDE VAUTIN having been invited to reply, said that Dr. Goldschmidt had so ably replied to questions that had been put that he had but little to say. Referring to Mr. Ackerman's remarks, however, he might observe that the temperature of burning iron into oxide was several thousand calories less than that generated by the burning of an equal number of molecules of aluminium. In fact, results were obtained by the combustion of aluminium that were not possible in the electric furnace. Dr. Goldschmidt had made some experiments for determining the temperature reached, and estimated it up to $2,900^{\circ}$ C. The process was already in practical operation, and the demand for chromium was so great that it was sufficient to use up the present production of aluminium for the purpose of reducing the chromic oxide. He understood the demand was attributable to the greater certainty of composition as compared with the use of ferrochromium and the freedom from carbon. He quite agreed with Mr. Blount that the specimen of iron shown was one of great chemical curiosity. He understood that although it contained a little silicon there was no carbon present.

Aluminium as a Reducing Agent, &c.

L. Franck. Chem. Zeit. 1898, 22, [25], 236-245.

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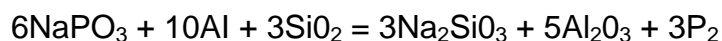
Action of Aluminium on Phosphorus Compounds—Phosphorus vapour when led over powdered aluminium, heated to a dull red heat in a current of hydrogen, combines with

it with incandescence, forming a dark greyish-black unfused mass, which is decomposed in contact with moist (normal) air, forming PH_3 , and leaving a greyish-white powder. It is decomposed also by water, aluminium also by water, aluminium hydroxide and a brownish-black residue being left ; and by acids and alkalis, which dissolve it almost completely with evolution of PH_3 . The compound remains unaltered when heated in air.

At more or less elevated temperatures, all phosphoric, acid compounds (meta-, pyro-, and ortho-salts alike) are decomposed by aluminium. Metaphosphates, however, undergo the most complete change, according to the equation—



The addition of silica effects the release of the remaining phosphorus, thus :—



Calcium and magnesium salts are as efficacious as those of sodium, but the superphosphates of commerce are not available for the production of phosphorus in this manner. If, however, bone ash be decomposed by hydrochloric acid instead of by sulphuric acid, a material suitable for the purpose is obtained.

Hence phosphorus may be produced, with almost quantitative completeness of yield, at relatively low temperatures, and the reduction may be demonstrated in the apparatus shown in the annexed figure. Hydrogen generated in A is dried by the sulphuric acid bottles B, and is then passed through the Fresenius safety-tube C to the combustion - tube D, which is 0.5 m. long, and contains a porcelain boat, d, carrying the charge of 2.1— 2.5 equivalents of Al, six equivalents of NaPO_3 , and two of silica (Kieselguhr). Beyond D is the condenser, E, and a trough of water, into which the outlet tube , F, is passed. On heating the boat at d, particles of phosphorus soon condense on the walls of the tube, in its cooler section, and in the condensing-bulb. If the flow of hydrogen be too rapid, some phosphorus is carried over, and is spontaneously kindled as it escapes into the air ; but with a slow current no phosphorus need be lost.

Action of Aluminium on Carbon Compounds : On Carbon Dioxide.— On passing dry CO_2 over aluminium powder, heated to redness of the mass rose rapidly [613] owing to the resulting reaction. After cooling in the same gas, the residue was found to consist of Al_2O_3 and amorphous carbon ; but it gave a small quantity of an evil-smelling gas when treated with hot dilute HCl so that traces of an aluminium carbide must have been formed. No carbon monoxide was detected throughout; but the reaction corresponded almost exactly with the equation $3\text{CO}_2 + 4\text{Al} = 2\text{Al}_2\text{O}_3 + 3\text{C}$. Aluminium sheet and wire heated in a current of CO_2 becomes covered with a black crust ; at the same time is brittle, and is partly oxidised, partly converted into a carbide.

Action on Carbon Monoxide.—An exactly similar result was obtained by beating aluminium powder in CO. The reaction is $3\text{CO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{C}$; but, as with CO_2 , a trace of carbide is formed.

Action on Carbonates.—Alkaline carbonates and aluminium mixed in equal proportions according to the equation $\text{Na}_2\text{CO}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + \text{C} + \text{Na}_2$, and heated to a red heat, became incandescent, and gave alkali-metal and amorphous carbon. Lithium, sodium, and potassium were thus reduced, the latter with almost theoretical yield. No potassium carbide was observable. Calcium, barium, and strontium were reduced in the same way, and barium crystals were sometimes obtained, but never crystalline carbon. Nevertheless, some aluminium carbide and a little nitride were also formed.

Aluminium and Carbon.—The author confirms Guntz and Masson's statement (this Journal, 1897, 244) that the presence of aluminium iodide or chloride favours the formation of carbide when Al is heated in CO or CO_2 , but he reaffirms the correctness of his own general equations given above. Aluminium powder heated with lampblack appears unchanged, but evolves much hydrocarbon gas when placed in water. The excess of lampblack could not, however, be removed. Much carbide may be formed by direct combination (Deville to the contrary notwithstanding), but the reaction is never complete ; and Moissan's carbide, Al_4C_3 , has not been obtained except in the electric furnace.

Action of Aluminium on Oxides.—Copper oxide (cuprous or cupric) mixed with the correct proportion of aluminium powder for reduction, and heated gradually, reacted suddenly, with a report like that of a gun. The glass tube was shattered and small copper shot were found. With an excess of aluminium, the residue was an aluminium bronze. Silver oxide was similarly attacked. Beryllium was also reduced at a red heat, but quietly, and with only slight incandescence. Calcium could be partly reduced from lime, and calcium alloys could thus be readily obtained. Strontium was reduced from the oxide with a more marked rise of temperature. Baryta is much more readily, and is indeed almost completely reduced, with distinct incandescence. Zinc oxide is reduced with quiet combustion and a blue white luminous flame. Cadmium and mercury and lead oxides also yield metal, the former quietly, the second almost at once, and the last-named with explosion. Boron, silicon, phosphorus, and arsenic also, are all separated in the elementary state on beating the oxide with powdered aluminium. Iron, manganese, cobalt, nickel, and molybdenum are all partly reduced ; in the electric furnace new compounds are thus produced.

Action on Sulphates and Chlorides.—Barium (or other) sulphate, mixed with excess of aluminium powder and heated, explodes with a loud report, shattering the glass tube in which it is held. Finely divided sulphur and sulphides are among the products of the reaction. Sodium, potassium, calcium, and barium chlorides, when melted, yield metal on the introduction of Al powder, the two latter reacting more rapidly and completely.

Action on Sodium Peroxide.—Aluminium powder mixed with sodium peroxide explodes at a red heat. If the mixture be moistened with water it inflames spontaneously.

—W. G. M.

High Temperatures, New Process for the production of, and for the Preparation of Metals Fusible with difficulty, and Free from Carbon. Goldschmidt. Zeits. f. Elektrochem. 1898, 4, [21],491-498.

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THE author shortly reviews previous work on the use of aluminium in producing high temperatures, and then describes the method he adopts. As is well known, an extremely violent reaction takes place when aluminium unites with oxygen, the estimated temperature of the reaction being about 3,000° C. In order practically to make use of the high temperatures thus obtained, the chief difficulty is so to moderate and-control the reaction that it will perform the required work.

The first point to be noted is that it is not necessary to heat up the whole of the reacting mass to the temperature of ignition. It is sufficient to start the combustion at a single point only, but this in itself presents some difficulties. In the preparation of metallic chromium from a mixture of its oxide with powdered aluminium, these difficulties may easily be overcome by applying at any convenient point a small quantity of a mixture of aluminium with a more easily reducible oxide, or preferably a peroxide. Lead oxide, copper oxide, potassium permanganate, and many other substances may be employed for this purpose.

One great advantage of this process is that it admits of the preparation of pure metals free from aluminium ; the only precaution which requires to be observed is that the oxide to be reduced must be present in slight excess.

The process is capable of two main applications. In the first place the heat given off by the combustion of a mixture of aluminium with any convenient oxide may be utilised for beating purposes only (welding, &c.), or, secondly, the reducing power of aluminium at a high temperature may be used for the preparation of pure metals, or alloys. In either case only slight alterations in the mode of working are necessary. If a moderate heat be required, the reacting mass is diluted by the addition of some inert substance, which, at the same time, prevents the whole mass from melting. A convenient mixture of this sort is composed of aluminium and the cheapest available oxide (e.g., iron ore, sand, &c.), which is then diluted either with a large excess of the same oxide or with magnesia, lime; &c. If, on the other hand, the metal itself be required, a large excess of the oxide must be avoided, so that the heat which is generated will not only melt the metal, but also the slag (corundum), which then protects the regulus from the action of the air.

The following experiments illustrate the applications of the process :—A rivet weighing 3 kilos., such as is used in the construction of bridges, is surrounded by a mixture of oxide of iron, sand, &c., and powdered aluminium, and almost wholly embedded in sand contained in a wooden box. On the top of the small exposed portion of the aluminium mixture is laid a small ball prepared by mixing aluminium powder with a more easily reducible oxide, and into which is inserted a short length of magnesium ribbon. The

reaction is started by setting fire to the magnesium ribbon, and as soon as this is done more sand is placed on the top in order to keep in the heat. If the contents of the wooden box are emptied out after a short time it will be found that the rivet is white hot and ready for forging.

In a somewhat similar way 1-in. iron pipes may be hard soldered at an estimated cost of about 2d. ; or, two pieces of wrought iron may be fused (welded) together. The joint so obtained is satisfactory, as can be shown by sawing the pieces through at the joint. It is claimed that such a joint is better than that produced by electric welding, owing to the greater uniformity of heat. By diminishing the quantity of inert material, the iron in the above experiment may easily be melted. Holes may be made through ½-in. wrought-iron plates by igniting some of the mixture on them, and adding more, if necessary, as soon as the reaction has started.

In order to reduce chromium from its oxide, a mixture of this and powdered aluminium is made and introduced into a crucible lined with magnesia. The reaction is started as before, and the mixture then added continuously until the crucible is full. After cooling, the crucible is broken open and the regulus of metallic chromium removed. At the meeting of the German Electrochemical Society, at which the author communicated his paper, he showed a mass of chromium weighing 25 kilos. prepared in this way. By making two apertures in the crucible, one for the introduction of the mixture and the other for the outflow of the chromium, the process may be worked continuously, as in the case of the electric furnace.

It is claimed that the temperature attained is higher than in the ordinary electric furnace, and that a given quantity of material can be put through in a shorter time. Moreover, the chromium is also free from carbon or carbides. The slag (alumina) produced in the furnace may be reconverted into aluminium and used over and over again, or it may be used for polishing, since it possesses certain advantages, over emery.

Almost all metals may be reduced from their oxides in this way, and the yield is nearly theoretical. The different alloys, e.g., "chrom-manganin," copper-chromium, &c., can also be prepared. The slag from the furnace contains minute rubies, which owe their colour to chromium.

For the preparation of pure metals it is necessary to use pure aluminium, but for heating purposes only, crude (50 per cent) aluminium may be employed. Besides oxides the oxy-salts of certain metals may be reduced in the same way.

The author, looks upon aluminium as a "*heat accumulator*," since it is possible to transport it, and by its union with oxygen develop, wherever necessary, an amount of energy corresponding to that which was originally required for its preparation.-J. S.