

divested of many complicating assumptions, and greatly simplified.

I should acknowledge my obligations to Mr. James Graham for assistance in the experimental work of this paper.

CASE SCHOOL OF APPLIED SCIENCE
CLEVELAND, OHIO

THE PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE¹

By HERBERT T. KALMUS

In connection with the work on cobalt it has been necessary to prepare considerable quantities of the metal in as pure a state as possible. Nearly 1000 pounds of commercial black cobalt oxide have been given to this laboratory for these researches by the Deloro Mining and Reduction Co. of Deloro, Ontario, to whom we take this opportunity of expressing our thanks.

The writer wishes to acknowledge the work of Messrs. C. Harper, W. L. Savell, C. W. Day and R. Wilcox, who, in the capacity of research assistants at these laboratories, have done most of the actual experimenting. To Professor S. F. Kirkpatrick of the Department of Metallurgy, Queen's University, thanks are due for many valuable suggestions.

The process for the preparation of fairly pure cobalt oxide has been very completely worked out, and has been practised on a large scale at several Canadian smelters. For this reason the oxide was chosen as a raw material from which to prepare the metal. As the work progressed, it became more and more apparent that some of the uses for cobalt which were being demonstrated at these laboratories and elsewhere, would lead to the preparation of the metal in large quantities. Hence, it became of increasing importance that the metallurgy of the preparation of the metal from the oxide be studied, and this has been done with greater care than was necessary merely for the production of the quantities required for experimental purposes. There are four important reducing agents for obtaining metallic cobalt in reasonably pure form from commercial cobalt oxide. They are: I, Carbon; II, Hydrogen; III, Carbon Monoxide; IV, Aluminum.

The Co_3O_4 used² for these experiments was made from cobalt hydrate, precipitated by bleach from a cobalt chloride solution. This hydrate, in contact with the atmosphere, is greenish black in color. It was calcined at 750°C ., yielding a black oxide of approximately the composition Co_3O_4 . This is shown by the following analyses, made at widely different times, which are typical of a large number:

ANALYSES OF PURIFIED COBALT OXIDE (PERCENTAGES)

	June, 1912	November, 1912	April, 1913
Co.....	71.99	71.52	72.3
Fe.....	0.11	0.27	0.10
Ni.....	0.040	0.020	Trace
S.....	0.020	Trace	0.052
Ca.....	0.030	...	0.15
SiO ₂	0.19	0.18	0.39

The oxides corresponding with the theoretical formulas would have cobalt content as follows:

Formula	Percentage, cobalt
Co_2O_3	71.1
Co_3O_4	73.4
Co_5O_7	76.0
CoO	78.8

It is obvious then, when we take into account the portion of the sample which is not cobalt oxide, that the oxide itself is largely Co_3O_4 . It is not necessary for the purpose of our calculations to assume that this oxide alone is present, for we shall base our computations upon the actual analyses as we have found them. However, in writing the reactions throughout this paper, we shall, for simplicity, consider the oxide to be Co_3O_4 .

PURIFICATION OF COBALT OXIDE

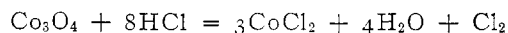
Cobalt oxide as we obtained it from the smelters, and as sold on the market, analyzed approximately as follows:

Barrel 1	Percentages	Barrels 3 and 4	Percentages
Co.....	70.36	Co.....	69.2
Ni.....	1.12	Ni.....	1.4
Fe.....	0.82	Fe.....	0.50
S.....	0.45	CaO.....	0.37
As.....	0.10	S.....	0.54
SiO.....	0.20	Insoluble.....	1.46
Ca.....	0.50	Ag.....	Trace

Analyses, of course, vary considerably from one shipment to another; the above samples are high in Fe, S and Ca, and would be considered by most smelters as No. 2 grade.

Metal produced from oxide analyzing as above, by the method to be described, is of sufficient purity for most purposes. This is especially true if lime be added to the melt to slag off the sulfur. However, for other purposes metal is required in which the impurities, nickel, iron, sulfur, arsenic and silica, are reduced to very small percentages. In this case it is best to remove these impurities from the oxide before reduction. Starting with a crude cobalt oxide, these impurities may be reduced as far as is desired by the following procedure:

SILICA—Dissolve the crude oxide in hydrochloric acid according to the reaction:



This may be done best by heating and agitating with steam. If silica is present, it will not dissolve, and may be removed by filtration or decantation. The same is true of silicates which are not decomposed by this treatment. Decomposable silicates would send a certain amount of silica into solution, which would be thrown out during the next step.

IRON AND ARSENIC—To the cobalt chloride solution formed by dissolving the oxide in hydrochloric acid,

¹ Author's abstract of report under the above title to the Canadian Department of Mines. Published by permission of the Director of Mines, Ottawa, Canada. The general investigation of the metal cobalt and its alloys, with reference to finding increased commercial usages for them is being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canada Department of Mines.

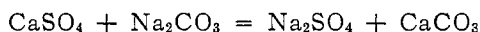
² For a consideration of the various oxides of cobalt, including the proof that the black oxide used for these reductions was largely Co_3O_4 , see the following article, page 115.

gradually add finely divided CaCO_3 or pure marble, until no further precipitate is formed. The heavy brown mud precipitated contains the iron and arsenic content of the original oxide.

NICKEL—For most purposes it will not be necessary to separate the small amount of nickel from the cobalt, but it may be done as follows: The cobalt chloride solution, containing a certain amount of nickel chloride, is of an intense red or claret color. Add a solution of bleach to the solution until it has almost completely lost its color. The bleach solution differentially precipitates hydrates of nickel and cobalt, so that the nickel is not appreciably brought down until the cobalt has been almost entirely precipitated.

The bleach will precipitate a black, hydrated oxide of cobalt, and the diminishing redness of the solution will indicate the end point. If all of the steps above outlined have been applied to the original oxide, this final black precipitate may be calcined at about 750°C ., to yield black Co_3O_4 .

SULFUR—Any sulfur present in the original oxide and carried through to the final product, or introduced with the bleach, may be removed by boiling the final dried oxide with sodium carbonate and dilute hydrochloric acid. The reaction is:



The soluble sodium sulfate formed is washed out with water. A further washing is given with dilute hydrochloric acid, which decomposes the calcium carbonate into soluble calcium chloride and CO_2 gas. The CaCl_2 is washed out with water. This method is, of course, applicable only for the removal of the small percentages of Ca and S found in the oxides in question.

A shipment of oxide from the smelter was analyzed before and after treatment by the above method, with the following results:

Percentages	Before	After
Co.....	70.36	71.99
Ni.....	1.12	0.041
Fe.....	0.82	0.11
S.....	0.45	0.020
Ca.....	0.50	0.021
As.....	0.10	None
SiO ₂	0.20	None

There are other obvious methods of purifying the Co_3O_4 . For example, the bleach solution may be freed of its SO_4 content with BaCl_2 , and the Ca and excess Ba precipitated with Na_2CO_3 , thus yielding a fairly pure solution of soda bleach. The SO_4 content of the CoCl_2 solution may be precipitated with BaCl_2 and the differential precipitation of cobalt and nickel accomplished with the purified solution of soda bleach.

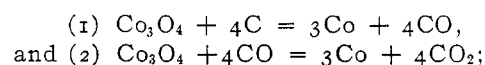
I—REDUCTION OF COBALT OXIDE WITH CARBON

METHOD OF EXPERIMENT—These experiments all consisted in intimately mixing definite amounts of finely divided carbon in various forms with Co_3O_4 , and heating the mixture to constant temperature for a measured time. The charges employed varied in size from a few grams to 10 lbs., and were heated in lined and unlined graphite crucibles, and in porcelain crucibles.

FURNACES—The reduction took place either in an

oil-fired "Steele-Harvey" furnace of 60 pounds, metal capacity, No. 20 crucible, which could be controlled at any temperature up to 1550°C ., or in a modified Hoskins electric resistor furnace. This latter has a heating chamber, 8 inches cube, which can be maintained constant to within about 10 – 20°C ., at any temperature up to 1650°C . Some of the small charges were run in porcelain crucibles heated within an electric resistor furnace.

The reactions for the reduction of cobalt oxide with carbon are:



or, combining (3) $2\text{Co}_3\text{O}_4 + 4\text{C} = 6\text{Co} + 4\text{CO}_2$.

If all the oxygen for the oxidation of the carbon be supplied by the cobalt oxide, and if all the carbon be burned to CO_2 then the reaction goes according to the last equation.

In practice, neither of these conditions is strictly obtained, but with proper design of furnace they may be closely approximated.

THE RUN—In each case the charge was made up by intimately mixing a weighed amount of finely divided oxide with a weighed amount of finely ground carbon. This mixture was placed in the crucible, which, with its charge, was placed either in the Steele-Harvey oil furnace or in the electric furnace. The mixture was frequently stirred with an iron rod during the reduction.

THE CARBON—The form of carbon chosen for the reduction, whether powdered charcoal, coke, coal, etc., depends somewhat upon the impurities from which it is desirable to keep the resulting metal free, but also this choice greatly influences the speed of the reduction.

Three sets of experiments were made with powdered anthracite coal, while further runs were made with lampblack or with powdered charcoal. The carbon was in all cases powdered to an extremely fine flour.

TEMPERATURE MEASUREMENTS—Temperature readings were made at frequent intervals with a platinum platinum-rhodium thermo-element, with a Wanner optical pyrometer, or with a Féry radiation pyrometer, and the furnace adjusted to keep the temperature constant to within about 20° .

The charge was put into the crucible which was within the furnace, both crucible and furnace being at a temperature somewhat higher than the intended temperature of the run. Some of the smallest charges were inserted with containing crucible. It was learned, by experience, for the different sizes of charge and qualities of crucible, at about what temperature to maintain the furnace prior to inserting the charge, in order that the charge might come to the desired equilibrium temperature, with proper furnace adjustment, in about ten minutes. There is, therefore, a period of about ten minutes, at the beginning of each run, during which the average temperature of the charge is not as high as that noted with the Wanner optical pyrometer, which observes the surface of the charge. We satisfied ourselves that the center of the charge was at the same temperature as the surface, within 20 or 30°C ., after the first ten minutes, by exploring the center with a thermo-element, and noting simul-

taneously its readings and those of another thermo-element near the surface, and of the Wanner optical pyrometer.

In the following runs we have not attempted to make a correction for the lag in coming to temperature during these first ten minutes. This lag would be considerably less than ten minutes for the smallest crucibles used, about ten minutes for the four-pound charges, and possibly as long as twenty minutes in the worst cases, with the ten-pound charges.

The oxides used for the runs reported in Tables I and II analyzed as follows:

Runs	Percentages	
	A-H	RI-RVIII
Co.....	71.36	69.2
Ni.....	1.12	1.4
Fe.....	0.82	0.50
S.....	0.45	0.54
Ca.....	0.50	CaO..... 0.37
As.....	0.10	Insoluble.... 1.46
SiO ₂	0.20	Ag..... Trace

The anthracite coal used was very finely powdered. In the typical runs A-H, No. 12 unlined carbon crucibles were used, and the charge was stirred every ten minutes during reduction. In these runs no

TABLE I—REDUCTION OF Co_3O_4 WITH POWDERED ANTHRACITE COAL (A)
RUNS A, C, H—HARVEY-STEEL OIL FURNACE
G, B, D, E, F—ELECTRIC CRUCIBLE FURNACE
Yield of cobalt

No. of run	Charge		Average temperature ° C.	Time of reduction Min.	Yield of cobalt		
	Co ₃ O ₄ Lbs.	Coal Oz.			Lb. Oz.	Per cent of theoretical	Per cent carbon in metal
A.....	5	8.3	1200	90	3 1.5	87	...
C.....	4	6.9	1200	30	2 12.5	98	0.18
H.....	10	16.0	1200	105	6 9	92	0.086
G.....	4	6.6	900	150	2 13	99	0.21
B.....	4	6.54	1200	60	2 13	99	0.29
D.....	4	6.9	1200	120	2 13.5	100	0.20
E.....	4	6.9	1500	60	2 11.75	96	0.22
F.....	4	6.6	1500	90	2 12.7	98	0.23

A—Considerable unreduced oxide slag. Carbon used is approximately the theoretical amount according to reaction (3).

C—Melt free from unreducible oxide slag. Carbon 10 per cent in excess of theoretical requirement.

H—3 oz. lime added shortly before pouring. Carbon, theoretical amount.

G—At end of 2.5 hours, charge not completely reduced, but completed during subsequent raising to melting point.

TABLE II—REDUCTION OF Co_3O_4 WITH POWDERED ANTHRACITE COAL (B)
HARVEY-STEEL OIL FURNACE

No. of run	Charge		Average temp. ° C.	Reduction time to removal of sample Minutes	Per cent Co in sample (a)	Reduction complete = 100
	Co ₃ O ₄ Lbs.	Coal Oz.				
I....	10	17.5	601	R2 82	73.6	Very slight
II....	10	16.5	750	R3b 91	74.1	Very slight
III....	10	16.5	888	R4b 90	73.8	Very slight
IV....	10	16.5	1057	R5b 95	80.8	28
VI....	10	16.5	1203	R6a 30	81.3	30
				R6b 49	93.0	74
VII....	10	16.5	1283	R7a 31	91.1	70
				R7b 47	93.9	77
VIII....	10	17.4	1502	1 11	76.7	12
				2 16	81.8	32
				3 21	91.0	66
				4 26	93.9	77
				5 31	93.9	Apparently some oxidation
				6 36	91.8	

(a) These analyses are for cobalt, nickel and iron combined, of which about 97 per cent was cobalt, as may be seen from the analysis of the original oxide. Carbon analyses were of course made, and the percentage of cobalt given in this column takes into account the residual carbon.

attempt was made to show the progress of the reduction, but at the close of the run the charge was raised as rapidly as possible to the melting point and the melt poured into an iron mould to be weighed. Considerable reduction must take place during the interval of melting the charge after the close of the run. The purpose of these particular runs was to study the yields under somewhat the same conditions which must necessarily obtain in practice. In the runs I-VIII, No. 20 unlined carbon crucibles were used; no attempt was made to obtain a yield. They are intended to show the progress of the reduction.

It will be noticed in the above runs with powdered anthracite coal that the reductions are extremely low. It was, therefore, thought advisable to check these runs with experiments on a very small scale in porcelain crucibles, in such a manner that there could be no doubt as to the time during which the charge was maintained at the temperature in question.

A number of such runs was made with a thermo-element near the center and at the outside of the charge. In the small furnace used, the crucible with its charge came to temperature in a very few minutes, so that the outside and inside thermo-element agreed to within 20° C. Approximately this condition was maintained throughout the run.

The results of the previous runs with powdered anthracite coal were confirmed by these small scale runs, and a satisfactory complete reduction could not be obtained at temperatures much below 1200° C.

REDUCTION OF Co_3O_4 WITH POWDERED CHARCOAL

Further experiments were tried on the reduction of Co_3O_4 with very finely powdered charcoal. A large number of these gave fairly concordant results, which showed a greater reduction at all temperatures than the corresponding powdered anthracite coal runs.

Without giving the details of about twenty-five runs, it may be said that complete reduction was obtained with from 20 to 30 per cent excess of powdered charcoal, at 900° C. or over, in less than an hour. At 1000–1100° C., the reduction with powdered charcoal was very much more rapid than at 900° C., often completing itself in less than 10 minutes. Of course, the time required depends, to some extent, upon the size of the furnace and charge.

REDUCTION OF Co_3O_4 WITH LAMPBLACK

Experiments on the reduction of Co_3O_4 with lamp-black were tried with results identical with those on the reduction of Co_3O_4 with powdered charcoal.

BRIQUETS—Experiments on the reduction of Co_3O_4 with powdered charcoal were tried, forming the charge into briquets. A small¹ percentage of molasses was used as a binder. These experiments were made under the same furnace and temperature conditions as those on the reduction of Co_3O_4 with powdered charcoal in bulk. Seven such runs showed, throughout, that the reduction was not very different in its velocity from the corresponding runs with powdered charcoal, although the difference was uniformly in favor of the briquetted charges. A satisfactory reduction

¹ The molasses would correspond to the addition of about 1 per cent carbon.

could probably not be made at temperatures below 800–850° C., even briquetting the charges, as compared with 900° C. for the charges in bulk.

The preparation of metallic cobalt by reduction in briquets or rondelles offers distinct commercial advantages in that the resulting metal is in a salable form without further melting and casting.

THE METAL—The metal produced by reduction of cobalt oxide with carbon is sufficiently pure for most purposes; it need not contain more than a few tenths of a per cent of carbon. The following characteristic analyses are taken at random from a large number to show the nature of the metal:

ANALYSES OF METALLIC COBALT PRODUCED BY REDUCTION OF COMMERCIAL COBALT OXIDE WITH CARBON (PERCENTAGES)

	7—12	8-15-12	10-10-12	10-11-12	6-11-13
Co.....	97.05	98.50	98.84	98.62	98.30
Ni.....	1.50	0.65	0.61	0.50	Trace
Fe.....	1.00	0.58	0.56	0.15	1.39
S.....	0.22	0.47	0.21	0.22	0.46
C.....	0.20	0.22	0.24	0.13	...
Ca.....	0.25	0.60	0.24	0.27	0.58
Mn.....	0.06
As.....	0.11
SiO ₂	0.12	0.13	0.14	0.11	0.12

It is obvious that the oxides taken for reduction with carbon were those directly from the smelter, which had not been treated by the method outlined above to remove the impurities. The iron, nickel, sulfur and silica content could have been reduced to mere traces by purifying the oxide before reduction in accordance with the method given. We have done this repeatedly, where a pure metal was required for experimental purposes. It is, however, of importance to note that metal with very low carbon content may be made by direct reduction of the oxide with carbon.

CONCLUSIONS

I. Reduction of Co₃O₄ with powdered anthracite coal does not take place rapidly enough to make it commercially interesting, either in the oil-fired crucible type of furnace or in the electric crucible type of furnace, until a temperature in the neighborhood of 1200° C. is reached.

II. In either the oil-fired crucible type of furnace or in the electric crucible type of furnace, substantially complete yields of metallic cobalt may be obtained by reduction of Co₃O₄ with powdered anthracite coal, in the neighborhood of 1200° C., for not more than 1 hour, with subsequent rapid melting and pouring.

III. With the oil-fired crucible furnace, using unlined graphite crucibles, complete yields are obtained with powdered anthracite coal only when there is an excess of approximately 10 per cent of this latter.

IV. With the electric crucible type of furnace used by us, complete reduction may be obtained, using only the theoretical quantity of powdered anthracite coal. In this furnace there is a considerable reduction due to the carbon monoxide atmosphere caused by the carbon resistor plates.

V. Both in the oil-fired and in the electric crucible type of furnace, greater reductions of Co₃O₄ are obtained using powdered charcoal than with powdered anthracite coal, at corresponding temperatures.

VI. With the oil-fired or electric crucible type of furnace, complete reduction may be obtained with powdered charcoal at 900° C. or higher. For this reduction a considerable excess of charcoal was required: under our conditions from 20 to 30 per cent.

VII. Powdered lampblack shows results in accordance with those for powdered charcoal.

VIII. Briquetting the charges with an organic binder tends to increase the rate of reduction at all temperatures. A minimum of about 800° C. may be employed for the reduction of Co₃O₄ with charcoal in the form of briquets as against 900° C. for the same charge in bulk.

IX. With sufficient carbon to get a complete yield of metal, the final product need contain only about 0.2 per cent of carbon.

X. At this laboratory, in an electric furnace not especially designed for this work, we reduce enough oxide to make 56 pounds of the metal in an eight-hour day, with the furnace absorbing 12 kw. Thus, on a commercial basis, the power charge for this reduction would be small.

II—PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH HYDROGEN

METHOD AND APPARATUS.—These experiments consisted in placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of hydrogen gas was passed through the furnace. A schematic sketch of the apparatus is shown in Fig. 1.

After purification, the hydrogen entered the furnace

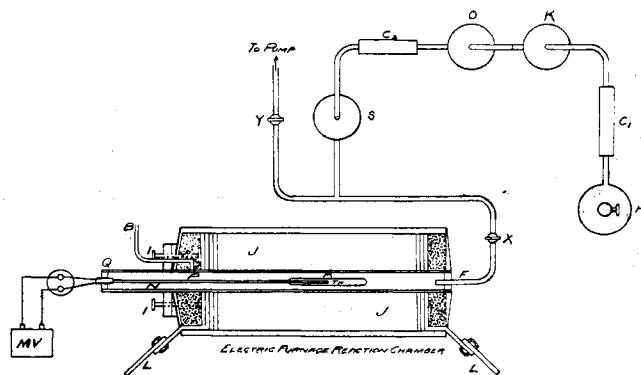


FIG 1—ARRANGEMENT OF APPARATUS FOR REDUCTION OF Co₃O₄ BY HYDROGEN

H = Hydrogen Tank O = KOH Tower Y = Stop Cock
C₁ and C₂ = Hot Copper S = H₂SO₄ Washer L = Leads to Ammeter and Bus Bars
K = K₂Cr₂O₇ Tower J = Carbon Rings

at F and the excess was burned at B. During the run the exit for the gas was through the by-pass PB, the end Q being sealed.

The heating element of the furnace itself was a series of co-axial carbon ring plates, which could be pressed together more or less tightly by suitable screws. The furnace was supplied with alternating current at 25 volts from a transformer, and could be controlled at any temperature up to 1350° C.

The details of the furnace are shown in Fig. 2.

The temperature measurements were made by a

platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivoltmeter. In this way, the temperature was maintained substantially constant by hand regulation of the screws I. All temperature measurements were made with thermo-elements calibrated at frequent intervals, in the usual way, against known melting points.

CONDUCTING A RUN—After having heated the furnace to the desired temperature, by a suitable current through the carbon rings, runs were made as follows:

(a) After closing the cock X, which separates the purifying system from the furnace, the air was exhausted from the hydrogen system by opening cock Y, and operating a pump.

(b) Gas burners were lighted to heat copper filings in tubes C₁ and C₂.

(c) Solutions of potassium bichromate, potassium hydrate and sulfuric acid were started flowing through the purifying towers K, O and S, which were partially filled with glass beads.

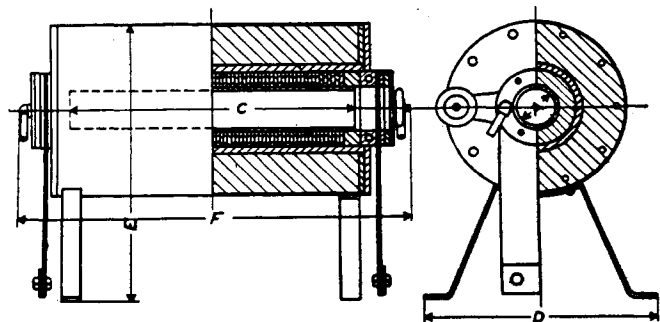


FIG. 2—DETAILS OF ELECTRIC FURNACE FOR REDUCTION OF Co_3O_4 WITH HYDROGEN

(d) Cock Y was closed and cock at outlet of hydrogen tank H was partially opened to allow a flow of hydrogen into the purifying system, until the pressure inside the system was a little greater than atmospheric pressure.

(e) Cock X was now opened to allow hydrogen to flow into the hot furnace.

(f) Flow of hydrogen was adjusted by cock at outlet of hydrogen tank H, until hydrogen burned freely at outlet end of furnace B. During the run the end Q was closed, and the gas escaped through the by-pass P-B.

(g) When adjustment (f) was satisfactory, assuring an excess of hydrogen within the furnace, the weighed dried alundum boat, containing the charge of cobalt oxide, was placed in the hot furnace at the position A, and the time noted.

(h) The run proper had now begun, during which observations of time, temperature, and power were made, and the furnace adjusted to keep the temperature constant.

(i) After a definite time, the boat, with its contents, was withdrawn from the centre of the furnace to the overhanging cool end of the furnace core N, in which it was allowed to cool, but through which, during the cooling, hydrogen was passed.

(j) When cool, the boat was removed to a desiccator and weighed.

II—COBALT OXIDE REDUCTION WITH HYDROGEN—COOLING IN AN ATMOSPHERE OF HYDROGEN

The cobalt oxide used for the following runs, I to IX, analyzed as follows in percentages:

Co.....	72.3	Ca.....	0.15
Ni.....	Trace	S.....	0.052
Fe.....	0.10	SiO ₂	0.39

It will be noticed that this oxide contained 72.4

TABLE III—REDUCTION OF COBALT OXIDE WITH HYDROGEN
Temperature ° C.

Number		Temperature ° C.		Time of reduction Minutes	Loss in weight Per cent	Reduction 100 = complete	
Run	Boat	Mean	Average deviation				
I	I	585	1.3	5	25.5	94.2	
				15	25.4	94.0	
II(b)	II(a)	584	1.0	5	25.8	95.6	
	I			15	26.0	96.2	
				30	26.6	98.3	
				60	26.2	97.0	
				II	15	26.1	96.8
	30			26.2	97.0		
	60			26.1	96.8		
	III			609	4.2	7	16.8
15		22.1	81.8				
30		22.4	83.0				
60		25.2	93.0				
IV	I	597	2.0	7	25.3	94.0	
				15	25.4	94.2	
				30	
				II	7	25.4	94.2
	15	25.2	94.1				
	70				
	V	IV(c)	598	1.7	15	25.5	94.3
					60	25.5	94.3
I(d)		60			25.8	95.7	
		120			25.7	95.3	
VI	I	727	1.5	5	26.5	98.1	
				10	26.5	98.1	
				30	26.6	98.5	
				60	26.6	98.5	
	II	5	26.6	98.5			
		10	26.5	98.1			
		30	26.6	98.5			
		VII(e)	I	824	4.3	2.5	26.6
5	26.6					98.5	
15	26.7					98.9	
30	26.75					98.8	
60	26.75		98.8				
150	26.8		99.0				
II	2.5		26.61	98.4			
	5		26.71	98.7			
	15	26.75	98.8				
	30	26.75	98.8				
VIII	I	965	1.0	60	26.80	99.0	
				1	25.6	94.8	
				5	26.9	99.7	
				30	27.1	100.0	
	60	27.1	100.0				
	II	1	26.8	99.1			
		5	26.9	99.4			
		30	26.9	99.4			
60		27.0	99.7				
IX	I	1073	2.1	2	26.28	96.8	
				5	26.90	99.4	
				30	27.00	99.7	
				60	27.05	99.9	
	II	1	24.38	90.0			
		5	26.90	99.7			
		30	27.00	99.8			
		60	27.10	100.0			

(a) It was noted at the close of this run that there was a slight oxidation at one point in the boat.

(b) All the reduced samples were steel-gray.

(c) Boat showed slight reoxidation at one end when removed from furnace.

(d) This final material analyzed 97.25 and 97.30 per cent cobalt on duplicates. The material resulting from this run contained 0.75 per cent of unreducible CaSO_4 , CaO and SiO_2 , and 1.4 per cent of oxygen presumably in the form of Co_3O_4 (the stable oxide at 598°C ., see following article, page 115), and 0.10 per cent of nickel and iron. It should, therefore, contain $100 - 2.3 = 97.7$ per cent of cobalt. This checks with the value determined by analyses, 97.3, to within the accumulative error in the analyses.

(e) The product from this run seemed to be of a slightly lighter gray shade than that from the runs at lower temperatures.

per cent of the metals cobalt, nickel and iron, in the form of oxides which may be computed without error to be cobalt oxide. Any sample contains, therefore, 0.75 per cent of unreducible calcium sulfate, calcium oxide and silica, 99.2 per cent of cobalt oxide running $72.4/99.2 = 72.9$ per cent in cobalt. This oxide, therefore, corresponds very closely to Co_3O_4 . The oxygen content of the substance which could be reduced by hydrogen, is equal to 27.1 per cent of 99.2 per cent = 27.0 per cent. This figure is accurate to within the experimental error of the runs, and is used as the basis of the following computations; that is to say, in the column headed "Percentage loss in weight," 27 per cent would represent complete reduction, and the last column headed "Reduction where 100 per cent is complete reduction" is computed in terms of 27 per cent actual reduction as total. The boats used ranged in weight from 5 to 6.5 grams and the charges of cobalt oxide from 2.0 to 2.1 grams.

The check between the composition of the oxide used for these hydrogen reduction experiments, as determined by analysis and as determined by the reduction experiments, is entirely satisfactory (see following article, p. 115).

A number of the early experiments to reduce Co_3O_4 with hydrogen were made allowing the reduced product to cool in the atmosphere. In every case reoxidation took place. These runs were made at various temperatures from 500°C . to 1000°C ., and curiously enough the reoxidation at the higher temperatures was progressively less than at the lower temperatures.

CONCLUSIONS

I. The reduction of Co_3O_4 to metallic cobalt by hydrogen gas takes place very rapidly at all temperatures above 500°C .

II. At temperatures between 500°C . and 700°C ., over 90 per cent of the reduction of Co_3O_4 to Co takes place in a few minutes, but a further reduction takes place very slowly, if at all.

III. Between 700°C . and 1100°C ., the amount of reduction of Co_3O_4 to Co which takes place during the first few minutes increases very rapidly with rising temperature, and at the higher temperatures it is complete.

IV. The hydrogen reduction method is to be especially recommended for the production of moderate quantities of very pure carbon-free cobalt for special purposes, just as it has been used for the production of metallic tungsten.

V. For the production of cobalt from Co_3O_4 by hydrogen, the charge must be completely cooled in an atmosphere of hydrogen.

III—PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH CARBON MONOXIDE

METHOD AND APPARATUS—These experiments were performed by placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of carbon monoxide was passed through the furnace (see Figs. 3 and 4).

CARBON MONOXIDE GENERATOR—The carbon mon-

oxide was supplied by passing carbon dioxide over hot wood charcoal, which reduced it according to the reaction, $\text{CO}_2 + \text{C} = 2\text{CO}$.

Carbon dioxide, after purification, entered the lower end of the carbon monoxide generating furnace at G.

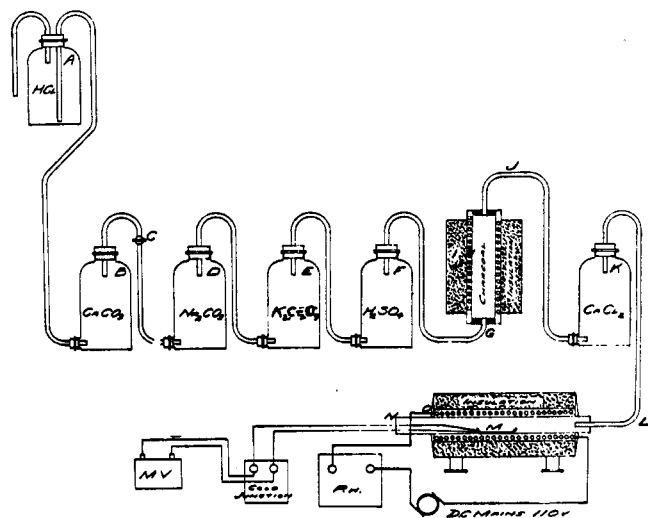


FIG. 3—APPARATUS FOR REDUCTION OF Co_3O_4 WITH CARBON MONOXIDE

This furnace was of the electric resistance type, made by winding nichrome wire over an alundum cylinder, the two being embedded in magnesite cement, and insulated within a cylindrical iron container. The wire is shown in section at H and the iron container at I. The entire core of the furnace was filled with wood charcoal, maintained at about 1000°C . by an appropriate current through the heating element. As a result, carbon monoxide gas left the generator at J, with a certain amount of moisture which was absorbed by passing through calcium chloride at K. Thus, substantially pure carbon monoxide entered the reaction furnace proper at L, passed over the alundum boat M, with its cobalt content, and the excess burned off at N.

THE REACTION FURNACE—The reaction furnace proper is shown in Fig. 3. It consisted of a central silica tube LN, 2 ft. in length, and 1 in. in internal

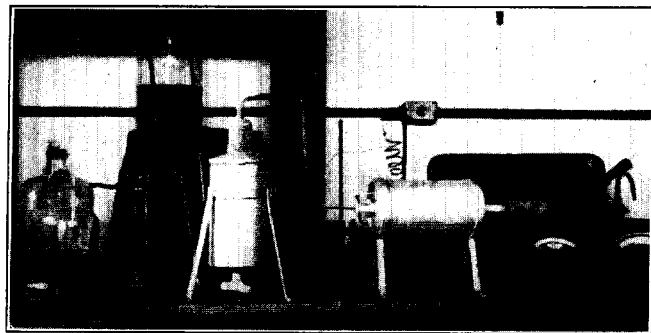


FIG. 4

diameter. This was wound with calorite or nichrome wire, of such resistance that it could be controlled by a suitable rheostat Rh on 110 volt direct current mains, to maintain a temperature constant to within less than 10° during a run, at any temperature up to 1000°C .

TEMPERATURE MEASUREMENTS—The temperature measurements were made by a platinum-platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivoltmeter Mv. The thermo-elements used for the temperature measurements were calibrated at frequent intervals.

COOLING CHARGE IN CARBON MONOXIDE ATMOSPHERE—The silica tube NL extended beyond the end of the furnace proper from O to N. The portion O-N was 1 ft. in length and was kept cool by a circulation of water, so that at the close of a run the boat was removed from the centre of the furnace to O-N, where it cooled to room temperature in the stream of CO gas.

CONDUCTING A RUN—After having heated the reaction furnace, and the CO producer furnace, by suitable currents, to the desired temperature, runs were made as follows:

(a) The cock C was opened to allow CO₂ gas to pass through the purifying system DEF into the producer furnace at G.

(b) The CO gas generated in the producer furnace GJ passed through the reaction furnace LN and was lighted at N.

(c) The weighed dried boat with its charge was introduced into the exterior ON of the reaction furnace.

(d) Temperature and time observations were begun, and when the desired temperature had been reached, the boat was moved to M.

(e) The run proper had now begun, during which observations of time and temperature were made and the rheostat Rh adjusted to keep the temperature constant.

(f) After a definite time the boat, with its contents, was withdrawn from M to ON, where it was allowed to cool in a current of carbon monoxide gas.

(g) When the boat was cool, the current of carbon monoxide was gradually diminished by closing the cock C, until it was finally entirely cut off.

(h) When the boat was cooled to room temperature, it was removed to a desiccator and weighed.

COBALT OXIDE FOR CARBON MONOXIDE REDUCTION EXPERIMENTS

The cobalt oxide for the CO reduction experiments was identical with that used for the hydrogen reduction experiments so that the column headed "Reduction where 100 per cent is complete reduction" is computed in terms of 27.0 per cent actual reduction as total.

A number of the first runs were made, reducing Co₃O₄ with CO and allowing the reduced product to cool in the atmosphere before weighing. Under these conditions, reoxidation took place rapidly, so that but a single pair of typical runs are given. The boats used weighed 10.5+ and 13.3 grams and the charges of cobalt oxide, 2—grams.

The reoxidation of cobalt oxide after reduction

with carbon monoxide takes place with great vigor. If the boat be withdrawn from the hot furnace directly into the atmosphere, it may be seen to glow with great brilliancy. If the content of the boat, while still warm, be snapped out on the floor, it will reoxidize with such vigor that a cracking sound, as of a mild explosion, attends the reaction, *i. e.*, the reoxidation taking place according to the reaction $6\text{CoO} + \text{O}_2 = 2\text{Co}_3\text{O}_4$ is extremely exothermic.

In the runs of Table IV, during the first part of the run, and up to the time that it began to gain in weight,

TABLE IV—REDUCTION OF Co₃O₄ WITH CO—COOLING IN AIR

Number		Temperature		Time of reduction Minutes	Per cent loss in weight	Reduction 100 = complete
		Mean	Average deviation			
I	I	602°	9	15	10.6	39.3
				30	11.1	41.1
				45	10.8	39.9
				60	12.9	47.8
				75	12.9	47.8
				82	11.8	43.6
				92	11.3	41.8
				107	7.8	39.6
				30	12.4	46.0
				45	11.7	43.3
II	II	594	12	75	13.2	48.8
				97	12.3	45.5
				112	11.9	44.0
				142	10.3	38.2

the Co₃O₄ in both boats gradually became a gray color. This gray material is CoO. At the end of the run it was black again.

On account of the irregularities of reoxidation, the furnace reaction chamber was lengthened by substituting a silica tube of length LN for the one of length LO as shown in Fig. 3. The overhanging tube ON, about 1 ft. in length, was cooled by water, and served as a cooling chamber for the boat while CO gas was still passed through it.

The following runs, representative of a large number, show the rate of the reduction of cobalt oxide by CO gas when the cooling was controlled so that no reoxidation could take place. The boats used weighed about 8 grams and the charges of oxide about 2 grams.

In Run III, Table V, the oxide became a greenish gray color at the end of the first five minutes, and a uniform steel-gray color at the end of fifteen minutes. From then on it began to gain in weight, due to a deposit of carbon. At the close of many runs at this temperature, there was an extremely heavy deposit of carbon in the boat.

This run was typical of a number, which showed a reduction from the original black oxide to the green, followed by a change from the green to the gray, and then a gain in weight, due to a deposit of carbon. The only possible source of carbon was from the carbon monoxide gas, so that the finely divided metallic cobalt, which was formed during the first stage of the reduction of the gray oxide, probably acted catalytically to decompose carbon monoxide gas at this temperature. This is an extremely interesting decomposition which might well be studied with considerable care.

TABLE V—REDUCTION OF COBALT OXIDE BY CARBON MONOXIDE GAS—COOLING IN CO GAS

Number		Temperature °C.		Time of reduction Minutes	Loss in weight Per cent	Reduction 100 = complete
		Mean	Average deviation			
III		347	3	5	18.2	67.3
				15	25.2	93.2
				45	Deposit of carbon
				60	
IV	I	451	3	5	22.1	81.8
V	I	453	3—	15	13.4	49.5
				5	21.4	79.2
				15	13.2	48.4
				45	Gain
VI	I	583	5	60	Gain
				5	16.2	60.0
				15	26.4	97.8
				35	26.8	98.0
				50	26.9	99.6
VII	II	596	3	65	27.0	100.0
				20	26.5	98.1
				30	26.6	98.4
VIII	I	600	5	10	21.0	77.9
IX	II	597	6	5	21.2	78.3
				15	24.7	91.0
X		611	6	49	26.3	97.7
				69	26.7	98.8
				86	27.2	100.0
				146	27.1	100.0
XI	I	594	6	5	25.7	95.0
				15	26.3	97.2
				45	26.7	99.0
				60	26.7	99.0
XII	II	601	1	5	25.6	94.9
				15	26.5	98.0
				45	26.5	98.0
				60	26.6	98.4
XIII		754	3	5	26.7	99.0
				15	26.8	99.3
				45	26.9	99.8
				60	26.9	99.8
XIV		752	4	5	26.8	99.6
				15	26.8	99.6
				45	26.9	99.8
				60	26.9	99.8
XV		749	3	5	24.9	92.3
				15	26.7	99.1
				45	26.8	99.6
				60	26.8	99.6
				150	26.8	99.6
XVI		751	3	5	26.0	96.2
				15	26.6	98.8
				45	26.7	99.1
				60	26.7	99.1
XVII		900	4	5	26.5	98.3
				15	26.9	99.8
				45	27.0	100.0
				60	27.0	100.0
XVIII		900	4	5	26.6	98.8
				15	26.8	99.7
				45	26.9	99.8
				60	26.9	99.8

A strong odor of hydrocyanic acid was noticed throughout run IV. After five minutes or so, a deposit of carbon began to form in the boat, due to the decomposition of carbon monoxide by finely divided cobalt, as in the runs at 350° C.

Throughout run V a strong odor of HCN was noticed. This is true of all the reductions of cobalt oxide with carbon monoxide in the neighborhood of 450° C.

These two runs are typical of a large number of similar ones. Our observations seem to show that the decomposition of CO by cobalt takes place only through a temperature interval in the neighborhood of from 300–450° C.

The check between composition of the oxide used for

these CO reduction experiments, as determined by analysis and as determined by the reduction experiments themselves, is entirely satisfactory. (See following article, p. 115.)

CONCLUSIONS

I. The reduction of Co_3O_4 to metallic cobalt by carbon monoxide gas takes place very rapidly at all temperatures above 600° C.

II. Between 350° C. and 450° C., carbon monoxide at first reduces Co_3O_4 to cobalt, but after a time the finely divided cobalt decomposes the CO gas, depositing carbon.

III. At temperatures between 500° C. and 750° C., over 90 per cent of the reduction of Co_3O_4 to Co takes place in a few minutes, but a further reduction to completion takes place very slowly.

IV. Between 750° C. and 900° C., the amount of reduction of Co_3O_4 to Co, which takes place during the first few minutes increases very rapidly, and at the higher temperatures it is complete.

V. Where producer gas is available it should offer a cheap and efficient means of producing large quantities of pure metallic cobalt from the oxide.

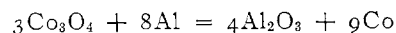
VI. For the production of cobalt from Co_3O_4 by CO, the charge must be completely cooled in an atmosphere of CO.

IV—REDUCTION OF COBALT OXIDE WITH ALUMINUM

The heat of formation of a molecular weight in kilograms of aluminum oxide (Al_2O_3) is 392,600 kilogram-calories, and is greater than that of any other metallic oxide. The molecular heat of formation of ferric oxide (Fe_2O_3) is correspondingly 195,600 kilogram-calories. It is therefore obvious that if finely divided aluminum be intimately mixed with ferric oxide (Fe_2O_3), the latter, possibly in the form of rolling mill scale, that the reaction $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$ will take place, provided the temperature be raised at some point in the mixture sufficient to start the reaction. This principle has been used by the Goldschmidt Thermit Co. to produce molten iron for welding purposes.

It is obvious that for every 160 kilograms of ferric oxide and 54 kilograms of metallic aluminum that are mixed together and fired in this way, there are developed $392,600 - 195,600 = 197,000$ kilogram-calories of heat. This is sufficient to raise the entire mass to a white heat, so that the molten iron readily settles to the bottom from where it may be tapped.

In a similar manner, metallic cobalt may be prepared by reduction of cobalt oxide with aluminum according to the reaction:



The molecular heat of formation of Co_3O_4 is 193,400 calories.¹

It is therefore obvious that for every 723 kilograms Co_3O_4 and 216 kilograms of aluminum that are mixed together and fired, there are developed $4 \times 392,600 - 3 \times 193,400 = 990,200$ kilogram-calories of heat. We would, therefore, expect a reaction

¹ Tables Annuelles Internationales des Constantes, 1, 428 (1910).

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

By HERBERT T. KALMUS

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 ,

¹ Published by permission of the Director of Mines, Ottawa, Canada. See footnote to previous article, page 107.

$\text{Co}_{12}\text{O}_{19}$, 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.