quite as vigorous, if not more vigorous, than the corresponding one with ferric oxide.

Experiments were tried, October, 1912, using a standard Goldschmidt Thermit conical welding furnace. Into this was charged 5-10 lbs. of finely divided Co_3O_4 with the theoretical amount of aluminum, according to the equation $3\text{Co}_3\text{O}_4 + 8\text{Al} = 4\text{Al}_2\text{O}_3 + 9\text{Co}$. The reaction was started by lighting a fuse of finely divided aluminum and potassium chlorate, rolled in a piece of tissue paper. The furnace fired with extreme violence, in every case becoming an intense white heat. The vigor of the reaction was so great that the lining of the furnace, although the best alundum-magnesite-cement mixture, would stand up for only two or three charges.

THE METAL—The metal produced in this manner was readily tapped from the bottom of the furnace into iron or sand moulds. It frequently contained less than 0.1 per cent of aluminum, and, of course, was carbon-free.

The various metals, chromium, molybdenum, etc., made by the Goldschmidt Co. by this method, as they have come to us, run about 0.5 per cent in aluminum and are carbon-free.

CONCLUSIONS

This aluminum reduction method can obviously be used with considerable satisfaction where absolutely carbon-free metal is required, and where a somewhat increased cost is not prohibitive. Moreover, it affords a method of preparing cobalt-aluminum alloys at once by adding an excess of metallic aluminum.

The price of crude aluminum, such as might be used for this purpose, is in the neighborhood of 17 cts. per lb. One pound of aluminum will reduce and melt in this way a little over two pounds of metallic cobalt. Therefore, there is a charge of 17 cts. in the form of 1 lb. of metallic aluminum, for the power for reducing and melting two pounds of metallic cobalt. There might, of course, be some return for the fused aluminum oxide which resulted from the process, but even allowing liberally for this, the costs are high as compared with the carbon and carbon monoxide methods of reduction described elsewhere in this paper.

It is obvious that the heating costs must be high by the aluminum method, for heat is being supplied at a temperature greater than 2100°C ., that is, at a temperature far in excess of what is required for the reduction of the oxide and the melting of the metal, and with consequent attendant increased losses, due to conduction and radiation.

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OXIDES OF COBALT¹

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The following oxides of cobalt have been described in various places throughout the literature: Co_2O_3 , CoO , Co_8O_9 , Co_6O_7 , Co_4O_5 , Co_3O_4 , Co_7O_{10} , Co_2O_3 ,

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$\text{Co}_{12}\text{O}_{19}$, Co_3O_5 , CoO_2 , and considerable disagreement is to be found among the statements concerning them.

The existence of many of these compounds is doubtful, and there are but three of them which particularly concern the commercial manufacturer of cobalt oxide: Co_3O_4 , Co_6O_7 , and CoO . These concern us in the production of metallic cobalt. We shall, therefore, describe these three oxides as we have observed them in the course of the experiments reported in our previous article, p. 107 of this issue of *THIS JOURNAL*.

COBALTO-COBALTIC OXIDE, Co_3O_4

The ordinary black commercial cobalt oxide which has been prepared from the hydrate, by calcining in the neighborhood of 750°C ., is a mixture of Co_3O_4 and Co_6O_7 , but largely the former.

There is an abundance of proof throughout the previous paper that this black oxide is largely Co_3O_4 , of which the following may be particularly noted:

(a) The purified cobalt oxide used for hydrogen reduction experiments, making allowance for the impurities according to the analyses, was computed to contain 72.9 per cent cobalt. The hydrogen reduction experiments, using this same oxide, showed, wherever the reduction was complete, a loss of oxygen amounting to 27.0 per cent. As was shown on p. 111, this checks with the 72.9 per cent of cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely Co_3O_4 , as may be seen from the following theoretical percentages:

Per cent cobalt	
Co_2O_3	71.1
Co_3O_4	73.4
Co_6O_7	75.9
CoO	78.8

(b) The purified cobalt oxide used for the carbon monoxide experiments, making allowance for the impurities according to the analysis, was computed to contain 72.9 per cent cobalt. The CO reduction experiments, using this same oxide, wherever reduction was complete, showed a loss of oxygen amounting to 27.0 per cent. As was shown on pp. 110 and 111, this checks with 72.9 per cent cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely Co_3O_4 according to the table under (a).

(c) As a further proof that the black oxide calcined at a good red heat is Co_3O_4 , the following experiment was tried:

A pure black hydrate of cobalt was made from electrolytic cobalt by the potassium-cobalti-nitrite method. This was calcined to constant weight at 105°C ., yielding a chocolate-brown powder, which was uniform under the microscope. Several samples of this brown powder were calcined to constant weight at 640°C ., and in each instance showed a loss of water between 11.5 per cent and 11.8 per cent. Therefore, the brown powder corresponds very closely to $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

The material resulting from these calcinations was a black powder identical in appearance under the microscope with the black cobalt oxide of commerce.

A sample of this previously calcined black oxide was calcined at a red heat to a constant weight of 0.8300 gram. The same sample was then completely reduced with a mixture of hydrogen and carbon monoxide gas at 900° C., which brought it to a constant weight of 0.6063 gram. Thus, the loss in weight was 27.2 per cent. Except for traces, this material was free from non-reducible substances, so that the oxide contained 72.8 per cent cobalt, against 73.4 per cent corresponding theoretically with Co_3O_4 . This was checked several times, which substantiates the statement that black cobalt oxide is Co_3O_4 .

(d) A further experiment was as follows: Black oxide was brought to constant weight at 640° C., and immediately thereafter brought to constant weight by heating to 1020° C. This experiment was tried several times and in every instance the percentage loss in weight was found to be very close to 7.1 per cent. The resulting gray oxide at 1020° C. analyzed 79.3 per cent Co, corresponding very well with CoO (78.8 per cent Co).

The theoretical loss in passing from Co_3O_4 to CoO is 6.6 per cent. As against this, the theoretical loss passing from Co_3O_4 to Co_6O_7 would be 3.3 per cent, and correspondingly, passing from Co_6O_7 to CoO the loss would be 3.3 per cent. Thus, there is very little doubt but that our reduction of the black oxide formed at red heat, to the gray at 1020° C., corresponds with the transition from Co_3O_4 to CoO.

(e) Two independent samples of brown $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$, calcined to constant weight at 640° C., analyzed for cobalt,¹ respectively, 74.7 per cent and 73.8 per cent. This analysis is between $\text{Co}_3\text{O}_4 = 73.4$ per cent Co and $\text{Co}_6\text{O}_7 = 75.9$ per cent Co. This black oxide is therefore largely Co_3O_4 with some Co_6O_7 .

The black hydrated cobalt oxide, as formed commercially by precipitation of a chloride or sulfate solution with bleach,² or the brown $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$, may be calcined at any temperature between 385° C. and 910° C., to yield substantially the same product, but in practice it is better to calcine at a good red temperature, in order that the calcination may take place with reasonable speed.

That there is a range between 385° C. and 910° C., through which very little oxidation or reduction of the black Co_3O_4 takes place, is shown by the following figures:

Starting with Co_3O_4 , heated to constant weight at 385° C. the loss in weight heating it to constant weight is

at 640° C.	0.7 per cent	at 860° C.	2.4 per cent
at 770° C.	1.2 per cent	at 910° C.	2.5 per cent

Just above 910° C., however, the reduction begins to take place very rapidly, and the black Co_3O_4 reacts to become gray CoO. Continuing the experiment for which the figures above are given, we have loss in weight heating it to constant weight

at 980° C. 7.0 per cent

This oxide, Co_3O_4 , shows no trace of being magnetic.

¹ Including very small amounts of Ni and Fe.

² See page 107.

THE OXIDE Co_6O_7

Co_6O_7 is not to be distinguished from Co_3O_4 either in appearance or in method of preparation; in fact, we have not succeeded in forming a pure oxide of cobalt which analyzed very close to 75.9 per cent. On the other hand, as will be noticed in many places throughout this paper, the analyses of the material obtained by calcining at a red heat are frequently something in excess of 73.4 per cent after making allowance for impurities. We, therefore, assume that a certain amount of Co_6O_7 accompanies the Co_3O_4 .

COBALT MONOXIDE, CoO

Cobalt monoxide is the stable oxide of cobalt when calcination takes place at a high temperature, that is, in the neighborhood of 1000° C. It is a gray powder and reacts to form the metal by heating with carbon monoxide gas at any temperature above 450° C., or with hydrogen gas at any temperature above 250° C.

Cobalt monoxide also exists in an allotropic form which is a yellow-green powder. Either the yellow-green or the gray cobalt monoxide oxidizes to Co_3O_4 , or to a mixture of Co_3O_4 and Co_6O_7 , when heated in the air to any temperature between 385° C. and 910° C. The yellow-green variety is readily formed by heating Co_3O_4 with 2 to 3% by weight of C at temperatures in the neighborhood of 900° C.

Numerous analyses of the purified gray oxide have been made, which range around the theoretical value 78.8 per cent. The following experiment was tried to prove that yellow-green oxide is an allotropic form of the gray CoO: Black Co_3O_4 calcined at 640° C. to constant weight was then calcined to constant weight at 1020° C. It lost, thereby, 7.1 per cent in weight, and the product was gray CoO. Yellow-green CoO, produced by the reduction of black Co_3O_4 with hydrogen at 300° C., was calcined to constant weight in air at 640° C., gaining, thereby, 6.5 per cent in weight and becoming black. This experiment, like the others, indicates that the gray and the yellow-green oxides are identical to within such limits that if the yellow-green be CoO, the gray cannot depart from it by more than the formula $\text{Co}_{19}\text{O}_{20}$. Such differences as there are, however, seem to show uniformly that the gray has slightly the greater oxygen content of the two.

A further experiment was performed with the yellow-green oxide as follows: Freshly prepared yellow-green oxide was reduced to metal with hydrogen and carbon monoxide gas, and brought to constant weight. During the reduction, the loss in weight was 21.5 per cent in one case and 21.3 per cent in another, corresponding very well with the reduction of CoO to metallic cobalt which would be 21.3 per cent.

Both the gray and the green CoO are nonmagnetic, and the samples of gray prepared by us, as well as those obtained from commercial sources, are homogeneous powders under 100 diameters magnification.