REDUCTION OF METALLIC CHLORIDES AND THE PHYSICAL PROPERTIES OF THE METAL PRODUCED

by

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ABSTRACT

This paper is a report on the investigations of the production of metals by the hydrogen reduction of metal chlorides and on the physical properties of the metal produced.

The study covers the hydrogen reduction of cobaltous chloride; crystallographic analyses of the cobalt powder produced under conditions of varying reduction temperature and hydrogen flow, and treated under various conditions of cooling and reheating; compacting and sintering of the powder under varying pressures and sintering temperatures; tensile tests on pressed and sintered cobalt bars; tests on growth of single crystals of iron and cobalt; crystallographic orientation of the iron single crystal; and Tukon hardness variation with orientation in the (001) plane of an iron single crystal.

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I. INTRODUCTION

A. PURPOSE

The purpose of this research is to investigate the properties of cobalt and iron, centering the investigations on the reduction of the metal chloride by various reductants and on the physical properties of the metal obtained.

A study of methods for the growth of metal single crystals and experimental work on single crystal growth is included in this investigation in an attempt to explain the anomalous crystal transformation characteristic of cobalt metal.

B. HISTORY OF THE REDUCTION OF METAL CHLORIDES

The reduction of metallic compounds to form the metal may be desirable for one or more reasons. Pyrometallurgical

methods may be impractical or impossible due to the high melting point of the metal or because of the absorption or solution of oxides into the molten metal. An example of this, of course, is tungsten. On the other hand, it is generally quite easy to get pure chlorides, even though the metal oxides are somewhat impure. Impure oxides may be reduced to form the impure metal. Chloridization followed by selective distillation or crystallization will yield a purer metal chloride. Reduction of this chloride by a process which permits clean separation of the reduction products will produce a pure metal.

Many metals, including cobalt, have been produced by the reduction of their metal chlorides. These include titanium, tungsten, copper, chromium, zirconium, iron, magnesium, and cobalt. In some instances, however, the reduction has been chiefly of thermo-chemical interest. In others, the reduction has been of metallurgical interest.

Ductile titanium[1] has been prepared by the reduction of titanium chloride by a more active metal such as sodium[2] or magnesium.[3] The Kroll process, using magnesium as the reductant, has proven best. Tungsten chloride has been reduced to the metal by means of hydrogen, carbon, and water gas, at temperatures from 1000 to 1500°C.[4] More work has been done, perhaps, on chromium chlorides and their reduction to chromium metal than has been done on any other of the metal chlorides. Preparation of the chromium chlorides has been explained in the literature[5,6]. Thermodynamic data on the hydrogen reduction

equilibria of $CrCl_3$ and $CrCl_2$ were obtained by K. Sano.[7,8] Details of the apparatus and operation for reduction of chromium chloride to chromium metal using dry hydrogen as reductant at 775°C is given by C. G. Maier.[9] A. B. Bagdasarian[10] made a physico-chemical study of the equilibria involved in the reduction of metallic chlorides by hydrogen for a few of the common base metals. Heats of fusion, heats of formation, and the free energies of Cu_2Cl_2, $PbCl_2$, $FeCl_2$, $ZnCl_2$ were obtained. The hydrogen reduction of silver chloride was investigated as far back as the late nineteenth century by Ribalquine[11] and Journiaux.[12] Crut[13] studied the hydrogen reduction of nickel and cobalt chlorides at 445°C. More recently, investigations on the hydrogen reduction were carried on by K. Sano[14] in Japan and by J. R. Partington and R. P. Towndrow.[15,16] Equilibrium constants and heats of formation were obtained for the reductions of cobaltous chloride. Lately, L.R. Michels[17] and co-workers reduced magnesium chloride by means of calcium carbide and finely divided magnesium. The process is not considered commercially promising. The report gives thermodynamic data for the reduction.

The foregoing covers but a few of the metal chloride reductions which have been investigated. Many more reductions using hydrogen, carbon, sodium, magnesium, calcium carbide, calcium hydride, and others could be mentioned here.

C. HISTORY, PROPERTIES, AND STRUCTURES OF METALLIC COBALT

Cobalt is a silvery coloured metal which takes a

lustrous polish. It is much like nickel in appearance. The atomic number of cobalt is 27 and the atomic weight is 58.94.

Its density, as determined by Kalmus[18] and Harper in 1914, is 8.7918 at 17.0°C when cast and unannealed, 8.8105 at 14.5°C when cast and annealed, and 8.9253 at 15.6°C when cast and swaged. Previous determinations ranged from 7.968 to 8.8. The density is now generally taken as 8.9.

Kalmus reports that the Brinell hardness of 99.1 per cent pure cobalt cast from just above the melting point and allowed to cool in an iron mould is in the neighborhood of 124.0, using a 3500 pound load. This is the mean of nine observations with an average deviation of 7.9.

Kalmus determined that the melting point of 99.9 per cent pure cobalt is 1478°C ± 1.1°C. Others have variously reported melting temperatures from 1455°C to 1530°C.

The tensile strength of commercial cobalt, 96.8 to 98.5 per cent pure, ranges, according to Kalmus, from 48,700 to 77,700 pounds per square inch in the cast and unannealed condition and from 42,600 to 75,200 pounds per square inch in the cast and annealed state. The tensile strength of pure cobalt, 99.9 per cent pure, produced by Kalmus, is about 34,400 pounds per square inch when cast from just above its melting point and allowed to cool in an iron mould, and machined in a lathe to test bars. Annealing seems to increase the tensile strength slightly to an average of 36,980 pounds per square inch.

Reductions in area up to 3 per cent are reported and

elongation in 2 inches up to 4 per cent.

Compressive strength of "commercial cobalt" (96.8 to 98.5 per cent pure), as reported by Kalmus averages 183,000 pounds for cast and unannealed samples and 140,000 pounds per square inch for the annealed samples. The compressive strength of the pure cobalt of Kalmus (99.9 per cent pure) when cast and unannealed is reported as 122,000 pounds per square inch and when cast and annealed as 117,200 pounds per square inch.

Kalmus states that the specific heat of 99.7 per cent pure cobalt is 0.1053 between 15 and 100°C., and $0.1058 + 0.0000457t + 0.000000066t^2$ between 0 and 890°C.

The latent heat of fusion is 58.38 calories per gram. The coefficient of linear expansion is 12.4×10^{-6} per degree centigrade.

Metallic cobalt has two crystal forms, the hexagonal close-packed and the face-centred cubic forms.

Hull,[19] in 1921, examined three samples prepared in three different ways. The first was a sample of filings from the pure cobalt of Kalmus. This sample showed a perfect hexagonal close-packed lattice with no trace of a cubic form. The side of an elementary triangular prism is 2.514A°, the axial ratio is 1.633, and the density from the X-ray data is 8.66. The same filings, after annealing in hydrogen at 600°C for 6 hours, showed a mixture of cubic and hexagonal close-packed structures in about equal proportions. The second sample was a fine cobalt powder, prepared by the reduction of cobalt oxide in hydrogen at about 600°C, gave a perfect cubic

lattice with a faint trace of hexagonal close-packed form. The side of the elementary cube is 3.554A° and the distance between nearest atoms is 2.514A°. The density from this X-ray data is 8.66. The third sample, prepared by dissolving a portion of cobalt filings of Kalmus in H_2SO_4 and rapidly electrolyzing, showed about equal amounts of the two forms.

Some confusion exists over the co-existence of the two crystal structures at any one temperature and over the position of the transformation temperatures.

Matsumoto,[20] in 1925, reported a phase transformation between 403 and 477°C. He states that below this temperature the lattice is hexagonal close-packed while above this temperature the lattice is face-centred cubic.

Sekito,[21] in 1927, melted some electrolytically pure cobalt in a Tammann furnace in hydrogen. The metal was forged and filed to shape. The cobalt was both cubic and hexagonal close-packed at room temperature. The pattern from this metal showed both forms at 700°C. He concluded from the relative intensities that the hexagonal close-packed form is the stable form at room temperature and that the face-centred cubic form is the stable form at 700°C. The lattice constant for hexagonal close-packed is given as 2.498A° with axial ratio of 1.622. The lattice constant for the face-centred cubic form is given as 3.558A°.

Hendriks, Jefferson, and Schultz[22] report that the powder formed by the reduction of Co_3O_4 yielded pure hexagonal close-packed cobalt at temperatures above 1120°C ± 20°C.

Sykes[23] reports that cobalt powder from hydrogen

reduction of Co_3O_4 yielded pure hexagonal close-packed form when reduced between 500 and 1000°C, and both forms when reduced at 1060°C ± 10°C. He also states that moderate deformation at room temperature changes the face-centred cubic form wholly or in part to the hexagonal close-packed modification, and that subsequent reheating at 800 to 1000°C causes but slight reversion again.

Edwards and Lipson[24] state that the high temperature structure of cobalt cannot be based on X-ray photographs at room temperature as often the high temperature structures of the element cannot be retained by quenching. They suggest that the free energies of the different forms of cobalt must be almost equal below 500°C, so that the approach to equilibrium is affected by factors other than the free energy difference. The increase of surface energy due to the transformation is one such factor, and this will account for the relative ease of transformation of the larger crystal grains.

X-ray examination of powder, compacted, or fine-grained samples does not reveal whether the specimen is composed of small integral crystals each of which contain both crystal forms by means of a lattice distortion phenomenon or whether the sample is composed of an intimate random mixture of fine crystals some of which are completely of the hexagonal close-packed structure and the rest of which are completely of the face-centred cubic structure. An attempt to solve this perplexity lead to a study and to experimental work in the growth of single crystals.

D. GROWTH OF LARGE SINGLE METAL CRYSTALS

E. Schmidt and W. Boas[25] break down the methods of growing large single metal crystals into three main groups. These are:

1. Preparation of single crystals from the solid state-recrystallization.
   (a) recrystallization after critical plastic deformation.
   (b) crystal formation through crystal agglomeration.
2. Crystal formation from the melt.
   (a) crystallization in the melt crucible.
   (b) crystal formation by drawing the molten metal from the melt as a wire.
3. Crystal formation by deposition.
   (a) crystal growth through deposition from the vapour state.
   (b) crystal growth by electrolytic deposition.

There are many reports in the literature giving particular methods of growth of large single metal crystals and procedures for investigating the mechanism of slip, plastic flow, orientation, and other properties of the single crystals. Some of these articles are given in references (26) to (44) in the bibliography of this report.

E. HARDNESS VARIATION IN A SINGLE METAL CRYSTAL

As part of the work in physical properties hardness as

related to crystal orientation was investigated for one of the iron single crystals.

Directional hardness effect has been measured on single crystals of zinc and silicon ferrite by F. W. Daniels and C. G. Dunn.[40] They showed that the Knoop hardness of single crystals of zinc and silicon ferrite varies with the crystal orientation. Also, the cyclic form of the variation in Knoop hardness for a particular plane of testing depends on the crystallographic plane.

A. A. Guy[41] and N. W. Thibault and H. L. Nyquist[42] have also performed experiments in this connection.

It was thought or, at least, suspected that, in single crystals produced by recrystallization by heating after plastic deformation in tension, one of the important crystallographic planes, (001), (110), or (111), would be in the surface plane of the specimen.

If this supposition were true it could be checked very easily by a procedure presented by H. J. Williams, R. M. Bozorth, and W. Shockley[43] in their work on magnetic domain theory related to silicon ferrite.

Williams and his co-workers produced domain patterns in silicon ferrite single crystals as shown diagrammatically in Figure (1).

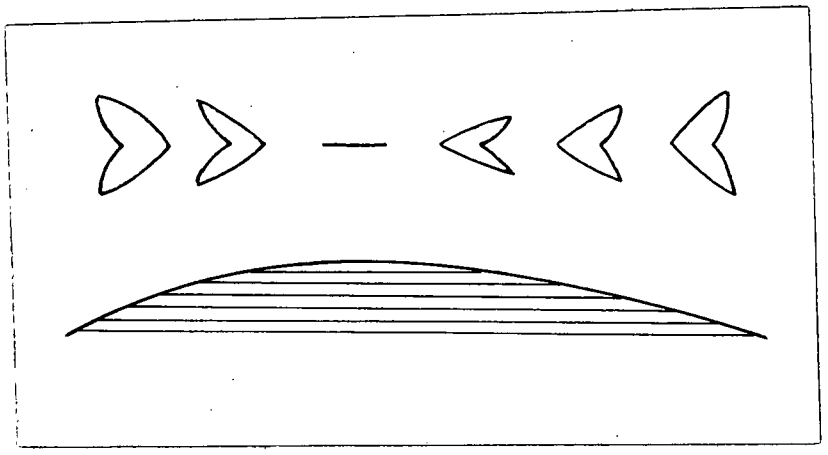


Fig. (1). Diagram of Domains on a Curved Surface.

This diagram shows domains on a curved surface having a gradually varying inclination with respect to the (001) plane. The tree-like domain patterns reverse direction as the inclination is reversed. The tree-like pattern becomes a straight line when the surface has zero inclination with respect to the (001) plane.

The specimen of silicon ferrite, used by Williams was electrolytically polished. After treating the specimen with a colloidal suspension of iron oxide, the specimen was examined under the microscope. Domain patterns were seen. The complete procedure used in preparing the crystals for examination is described in detail in the experimental part of this thesis.

It is convenient to index the Knoop diamond diagonal in relation to the <110> direction. This orientation may be determined by the etch-pit method outlined in Barrett.[44]

II. SUMMARY

The following phases of the research project have been reported in this thesis:

A. Production of cobalt powder by the hydrogen reduction of cobaltous chloride.

B. Effect on ratio of hexagonal close-packed to face-centred cubic cobalt of:

1. temperature of hydrogen reduction
2. rate of cooling
3. temperature of reheating
4. cold pressing and sintering.

C. Density of compacted cobalt powder.

D. Determination of particle size of the cobalt powder.

E. Tensile tests on pressed and sintered cobalt bars.

F. Investigation of methods of producing large single metal crystals.

G. Hardness variation in a single crystal.

A. PRODUCTION OF COBALT POWDER

Hydrogen was used as the reductant to produce cobalt powder from cobaltous chloride according to the chemical re-

action

$$CoCl_2 + H_2 \rightarrow Co + 2HCl.$$

The only variables in the reduction process were the temperature of reduction and the rate of flow of the reductant. Reductant temperatures from 300°C. to 800°C. were used. At 300°C., the reaction of the hydrogen on the cobaltous chloride was very slow. The reaction rate increased with increases in reduction temperature. From 400 to 700°C., the rate of reaction was satisfactory and a soft spongy layer of cobalt was formed in the reduction boat or tray. Reduction temperatures above 700°C. caused the cobalt to become partially sintered thereby forming hard sintered aggregates of particles, most of which were unable to pass a 65 mesh sieve. The cobalt produced at temperatures between 400 and 700°C. however passed readily through a 200 mesh sieve.

B. EFFECT OF VARIABLES ON CRYSTAL FORM RATIO

X-ray analyses of the cobalt powder revealed two crystal forms, the hexagonal close-packed and the face-centred cubic lattices. These allotropic coexistent forms have already been identified several times by former investigators.

1. Effect of Hydrogen Reduction Temperature

In the course of the present work it has been found that pure cobalt of almost any desirable ratio of hexagonal close-packed to face-centred cubic cobalt may be produced by varying the temperature of the hydrogen reduction. Hydrogen reduction

of the cobaltous chloride at the lower temperatures, 300 to 400°C, gave almost 100% hexagonal close-packed structure. Higher reduction temperatures produced cobalt of progressively decreasing amounts of hexagonal close-packed and, of course, increasing amounts of the face-centred cubic structure. The per cent of hexagonal close-packed cobalt when produced at 700°C is about 14 per cent.

2. Effect of Cooling Rate

The cooling rate appeared to have little effect on the crystal form ratio. Samples were water-quenched, air-cooled, and furnace-cooled, but the crystal ratios did not differ significantly on these cooling rate tests.

3. Effect of Reheating Temperature

Reheating causes a crystal transformation from hexagonal close-packed to face-centred cubic form. When samples of cobalt powder produced at a temperature to give nearly 100 per cent hexagonal close-packed structure were reheated at temperatures up to 900°C, it was found that the percentage of face-centred cubic structure increased to about 50 per cent. Temperatures above 500°C, however, did not increase the amount of the cubic form above about 50 per cent.

4. Effect of Cold Pressing and Sintering

Cold pressing causes a face-centred cubic to hexagonal close-packed transformation. Sintering

causes, or permits, some recovery of the face-centred cubic form. Powder compacts have been examined by X-ray diffraction methods for crystal transformation. The results of these tests have been included in the report but the validity of the X-ray results is somewhat uncertain.

C. DENSITY OF COMPACTED COBALT POWDER

Samples of cobalt powder were compacted at various pressures and sintered at various temperatures. The compact density was calculated from dimension measurements on green and sintered compacts. The density increased with compacting pressure and sintering temperature and approached a maximum at the upper pressure and temperature used. Pressures up to 100 tons per square inch and sintering temperatures to 2000°F were employed. The maximum density obtained in a green compact was 7.08 grams per cubic centimeter and in a sintered compact, 8.03 grams per cubic centimeter. Photomicrographs of compacts are included to show the density trend.

D. DETERMINATION OF PARTICLE SIZE

In all powder pressing operations, particle size is of great importance. Therefore, where tests are being performed on pressed powder compacts, the effect of particle size and shape must be known or standardized for correlative physical tests. Unfortunately, owing to the spongy and agglomerate nature of the reduced powder, no accurate particle size tests

could be made. Both the Andreasen pipette method and a photoelectric device method failed. The photoelectric particle size measuring apparatus was built in the course of the research for particle size measurement.

E. TENSILE TESTS ON PRESSED AND SINTERED BARS

Tensile specimens pressed from powdered cobalt at 50 tons per square inch and sintered in hydrogen for 4 hours at 2000°F were machined to a standard size. The tensile strengths varied from 40,000 to 68,000 pounds per square inch.

F. INVESTIGATION OF METHODS OF PRODUCING LARGE SINGLE METAL CRYSTALS

Work on single crystals was initiated in an attempt to explain the phenomenon of the coexistence of two crystal forms in cobalt metal at room temperatures. Single crystal growth experiments were performed on iron as well as cobalt on the supposition that, since iron and cobalt have somewhat similar properties and characteristics, a method which causes crystal growth in iron would also cause crystal growth in cobalt. However, although large single crystals were grown successfully in iron, no large crystals were obtained in cobalt.

Two methods for growth were investigated;

1. recrystallization in the solid state

and 2. crystal formation from the melt.

Of these two, only the recrystallization method produced large crystals. Two factors contributed to the inability of the recrystallization method to produce single crystals in cobalt.

The specimen of cobalt available for use was very small and thus controlled critical plastic deformations could not be obtained. In addition, the peculiar crystal transformation characteristics of cobalt offered complications not present in iron recrystallization.

It is worthy of note, in connection with the iron single crystals that the (001) crystallographic plane is very nearly in the plane of the specimen surface. This was very conveniently shown by an application of the magnetic domain theory as used by Williams, Bozorth, and Shockley.[43] The <110> crystallographic direction was found by the etch-pit method outlined in Barrett.[44]

G. HARDNESS VARIATION IN AN IRON SINGLE CRYSTAL

The Knoop diamond hardness tests showed that hardness of the iron crystal in the (001) plane varies from 111 to 137, using Knoop diamond indenter and 300 gram load, depending on the angular relation to the <110> direction. The hardness has a 22 per cent variation and the hardness values repeat every 90 degrees in the (001) plane.

III. DATA

Reaction Data for Cobaltous Chloride Reduction by Hydrogen[15] (Partington & Towndrow).

$$CoCl_2 + H_2 \longrightarrow 2HCl + Co.$$

Gas flow cc/min.	$\frac{pHCl}{pH_2}$	t. °C	Material
10.8	2.09	600	$CoCl_2$
6.9	3.13	600	"
4.0	3.81	600	"
0	4.40	600	"

t. °C	T °K	$\frac{10^6}{T}$	$4 + \log_{10} K$	K
400	673	1486	0.413	0.92
485	698	1433	0.733	0.76
450	723	1383	0.990	0.65
475	748	1337	1.350	0.78
500	773	1294	1.621	0.86

U = - 31.7 K Cal = energy of reaction.

$$K = \frac{HCl^2}{H_2} = \frac{4x^2\ Pt}{(1-x^2)RT}$$

R = 76 x .08207 litre cm Hg/deg.

$$1 + x = \frac{Pt,o}{Po}$$

$$pHCl = \frac{2x\ pt}{(1+x)}$$

$$pH_2 = \frac{(1-x)pt}{(1+x)}$$

where x = fraction of original number of molecules of H_2 reacted.

Analysis of the C.P. Cobaltous Chloride ($CoCl_2 6H_2O$) used throughout the tests for all reductions.

SO_4	0.005%	Ni	0.10
Zn	0.01	Pb	0.002
Cu	0.002	Earth & Alks(as SO_4)	0.20%
Fe	0.002	N comp	0.003%

A. TEST OPERATIONS AND DETAILS

1. Drying of Cobaltous Chloride

The drying of this hydrated cobaltous chloride ($CoCl_2 \cdot 6H_2O$) was rather difficult because the salt not only contains six molecules of water of hydration, but it absorbs water from the air. The hydrated salt is very unstable but, nevertheless, heating at 100°C failed to remove the water completely. Various quantities of water, ranging from about one-half to one and one-half molecules of water were found in the test samples after drying at 105°C. An attempt was made to reach a constant value for water present in each chloride sample used in reduction: but

this constant value was not definitely obtained. Recovery calculations were made on basis of $CoCl_2 \cdot H_2O$. Potentiometric titrations using calomel and silver electrodes were used as checks on gravimetric analyses of chloride ion for the calculation of the water present.

The drying of the hydrated chloride salt served three purposes:

(a) eliminated evaporation and subsequent condensation in the reduction tube,

  (i) the water vapour would decrease the partial pressure of the hydrogen

  (ii) the condensate would absorb some of the hydrochloric acid gas given off, thereby making reaction rate tests impossible, and would permit greater attack by hydrochloric acid on the 18-8 stainless steel tube used;

(b) eliminated fusing of the salt in reduction boats prior to reduction.

  (i) fusion hinders hydrogen diffusion between the salt particles.

  (ii) the fused salt is absorbed in the pores of the alundum boats, thereby decreasing recovery;

and (c) brought variable water content to a fairly constant amount.

  (i) this permits better calculation of metal recoveries.

Two methods of drying the cobaltous chloride were tested:

(a) air-drying in oven at 105°C.

(b) drying at 105°C with nitrogen atmosphere protection.

Because air-drying is so much easier when drying large batches, both methods were tested to see if drying in a nitrogen atmosphere offered any advantages. The possible advantages are:

(a) nitrogen drying may prevent formation of oxychlorides

and (b) the ratio of face-centred cubic to hexagonal close-packed structures in the metal may be increased by nitrogen drying at 105°C.

Tests showed that if oxychlorides are formed:

(a) the oxychlorides are water soluble

and (b) the ratio of face-centred cubic hexagonal close-packed structures in the metal reduced by hydrogen from the dried chloride is not noticeably affected by the drying method.

Therefore, air dried cobalt chloride is used in all the bath reductions.

Drying Procedure

(a) Three undried 0.500 gm samples of the cobaltous chloride were dried on watch glasses in the drying oven, and in direct contact with the air.

- the temperature was kept at 50-60°C for one hour. - this treatment removed excess water and caused a colour change from red-violet to whitish pink.

- the temperature was gradually raised to 105°C the treatment caused colour change from whitish pink to pale blue and finally to darker blue.

- the samples were reweighed and dissolved in water.

(b) Two 0.500 gm samples were placed in dessiccator with $CaCl_2$ as drying agent for 48 hours, reweighed, then dried in drying tube at 105°C under a flow of nitrogen.

- the samples were reweighed and dissolved in water.

(c) Procedure (b) was repeated using P_2O_5 as well as $CaCl_2$ in the dessiccator.

(d) All solutions were analysed for chlorine as silver chloride. The amount of $CoCl_2$ and hence the amount of water present was calculated.

Results of Drying Tests

(a) Dessiccation of samples for periods longer than two days produced no better drying.

(b) The samples are prone to fuse to a moist dark blue crystal form between 50 and 105°C but revert to a lighter blue colour when drying at 105°C is complete. Water content and crystal structure of metal subsequently produced differ little from non-fused dried chloride.

(c) Recovery calculations are based on the weight of dried cobaltous chloride using formula $CoCl_2 \cdot H_2O$. The water in undried $CoCl_2 \cdot 6H_2O$ seems most constant and perhaps should be used for recovery calculations.

(d) Dried weight may be taken as 60% of the undried weight.

2. Reductants and Reduction Methods

Three reductants, hydrogen, magnesium, and cal-

cium carbide were used in the tests. Of these three, hydrogen proved best because of the ease, simplicity, cleanliness, and purity of the reduction process.

Although the magnesium reduction took place in a nitrogen atmosphere, the only products of reduction were CaO, Co_3O_4, MgO, Mg, MgCl, and various combinations of the above oxides. X-ray analysis revealed no cobalt. Further work, using purified oxygen-free nitrogen, or argon, and gas-tight crucibles, is justified.

Calcium carbide reductions have several undesirable features;

(a) pure CaC_2 is not commercially available,
(b) separation of carbon and the other impurities, such as CaO, Fe_3O_4, SiO_2, from the finely divided cobalt is difficult.

Fe_3O_4-free calcium carbide would permit some form of rough magnetic separation. Small-scale flotation might also be used to separate the CaO and C from the cobalt.

One test of each reduction, magnesium and calcium carbide, was performed. The reduction temperature chosen was 500°C for each test.

The hydrogen reduction of the chloride seemed to warrant further work. For this reason many detailed tests were carried out to obtain data. A tube furnace of the type shown in figure (2) was used for all the test runs. The tube was one-inch 18-8 stainless steel tubing, threaded on one end to take a standard

gas-tight valve. This valve permitted the flushing of air from the charging chamber before the charge entered the reduction chamber itself. The nitrogen, used for flushing, entered the combustion tube directly, whereas the hydrogen passed through a flowmeter, a calcium chloride drying tower, and a phosphorous pentoxide U-tube as shown in figure (2). The hydrogen-hydrochloric acid gas mixture, that leaves the combustion tube, is bubbled through a known normality solution of sodium hydroxide so that the reaction rate can be calculated. Alundum boats were used for the chloride charge in the first test runs, but these boats have two disadvantages. The boats were easily overturned. Also, if any of the cobalt chloride melted before the reduction took place, it was absorbed in the alundum boats. Later test runs were made using a small boat and insert lid of 18-8 stainless steel. This boat overcame the previous weaknesses. The temperature was measured and controlled by a chromel-alumel thermocouple with a Wheelco Capacitrol control meter. The couple was inserted in a silica protection tube into the reduction chamber as shown in the diagram.

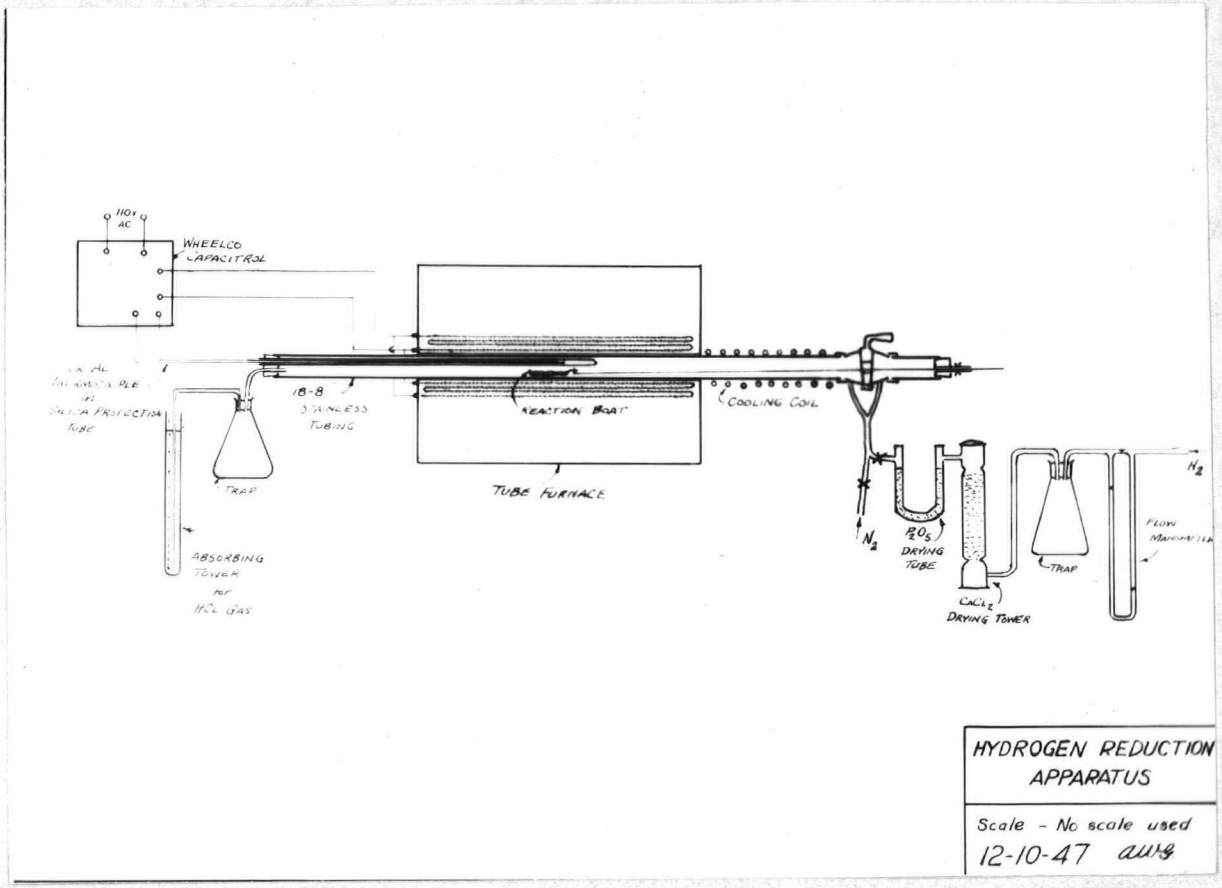


Fig. (2). Diagram of Hydrogen Reduction Apparatus.

3. Hydrogen Reduction Procedure

Using a hydrogen flow of 75 ccs per minute, tests were run at 400°C, 500°C, 600°C, 700°C, 750°C, and 800°C. The reaction rate, measured as the volume of HCl gas given off and absorbed per hour at intervals of time throughout the reaction, was obtained for the various temperatures of the test runs. The reaction rate curves for the test runs of varied reduction temperatures are shown in figure (3).

Similarly, tests were run at 500°C, using varied hydrogen flow from 35 - 200 ccs of hydrogen per minute. The reaction rates were obtained as before. The reaction rate curves for varied hydrogen flow are shown in figure (4).

The samples of cobalt obtained from the varied temperature runs were crystallographically examined by X-ray diffraction to find the per cents of face-centred cubic and hexagonal close-packed structures at these reduction temperatures. The results are shown in Table I.

4. Effect of Cooling Rate

The cobalt obtained by the above reductions were given the equivalent of an air cool in the cold end of the tube. Rapid cooling (water quench) and very slow cooling (furnace cooling) were performed on the cobalt. X-ray examinations were made of the cobalt samples which underwent these cooling treatments.

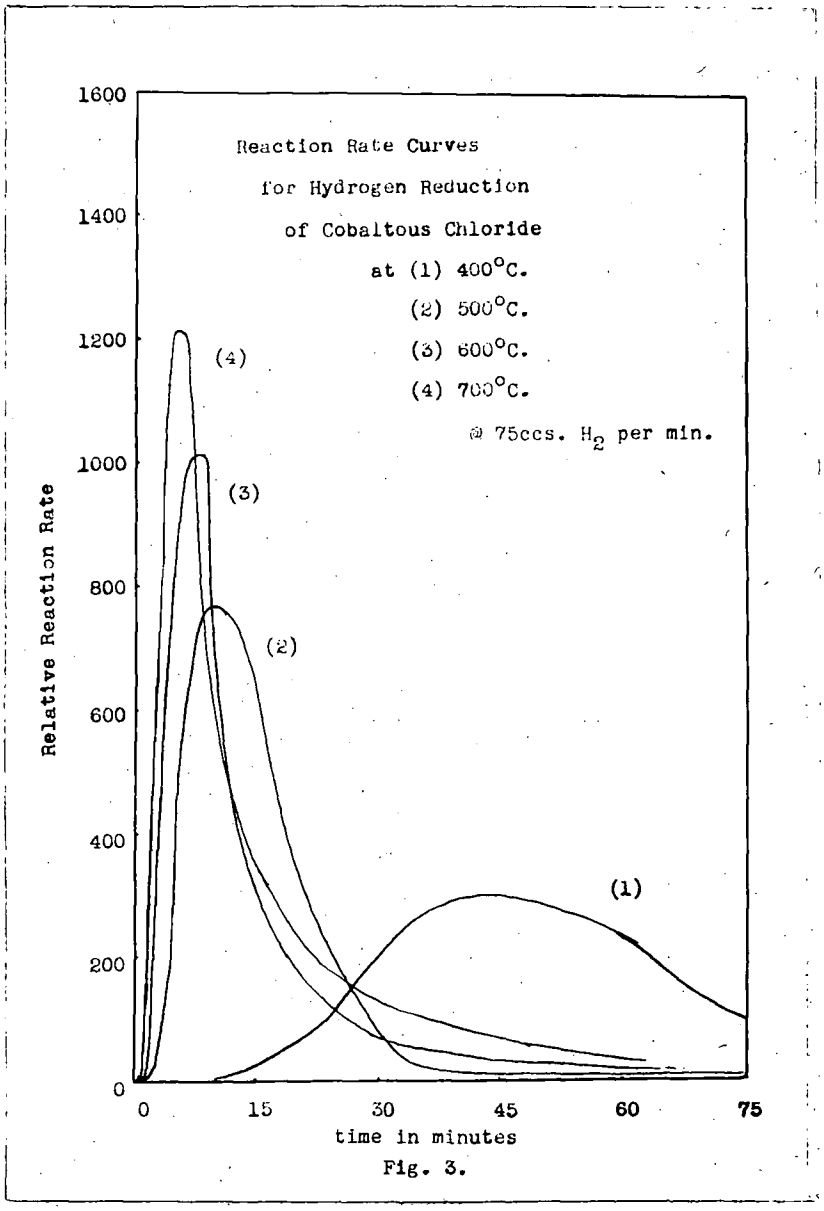


Fig.(3). Reaction Rate Curves.

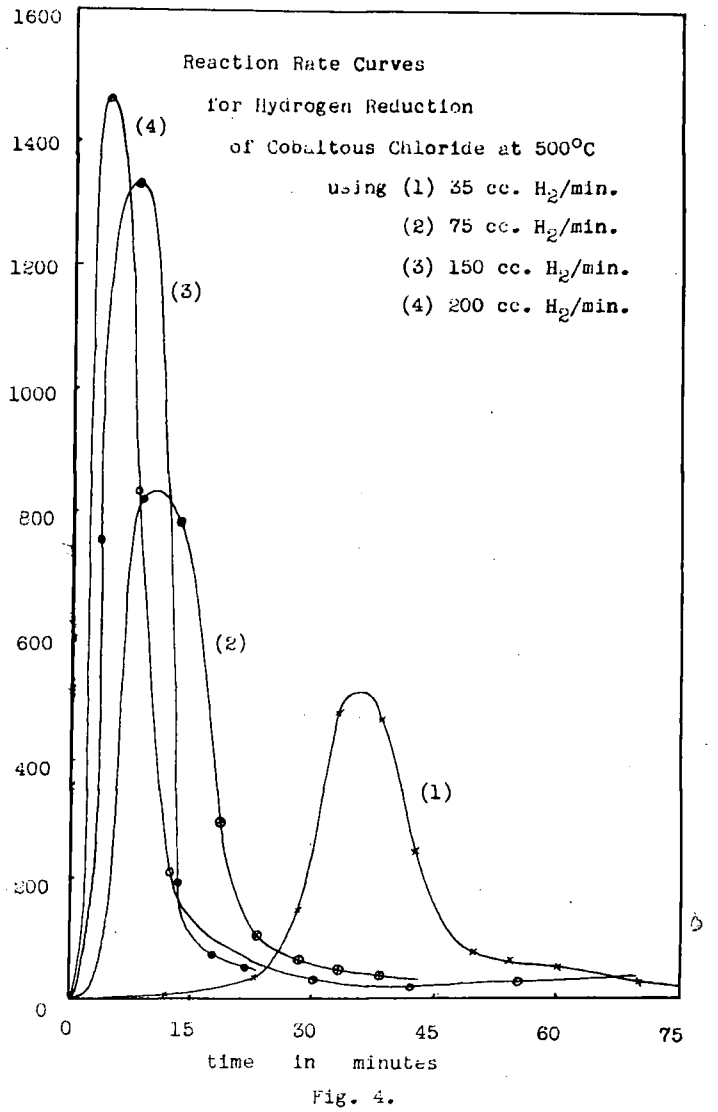


Fig. 4.

Fig. (4). Reaction Rate Curves.

The results are listed in Table II. Very little variation occurred in the F.C.C. to H.C.P. ratio as a result of the cooling tests.

5. Effect of Reheating

A cobalt sample was produced at 400°C and cooled in the cold end of the tube in the protective hydrogen atmosphere. This sample was divided into several portions which were reheated to various temperatures. These tests were made to see if any crystal transformation would occur; that is, to see if the ratio of face-centred cobalt to hexagonal close-packed cobalt would increase due to a hexagonal close-packed to-face-centred cubic transformation at higher temperatures. The cobalt before reheating was nearly 100% hexagonal close-packed. The X-ray diffraction patterns were obtained and the results listed in Table III.

6. Particle Size of the Cobalt Powder

In spite of the great importance of particle size measurement in powder metallurgy work where compacting is encountered, no accurate size measurements could be made in the cobalt powder produced in this research. This was due to the spongy and agglomerate nature of the reduced powder. However, microscopic examination shows that much of the powder is in the 0-10 micron range. This is especially so in powder produced at the lower reduction temperatures. High temperature reduction tended to sinter the particles

together.

Both the Andreasen pipette method and a photo-electric device method were used in particle size tests. The photoelectric apparatus was constructed during the course of the research and is shown in figures (5), (6), (7), and (8). The essential parts are:

(a) light source

(b) settling tube for the powder,

and (c) a light-measuring device.

The light-measuring device consists of a balanced bridge circuit which becomes unbalanced when the current from the vacuum photocell changes. This photocell current change is caused by change in light intensity of the light beam which passes through windows in the settling tube onto the photo tube. The electrical circuit used has been adapted from a light measuring circuit suggested in Canadian General Electric Bulletin No. PT20RI.

TABLE I
X-RAY DIFFRACTION ANALYSES FOR COBALT CRYSTAL FORM
(varied reduction temperature)

Sample Number	Reduction Temp. °C.	Percent H.C.P.	Percent F.C.C.	Impurities CoO	Impurities Co_3O_4
11A	300	90	10	-	-
7A	400	83	17	some	-
9A	500	50	50	trace	-
3A	600	19	81	trace	trace
5A	700	14	86	-	-
18A	750	5	95		very considerable

Notes.
(1) Cobalt produced by hydrogen reduction of cobaltous chloride.
(2) All samples were cooled in hydrogen at room temperature.
(3) All powder samples were -200 mesh.
(4) Percentages of F.C.C. and H.C.P. are approximate and are the percentages of free cobalt present, not percentage of total cobalt.

TABLE II
X-RAY DIFFRACTION ANALYSES FOR COBALT CRYSTAL FORM
(varied cooling rate)

Sample Number	Reduction Temp. °C.	Percent H.C.P.	Percent F.C.C.	Impurities CoO	Impurities Co_3O_4
21 A	700	17	83	some	?
5 A	700	14	86	-	-
20 A	700	18	82	trace	trace

Notes.
(1) Sample 21A was furnace-cooled in hydrogen (20°C/min.)
(2) Sample 5A was cooled in hydrogen at room temperature.
(3) Sample 20 A was water-quenched from the furnace tube.

TABLE III

X-RAY DIFFRACTION ANALYSES FOR COBALT CRYSTAL FORM
(varied reheating temperature)

Sample Number	Reduction Temp. °C.	Temp °C of Reheating	Percent H.C.P.	Percent F.C.C.	Remarks
23A1	400	----	100	-	
23A2	"	500	58	42	
23A3	"	600	49	51	
23A4	"	700	47	53	trace CoO
23A5	"	800	47	53	
23A6	"	900	50	50	

Notes.
(1) Sample 23A was produced by hydrogen reduction of cobaltous chloride at 400 C and divided into six portions, 23A1 to 23A6.
(2) The samples were reheated in hydrogen for two hours.
(3) All samples were -200 mesh.

TABLE IV

X-RAY DIFFRACTION ANALYSES FOR COBALT CRYSTAL FORM
(varied drying porcedure)

Sample Number	Reduction Temp. °C.	Drying Method	Percent H.C.P.	Percent F.C.C.	Remarks
24A	700	air	24	76	one unident-
25A	"	N_2	21	79	ified comp- onent.

Notes.
(1) All samples are -200 mesh.

TABLE V

X-RAY DIFFRACTION ANALYSES OF COBALT POWDER COMPACTS

Sample Number	Compacting Press T/in^2	Sintering Temp. ^{o}F.	Percent H.C.P.	Percent F.C.C.	Remarks
C9A	20	green	72	28	flat
"	"	"	71	29	edge
C10A	40	"	83	17	flat
"	"	"	90	10	edge
C14 A	50	"	83	17	flat
"	"	"	86	14	edge
C11A	60	"	81	19	flat
C12A	80	"	84	16	flat
C13A	100	"	85	15	flat
"	"	"	100	--	edge
C9B	20	1600	35	65	flat
"	"	"	57	43	edge
C10B	40	"	40	60	flat
"	"	"	55	45	edge
C11B	60	"	41	59	flat
C12B	80	"	45	55	flat
C13B	100	"	48	52	flat
"	"	"	67	33	edge

Notes.

(1) All specimens were compacted form cobalt powder sample 29A which was produced by hydrogen reduction of cobaltous chloride at 700^{o}C. The powder was 14% H.C.P. and 86% F.C.C.

(2) All sintering was performed in a hydrogen atmosphere.

(3) The term "flat" refers to plane perpendicular to pressing direction. The term "edge" refers to plane in pressing direction.

7. Compacting of the Cobalt Powder

A small steel compacting die of the type shown in figure (9) was used for all of the small compacts. The die was made from an abrasion resistant steel and treated to a hardness of R_c60. The diameter of the compacts was 0.500 inches and the thickness was about 0.10 inches. The thickness, of course, depends on the powder weight and the compacting pressure used. A small hydraulic press with a range from 0 to 60,000 pounds was used for the pressures up to 100 tons per square inch.

A larger collapsible die has been made for producing compacted bars. It is shown in figure (10).

8. Compacting and Sintering Procedure

(a) Two compacts of powder produced at 400°C were pressed at 50 tons per sq. inch. One compact was sintered in hydrogen at 1800°F for two hours.

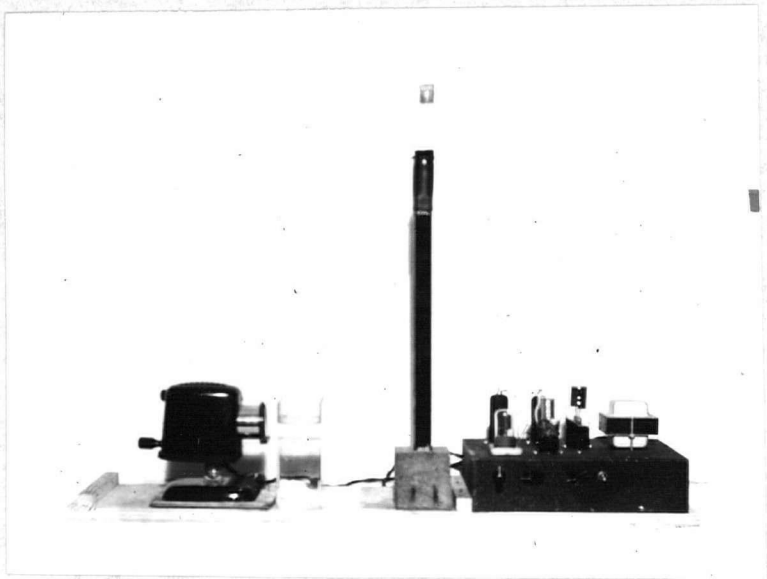
(b) A series of compacts of powder produced at 700°C were pressed at 50 tons per sq. inch for treatment under various sintering conditions. The sintering temperatures were 1600, 1700, 1800, 1900, 2000°F for two hours. Three samples were sintered at 1600°F for sintering times of 2, 4, and 8 hours.

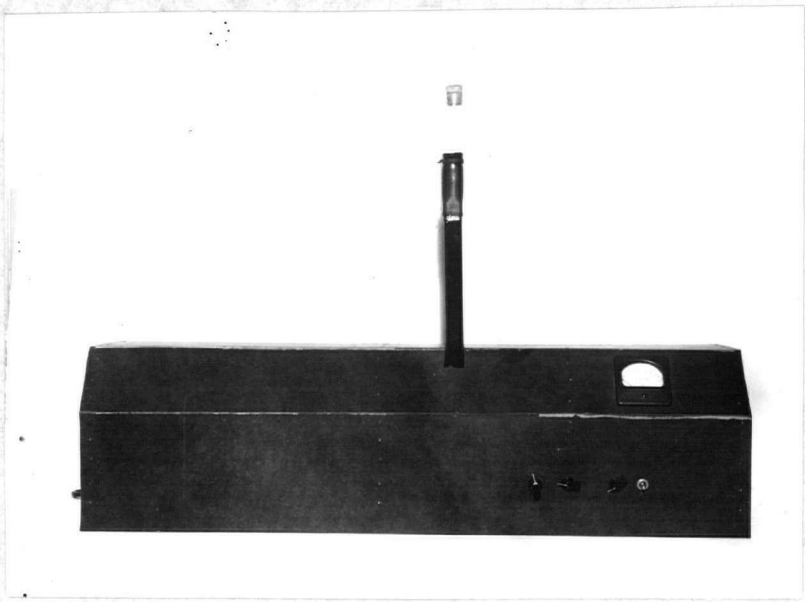
(c) A series of compacts of powder produced at 700°C were pressed using pressures of 20, 40, 50, 60, 80, and 100 tons per square inch. This series was sintered at 1600°F for two hours.

(d) Two compacts of a commercial cobalt powder were pressed at 50 tons per square inch. One compact was sintered at 1600°F for two hours.

All sintering was performed in a hydrogen atmosphere to remove any cobalt oxide and to prevent any oxidation.

From the results of the above, shown in Tables VI, VII, and VIII, curves of density vs. compacting pressure, density vs. sintering temperature, and density vs. sintering time were obtained. These curves are shown in figures (11), (12), and (13).





Figs. (5) & (6). Particle Size Measuring Apparatus.

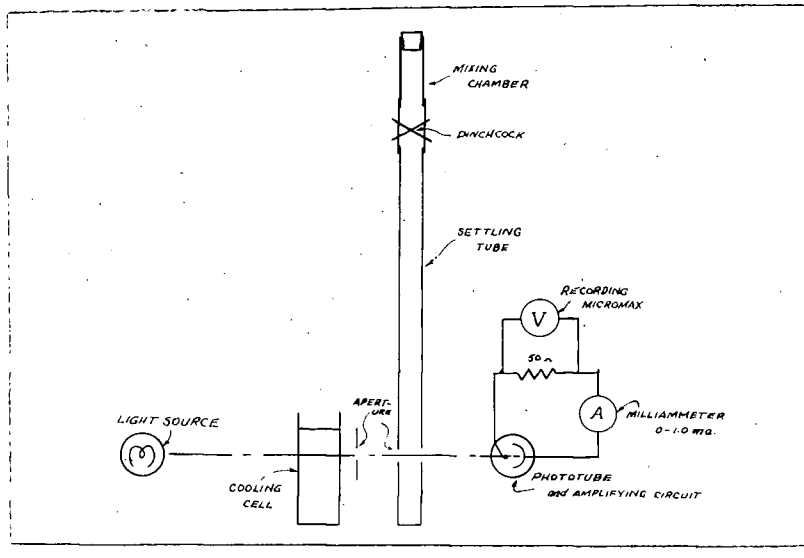


Fig. (7). Diagrammatic Sketch of Particle Size Measuring Apparatus.

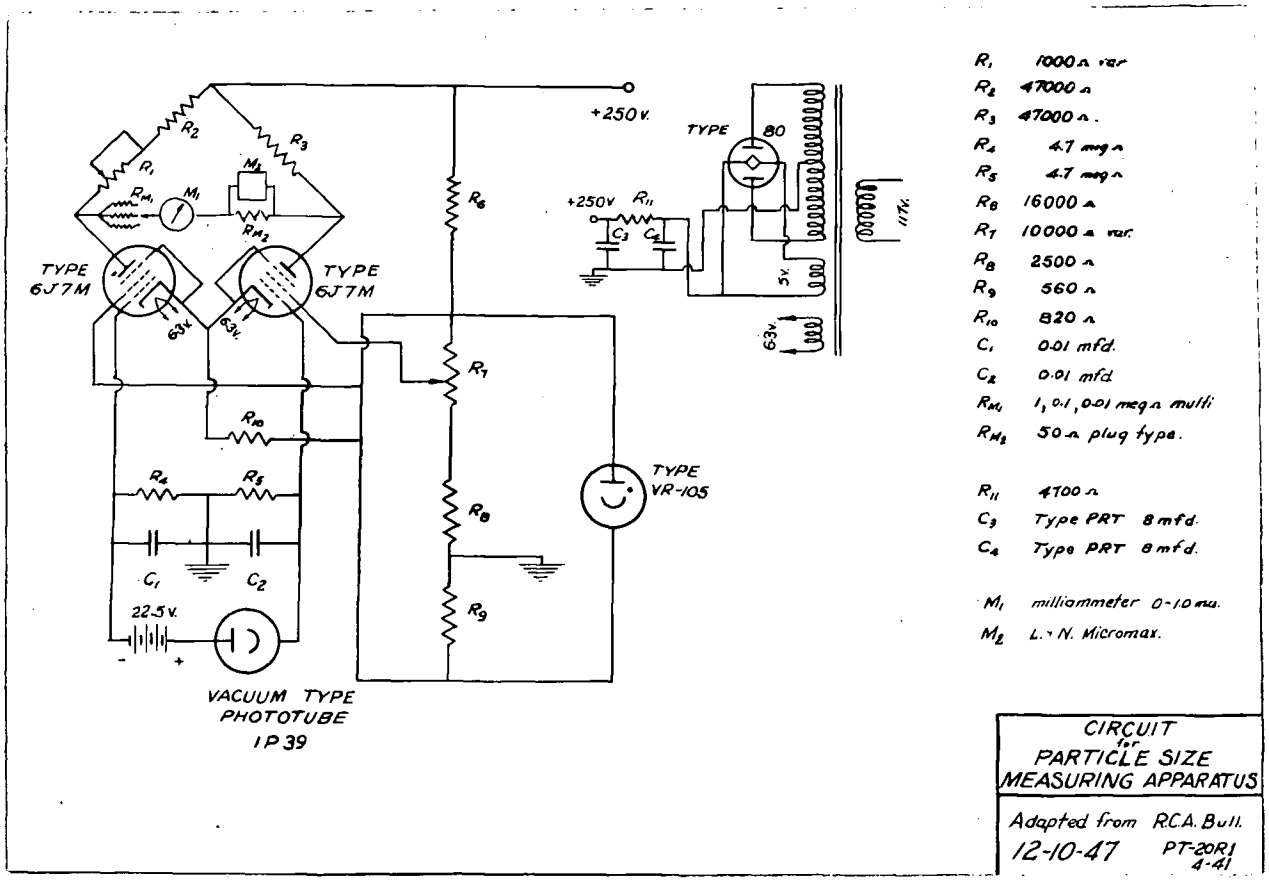


Fig. (8). Circuit Diagram of Particle Size Measuring Apparatus.

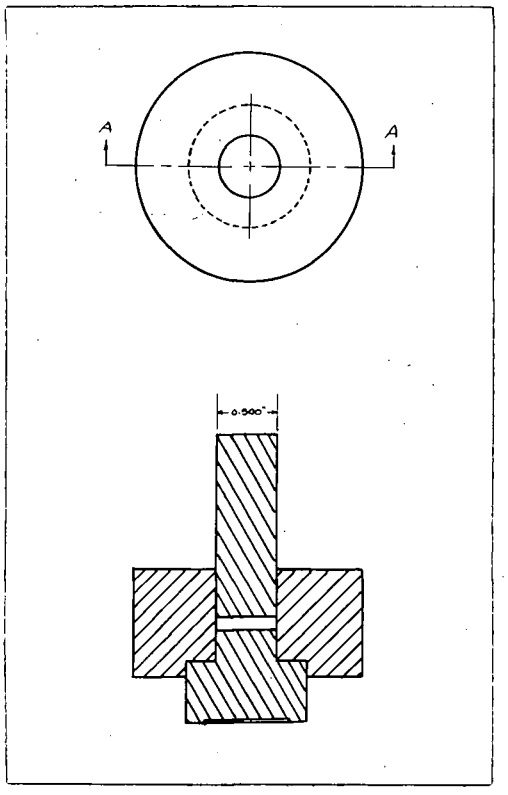
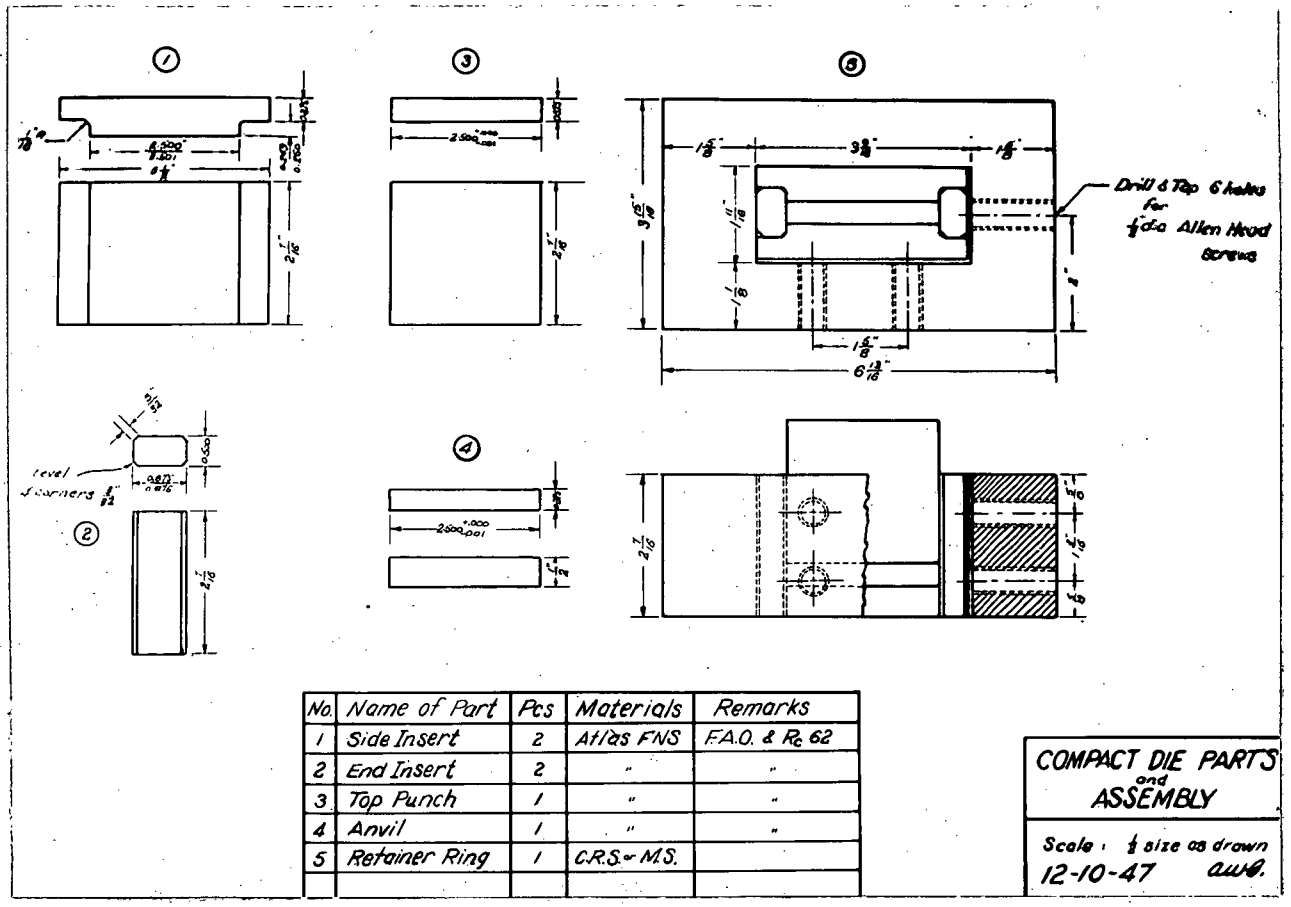


Fig. (9). Assembly of Small Powder Compact Die.



No.	Name of Part	Pcs	Materials	Remarks
1	Side Insert	2	Atlas FNS	F.A.O. & Rc 62
2	End Insert	2	"	"
3	Top Punch	1	"	"
4	Anvil	1	"	"
5	Retainer Ring	1	C.R.S. or M.S.	

COMPACT DIE PARTS and ASSEMBLY

Scale : 1/4 size as drawn
12-10-47 awg.

Fig. (10). Bar Compact Die.

9. X-Ray Crystallographic Analyses

X-ray diffraction patterns of the various powders and compacts were obtained from the Philips' Geiger-counter X-ray Spectrometer in the laboratories of the British Columbia Research Council. The tests were made using K_{α} radiation from an iron target and a manganese filter. The line locations and intensities were measured by a Geiger-counter which traverses at constant speed. The pattern is traced on a Brown Instrument Recorder. The motors, which drive the counter and recorder roll, run at the same speed but are not synchronized. Figures (14) and (15) show the diffraction patterns of two cobalt samples. Cobalt trace in figure (15) shows 86 per cent F.C.C. and 14 per cent H.C.P. structure. The relative per cents of F.C.C. and H.C.P. are calculated from the relative intensities of the face-centred cubic and hexagonal close-packed lines on the trace.

The powder samples were mounted in a hole in a microscope slide with a minimum of crystal orientation. Where the powder does not compact properly in the slide, a binder such as collodion must be used.

The green and sintered compacts were mounted in transoptic mounting plastic. The mounted specimens, after being polished, were used directly in the X-ray apparatus. The relative intensities of the lines are somewhat less accurate for the compacts than for the

loose powder because slight orientation in compacting is inevitable.

The X-ray results are listed in Tables I, II, III, IV, and V.

The crystallographic analyses of compacted specimens are of somewhat doubtful validity because of the factor of preferred crystal orientation. X-ray tests were run on the flat and edge surfaces of the compacts for comparison. Tests on specimens etched to remove manual polishing effects produced non-significant results. The difference between flat- and edge-tested specimens varied from 0 - 22 per cent in the hexagonal close-packed analysis. Obviously the validity of X-ray analyses on compacted samples is questionable.

10. Microscopic Examination.

A series of compacts were pressed and sintered with compacting pressure, sintering time, and sintering temperatures as variables. Photomicrographs to show the trend of compacting and bonding with pressure, sintering temperature and sintering time are presented in figures (17) to (37).

Physical Testing

Bars $\frac{3}{8}$" x $\frac{3}{8}$" x $2\frac{1}{2}$" were pressed at 50 tons per square inch and sintered for 4 hours at 2000°F in a hydrogen atmosphere. Two bars were compacted from high hexagonal close-packed powder and two bars from high face-centred cubic powder.

After sintering, the bars were machined to $\frac{3}{16}$" Standard U.S. Machined Round Test Piece specifications, as shown in figure (16).

The tensile strengths varied from 40,000 to 68,000 pounds per square inch. The tests did not show conclusively which type of powder gave the greatest strength.

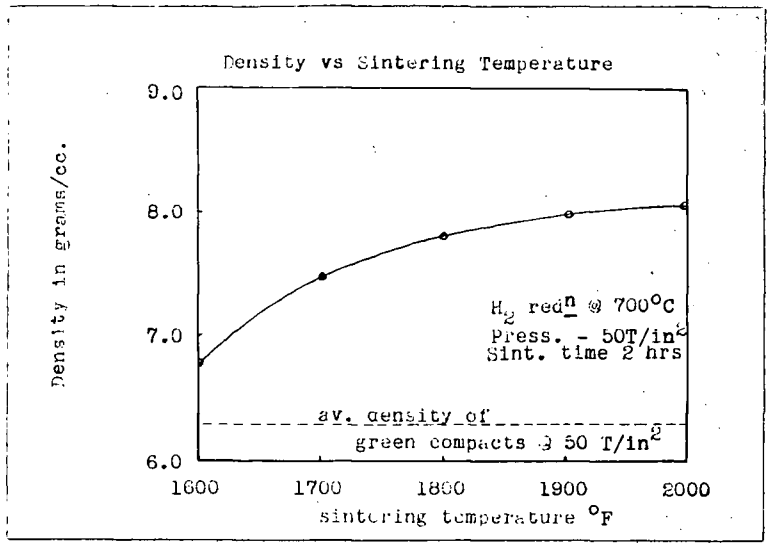


Fig. (11). Density vs Sintering Temperature.

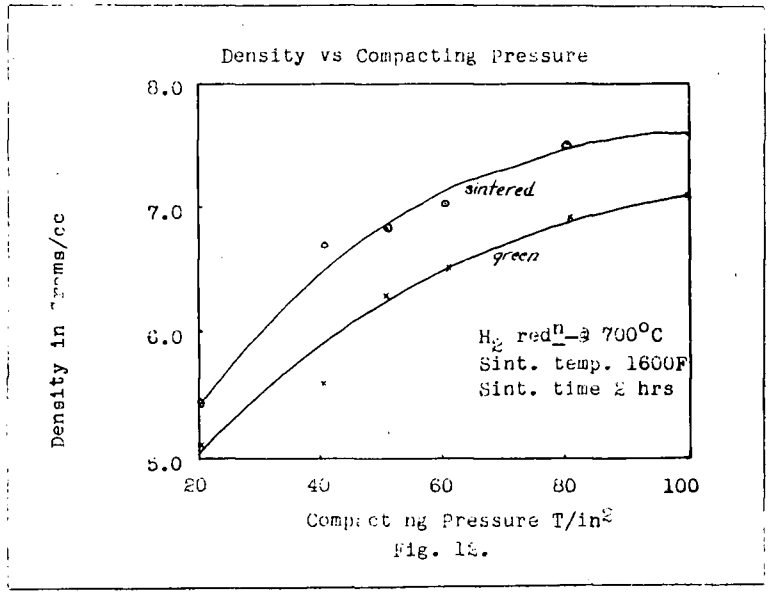


Fig. (12). Density vs Compacting Pressure.

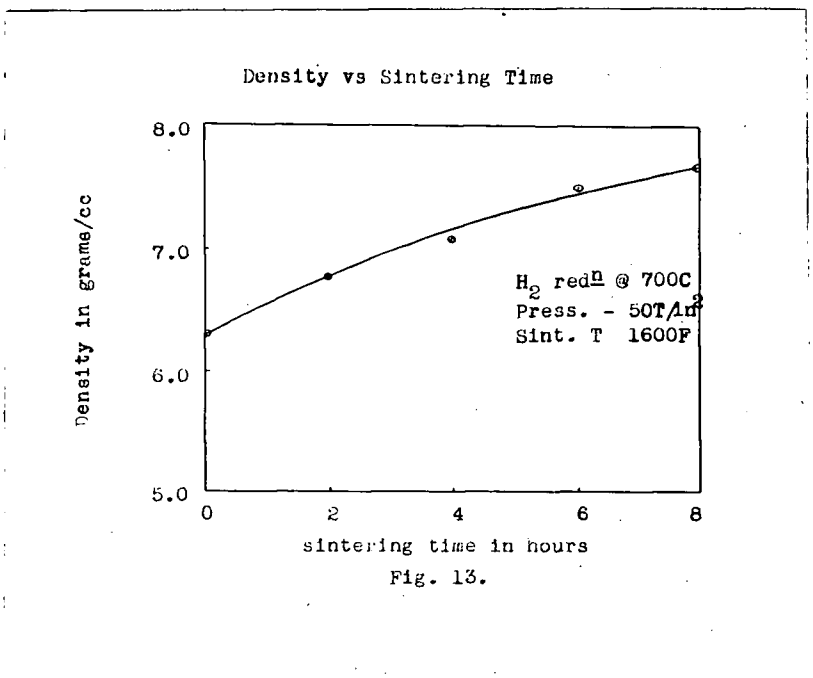


Fig. 13.

Fig. (13). Density vs Sintering Time.

TABLE VI
DENSITY OF GREEN AND SINTERED COBALT COMPACTS
(varied compacting pressure)

Sample Number	Compacting Press T/in^2	Sintering Temp. ^{o}F.	Sintering Time hrs.	Density gm./cc.
C9A	20	---	---	5.13
C9B	"	1600	2	5.36
C10A	40	---	---	5.64
C10B	"	1600	2	6.70
C14A	50	---	---	6.39
C14B	"	1600	2	6.75
C11A	60	---	---	6.51
C11B	"	1600	2	7.00
C12A	80	---	---	6.90
C12B	"	1600	2	7.52
C13A	100	---	---	7.08
C13B	"	1600	2	7.55

TABLE VII
DENSITY OF GREEN AND SINTERED COMPACTS
(varied sintering temperatures)

Sample Number	Compacting Press T/in^2	Sintering Temp. ^{o}F.	Sintering Time hrs.	Density gm./cc.
C14A	50	---	---	6.39
C14B	"	1600	2	6.75
C15A	"	---	---	6.24
C15B	"	1700	2	7.53
C16A	"	---	---	6.29
C16B	"	1800	2	7.88
C17A	"	---	---	6.18
C17B	"	1900	2	8.05
C18A	"	---	---	6.34
C18B	"	2000	2	8.03

TABLE VIII
DENSITY OF GREEN AND SINTERED COBALT COMPACTS
(varied sintering times)

Sample Number	Compacting Press T/in^2	Sintering Temp. ^{o}F.	Sintering Time hrs.	Density gm./cc.
C14A	50	---	---	6.39
C14B	"	1600	2	6.75
C19A	50	---	---	6.30
C19B	"	1600	4	7.02
C20A	50	---	---	6.33
C20B	"	1600	8	7.66

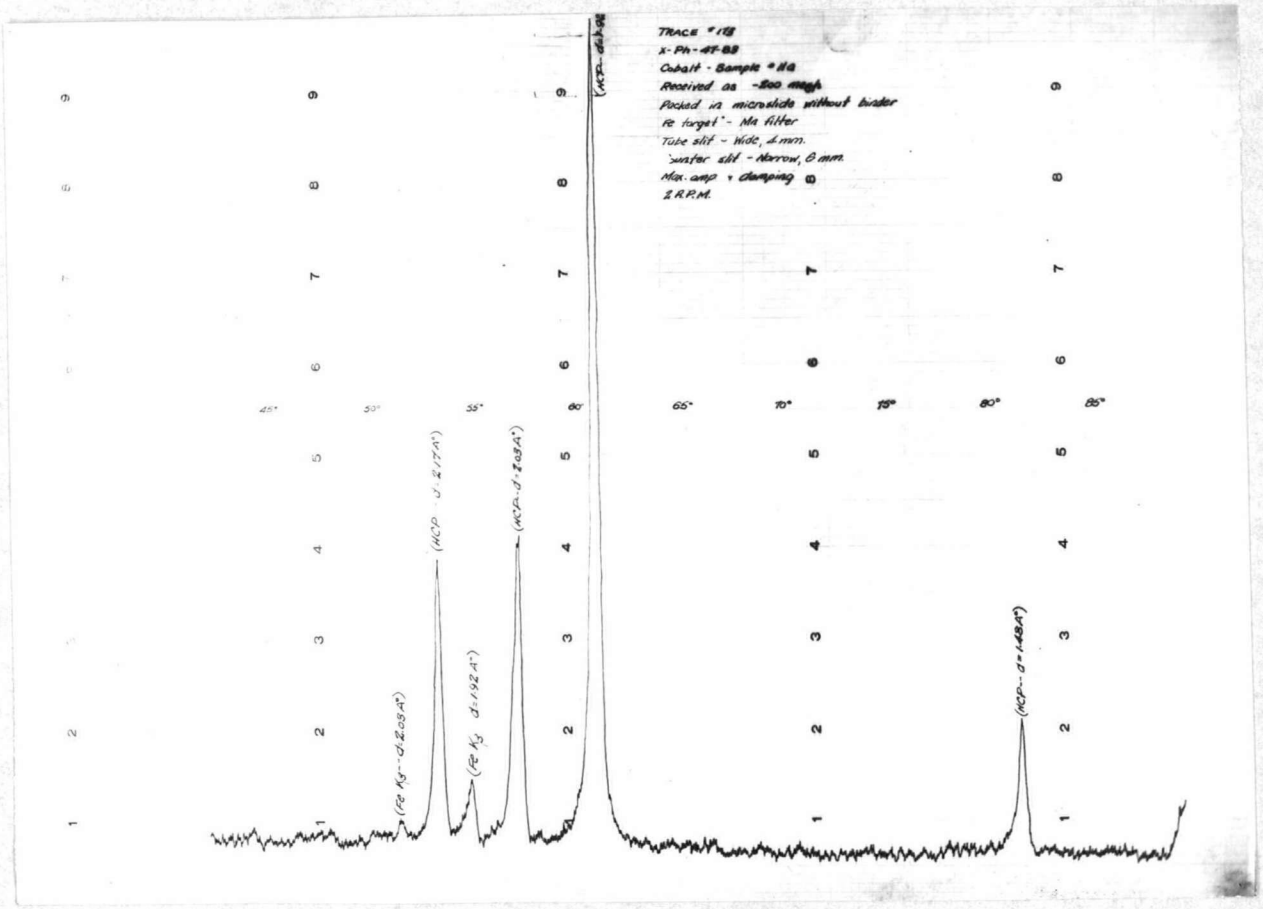


Fig. (14). X-ray Diffraction Pattern of 300°C. Cobalt
90% H.C.P. - 10% F.C.C.

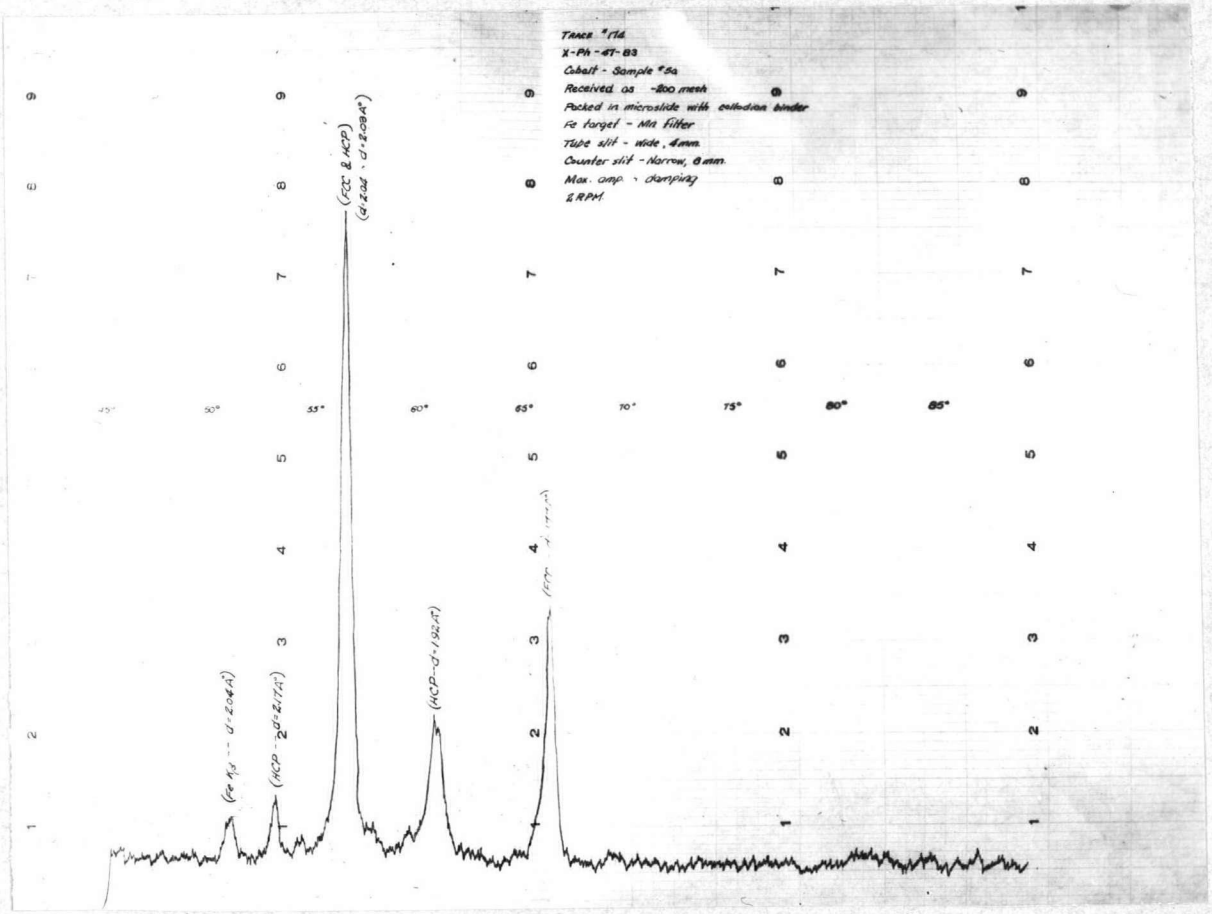
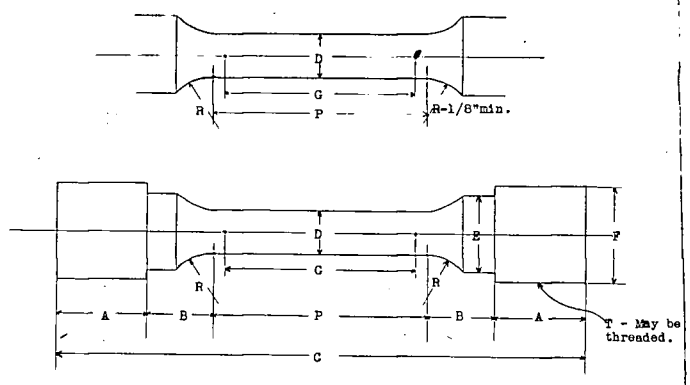


Fig. 15. X-ray Diffraction Pattern of 700°C Cobalt
14% H.C.P. - 86% F.C.C.

STANDARD U. S. MACHINED ROUND TEST PIECE.



Specimen	D	G	P	A	B	C	E	F	T
1/2"	.500 ±.005	2	2-1/4	1	5/8	5-1/2	19/32	3/4	3/4--10 Thrds.
7/16"	.438 ±.004	1-3/4	2	7/8	5/8	5	1/2	5/8	5/8--11 Thrds.
3/8"	.375 ±.003	1-1/2	1-3/4	3/4	1/2	4-1/4	29/64	9/16	9/16-12 Thrds.
5/16"	.313 ±.002	1-1/4	1-1/2	5/8	1/2	3-3/4	25/64	1/2	1/2--13 Thrds.
1/4"	.250 ±.001	1	1-1/4	1/2	3/8	3	11/32	7/16	7/16-14 Thrds.
3/16"	.188 ±.001	3/8	1	1/2	3/8	2-3/4	9/32	3/8	3/8--16 Thrds.
1/8"	.125 ±.001	1/2	3/4	3/8	5/16	2-1/8	3/16	1/4	1/4--20 Thrds.

Note 1. These specimens may have either headed or threaded ends, thread dimensions being given under T in table.
Note 2. Radius R to be equal to or greater than diameter D.

Fig. (16). Standard U.S. Machined Round Test Piece.

Photomicrographs of Green Cobalt Powder Compacts.
(figures 17 - 22)

Cobalt powder produced by hydrogen reduction of cobaltous chloride at 700°C.

Compacting pressure - as under each figure.

Magnification - 675X.

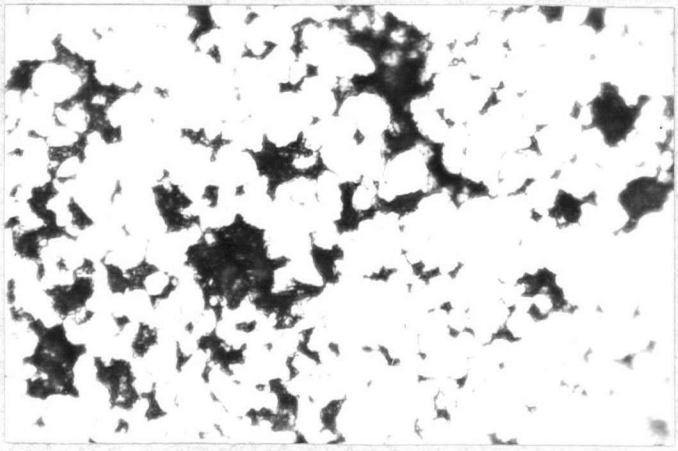


Fig. (17).

20 tons / sq. in.

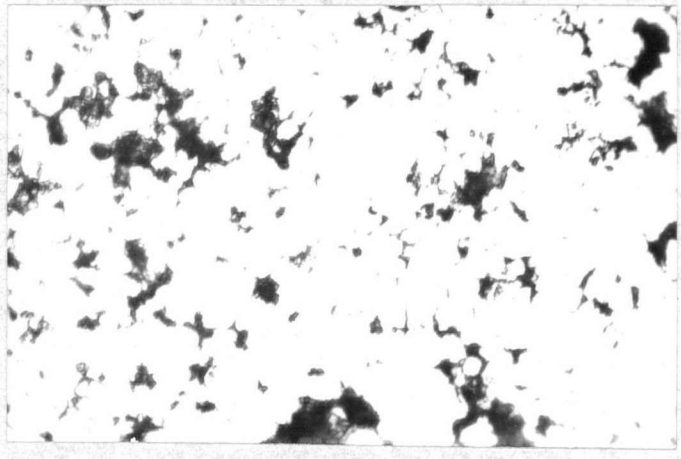


Fig. (18).

40 tons / sq. in.

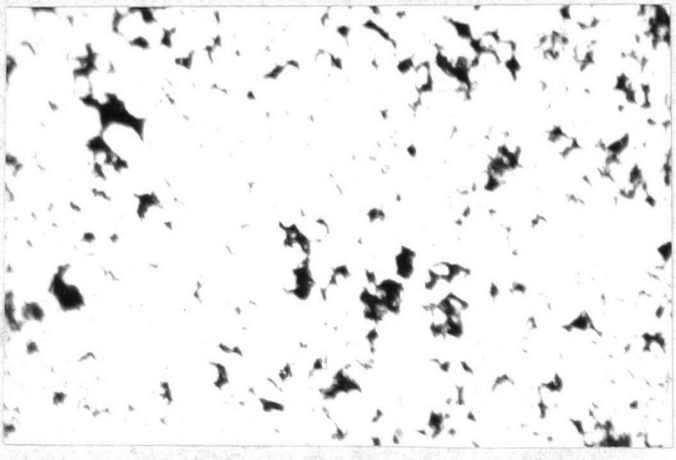


Fig. (19).

50 tons / sq.in.

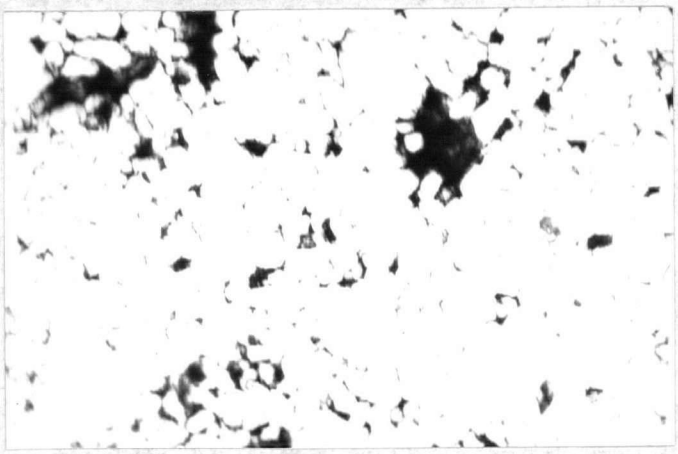


Fig. (20).

60 tons / sq. in.

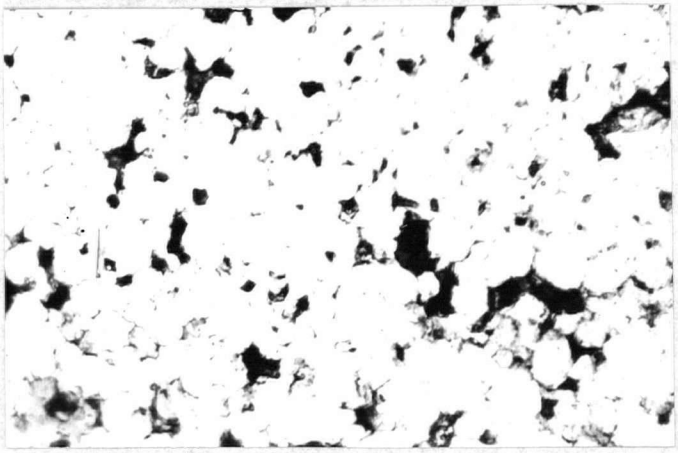


Fig. (21).

80 tons / sq. in.

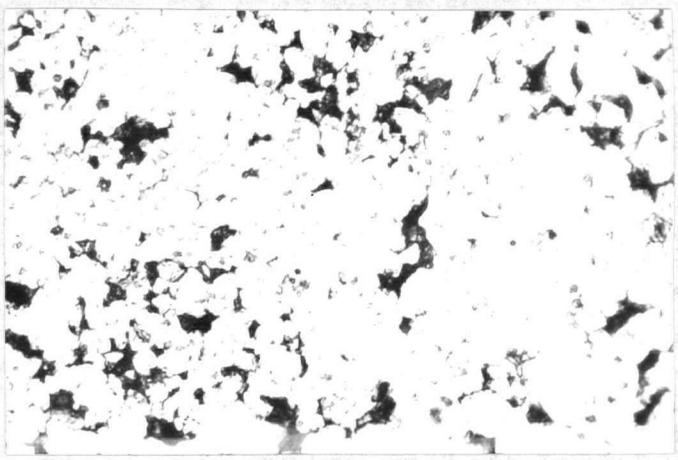


Fig. (22).

100 tons / sq. in.

Photomicrographs of Sintered Cobalt Powder Compacts.
(figures 23 - 28)

Cobalt powder produced by hydrogen reduction of cobaltous chloride at 700°C.

Compacting pressure - as under each figure.

Sintering temperature - 1600°F. in hydrogen for 2 hours.

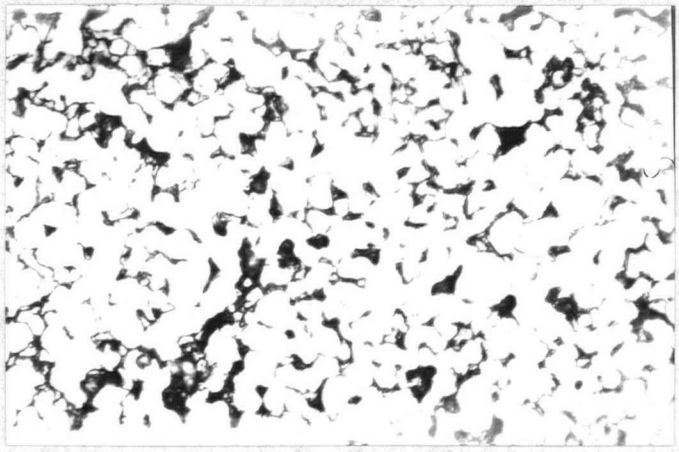


Fig. (23).
20 tons / sq. in.

Fig. (24).
40 tons / sq. in.

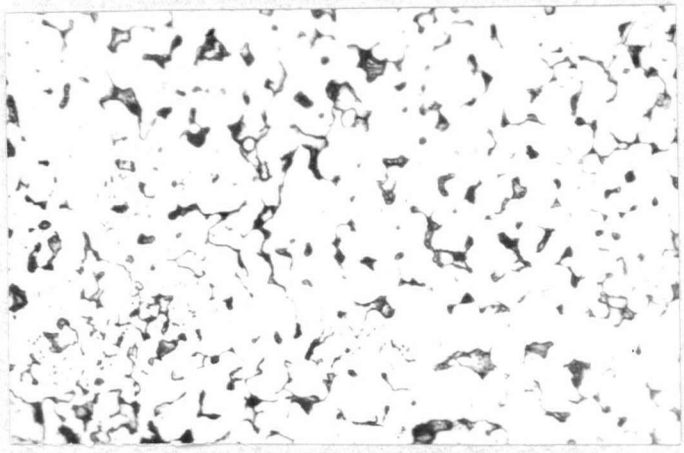


Fig. (25).
50 tons / sq. in.

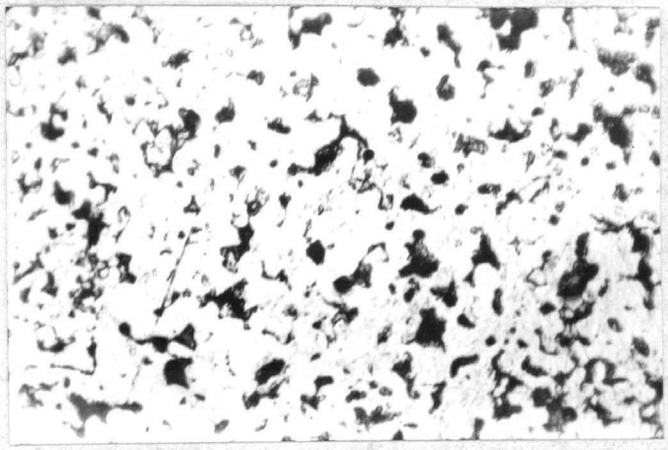


Fig. (26).

60 tons / sq. in.

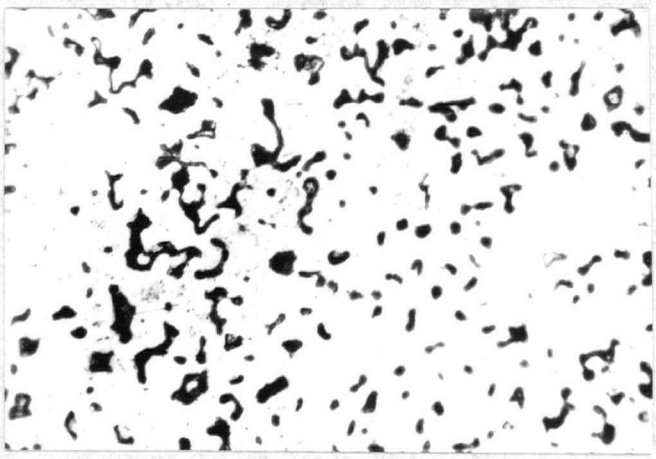


Fig. (27).

80 tons / sq. in.

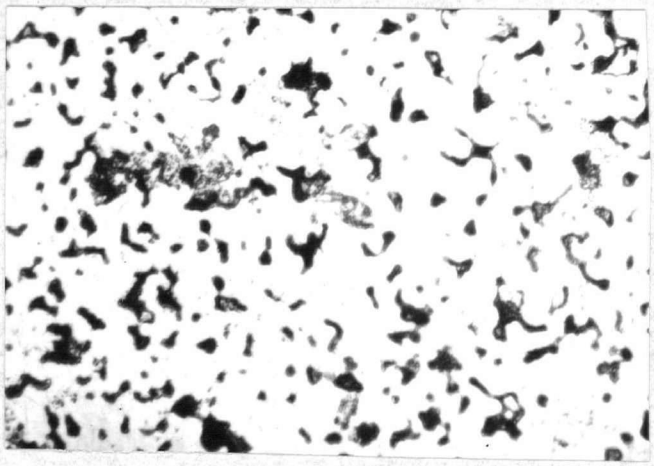


Fig. (28).

100 tons / sq. in.

Photomicrographs of Sintered Cobalt Powder Compacts.
(figures 29 - 33)

Cobalt Powder produced by hydrogen reduction of cobaltous chloride at 700°C.

Compacting pressure - 50 tons / sq. in.

Sintering temperatures - in hydrogen for 2 hours at various temperatures as listed under figures.

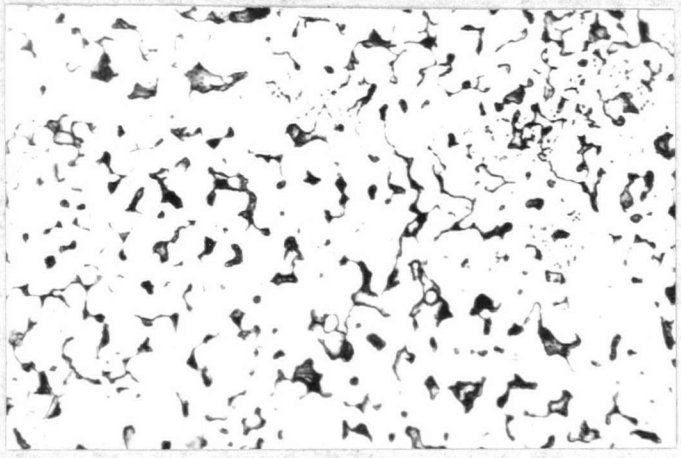


Fig. (29).
1600°F.

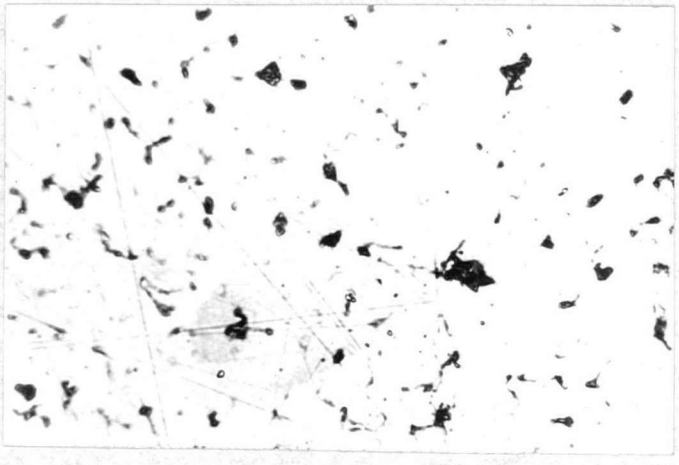


Fig. (30).
1700°F.

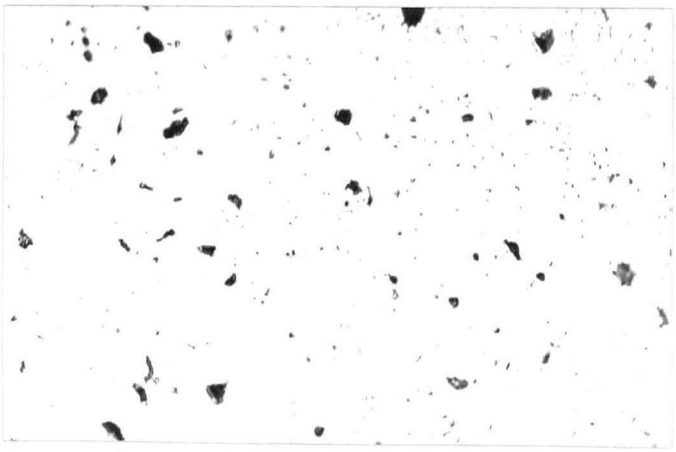


Fig. (31).
1800°F.

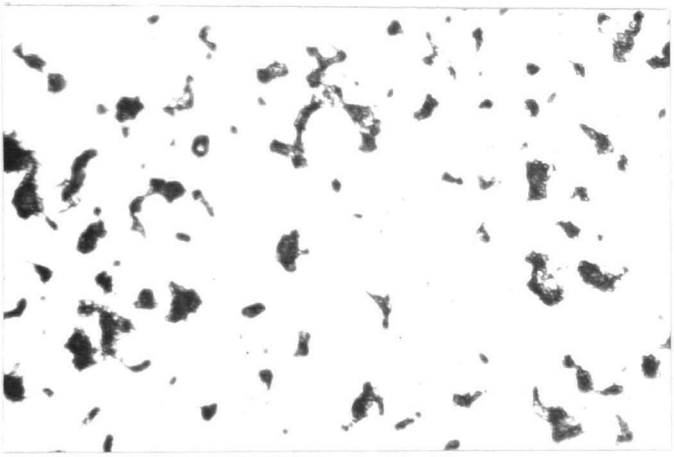


Fig. (32).
1900°F.

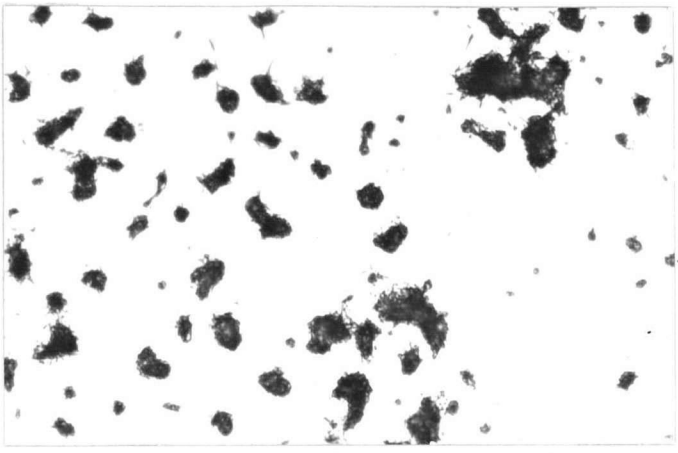


Fig. (33).
2000°F.

Photomicrographs of Sintered Cobalt Powder Compacts.
(figures 34 - 36)

Cobalt powder produced by hydrogen reduction of cobaltous chloride at 700°C.

Compacting pressure - 50 tons / sq. in.

Sintering time - in hydrogen at 1600°F. for various sintering times as listed under figures.

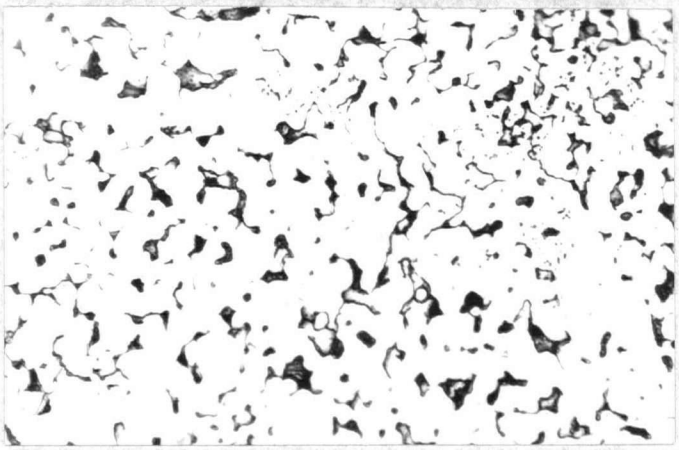


Fig. (34).
2 hours.

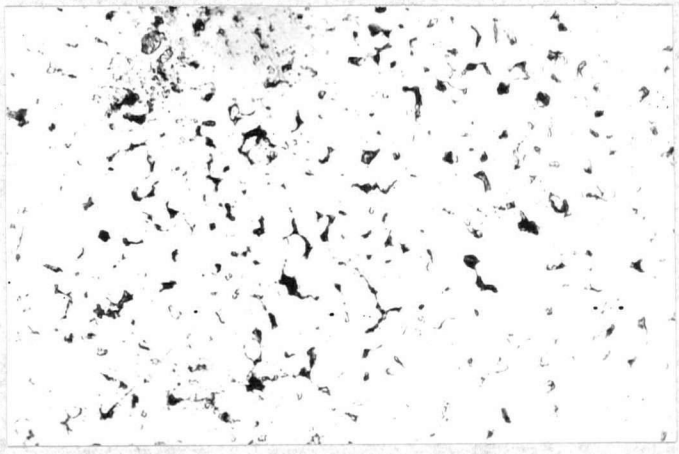


Fig. (35).
4 hours.

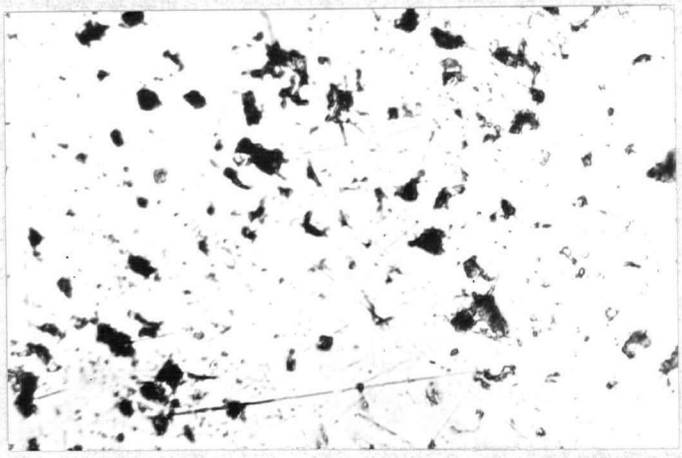


Fig. (36).
8 hours.

Photomicrographs of Commercial Cobalt Powder Compacts.
(figures 37 - 38)

Commercial Cobalt Powder.

Compacting pressure - 50 tons / sq. in.

Fig. (37). - green compact.

Fig. (38). - sintered in hydrogen at 1600°F. for 2 hours.

Magnification - 675X.

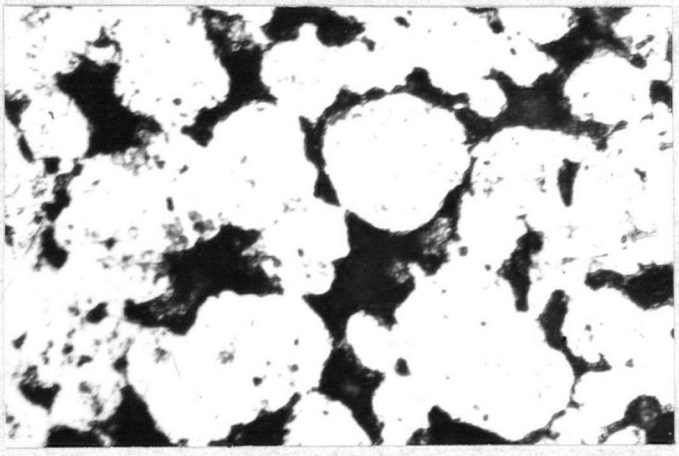


Fig. (37).
green.

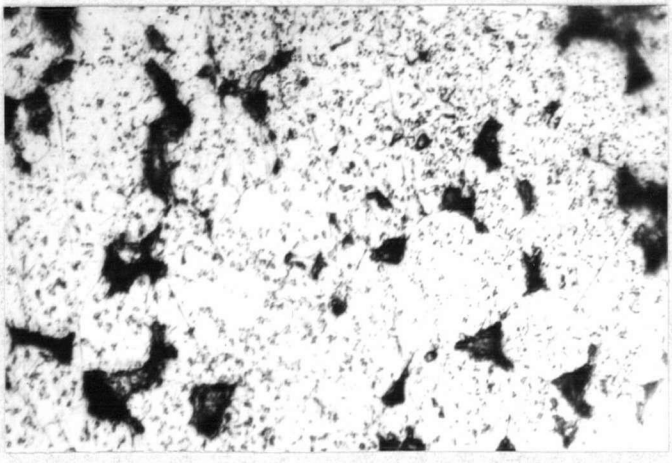


Fig. (38).
sintered.

11. Production of Single Metal Crystals

The work at this time was confined to two of the methods for large grain growth:

(a) recrystallization from the solid state and (b) crystal formation in the melt.

Of these two methods only one proved favourable to the growth of large crystals in metals of high melting points.

The materials used in the tests were:

(a) Norway iron bar stock

(b) Armco ingot iron C = 0.03%

(c) Pure cobalt.

The recrystallization method consists of plastically deforming the metal and reheating very slowly to elevated temperatures. The amount of plastic deformation is critical.

Compressive deformation was used in the first tests performed. Small specimens of enamelling steel (Armco ingot iron 0.03% C) were compressed by a manually operated hydraulic press after annealing in hydrogen at 1670°F. After compression, the specimens were heated for 4 hours in a hydrogen atmosphere at 1275 - 1280°F (that is, at a temperature above the recrystallization temperature for pure iron).

The grain size of the annealed specimens was about No. 1 on the A.S.T.M. grain size chart. The

maximum grain size obtained by the foregoing procedure was approximately 6 - 7 mm.

Reductions in thickness used were 0.6, 1.2, 3.1, 5.3, 8.7, 11, 17, and 21%. The increase in grain size occurred only in those specimens with 5.3% reduction in thickness or less, and as mentioned before, the maximum grain size obtained was 6 - 7 mm. Those specimens reduced more than 5.3% appeared to have an A.S.T.M. grain size of 3.

In addition to these ingot iron compression specimens, Norway iron specimens were compressed to a reduction in thickness of 1 - 2% and heated to 1275°F in a hydrogen atmosphere. Once again small grains resulted. Although Norway iron is very pure, it contains many slag inclusions which might cause small grains due to grain nucleation at many points.

Further tests on compressed specimens were abandoned because the procedure failed to show promise of producing larger grains. It is not impossible to produce large grains by compressive deformation, however, since large grains have been frequently found in sheet steel after rolling operations.

At this time an article appeared by F. G. Stone[36] showing photographs of grain growth in iron tensile bars. The process for growth consisted of plastically deforming the bars in tension and reheating slowly

to 1670°F. A similar process was tried on ingot iron sheet. The tension test bars were filed out of 16 gauge sheet with a three-inch guage length. These tension specimens were deformed to a 2% plastic strain in three inches in the laboratories of the British Columbia Research Council. The specimens were then inserted into a tube furnace at 800°F in a hydrogen atmosphere. The tube temperature was gradually increased at a rate of 200°F per day, by means of a clockwork mechanism connected to the pyrometer control, until 1660°F was reached. Care was taken to avoid passing 1670°F, the temperature of the alpha to gamma transformation in pure iron. The current to the furnace was controlled by a Variac transformer to keep the temperature steady and to prevent overshooting. Absence of thermal fluctuations would keep crystal nucleation to a minimum.

This process yielded crystals up to 1½ inches in length, some of which were the full width and thickness of the specimens. The largest crystals formed at the shoulder fillets but, generally, the whole section between the shoulders was composed of large crystals. Figure 39 shows two bars after treatment. These were the first single crystals obtained but were not the largest grown by this procedure.

A modification of the foregoing process was used on two other tensile specimens of ingot iron. Once again the specimens were deformed to 2 per cent plastic strain in 3 inches. These specimens were inserted into the cold end of a tube furnace. The centre zone of the furnace was maintained at a constant temperature of 1660°F. The specimens were drawn into the hot zone at a rate of 1.2 mm per hour and finally into the cold zone at the other end. The results from the procedure were unsatisfactory. Although the deformation with subsequent reheating process was effective in producing large single crystals in the iron specimens, it was ineffective in producing single crystals in a cobalt specimen. The reasons for this inability have not been determined. However, possible explanations may be that (a) the cobalt specimen was small and made controlled deformations difficult, (b) too few tests were made because of the scarcity of pure bar or sheet cobalt, and (c) the peculiar transformation characteristics of cobalt presented complications not present when working with iron samples.

Failure to obtain single crystals of cobalt by the recrystallization method lead to experiments for producing large crystals from the molten state. The formation of large crystals of iron and cobalt present difficulties not encountered in metals of lower

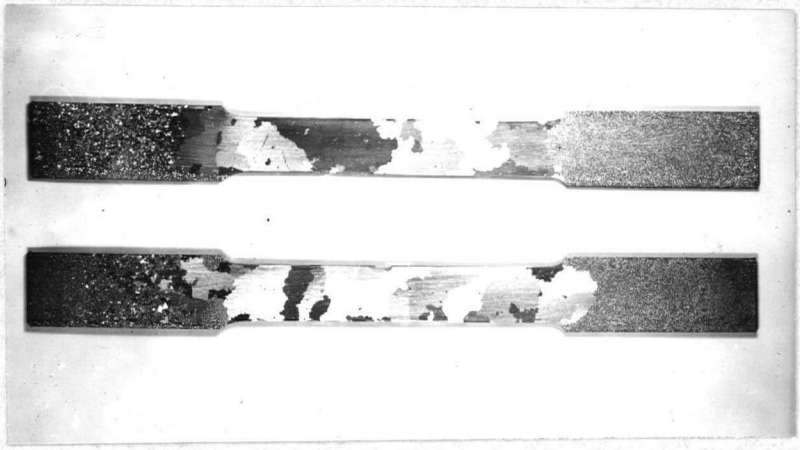


Fig. (39). Grain Growth in Iron Tensile Specimens.
(one-half size)

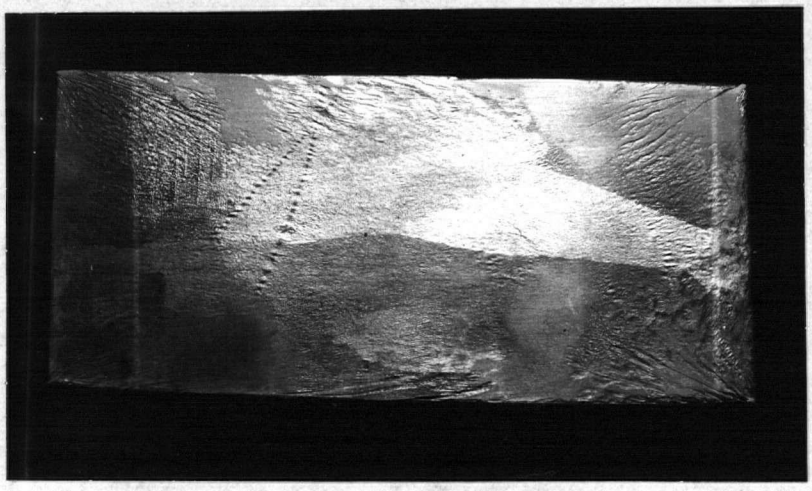


Fig. (40). Grain Growth in 2S Aluminum Sheet.
(one-half size)

melting points. As an example, single crystals two to three inches in length were formed from the molten state in 2S aluminum sheet with no special precautions. The method of L. Beaujard and P. Lacombe[39] was followed generally. A 10°C temperature gradient between the ends of the sheet specimen was not necessarily attained. The natural temperature gradient found in the box furnace was used. The large grains are shown in figure (40).

At 2900°F, however, the oxidation of iron and cobalt is very rapid, and, for this reason, the specimens could not be melted in an open crucible to give sound cast metal. Some specimens were sealed after evacuation in silica tubing. This was unsatisfactory also. At temperatures approaching 3000°F, the silica tube begins to soften, and on prolonged heating a phase change takes place in the silica so that on cooling only a chalky residue is left. Grains of cobalt up to 2 mm were produced by this procedure but, in each case, carbon pick-up was evidenced in the microstructure.

12. Determination of Crystal Orientation

The orientation of the single crystals must be determined before physical properties can be obtained because single crystals have directional properties. The orientation may be determined completely by X-ray, the Greniger method,[35] or the etch-pit method.

However, if one of the important crystallographic planes, (001), (110), or (111), of an iron single crystal, produced by recrystallization after deformation in tension followed by reheating, were in the surface plane of the crystal, it could very easily be checked by a procedure presented by H. J. Williams, R. M. Bozorth, and W. Shockley[43] in their work on magnetic domain patterns in silicon ferrite.

The domain patterns on the iron crystals grown by the recrystallization method were made by two engineering physics students D. Shaeffer, L. Couling. Photographs of these patterns appear in figure (41).

The shape of the patterns in these photographs indicate a slight waviness in the (001) plane due to polishing technique. However, the patterns show that the (001) crystallographic plane is substantially in the plane of the specimen surface.

The procedure used in preparing these iron crystals was essentially the same as that used by Williams, Bozorth, and Shockley. The surface of the specimen was polished manually to a metallographic surface through grades 2, 1, 0, 00, 000 emery paper, 600 alundum on a wax lap, and 1 hour suspension of levigated alumina on a cloth lap. The specimen was then electrolytically polished in a bath composed of 100 grams solid chromic acid, Cr_2O_3, and 900 grams of 85% solution of phosphoric acid to remove cold

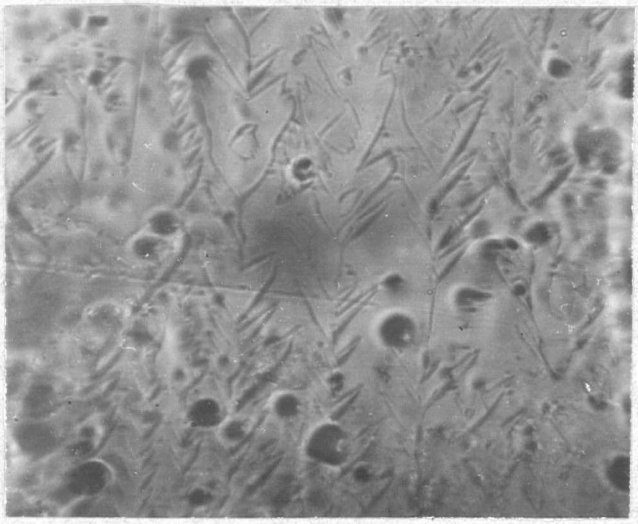


Fig. (41). Domain Pattern in Iron Single Crystal.

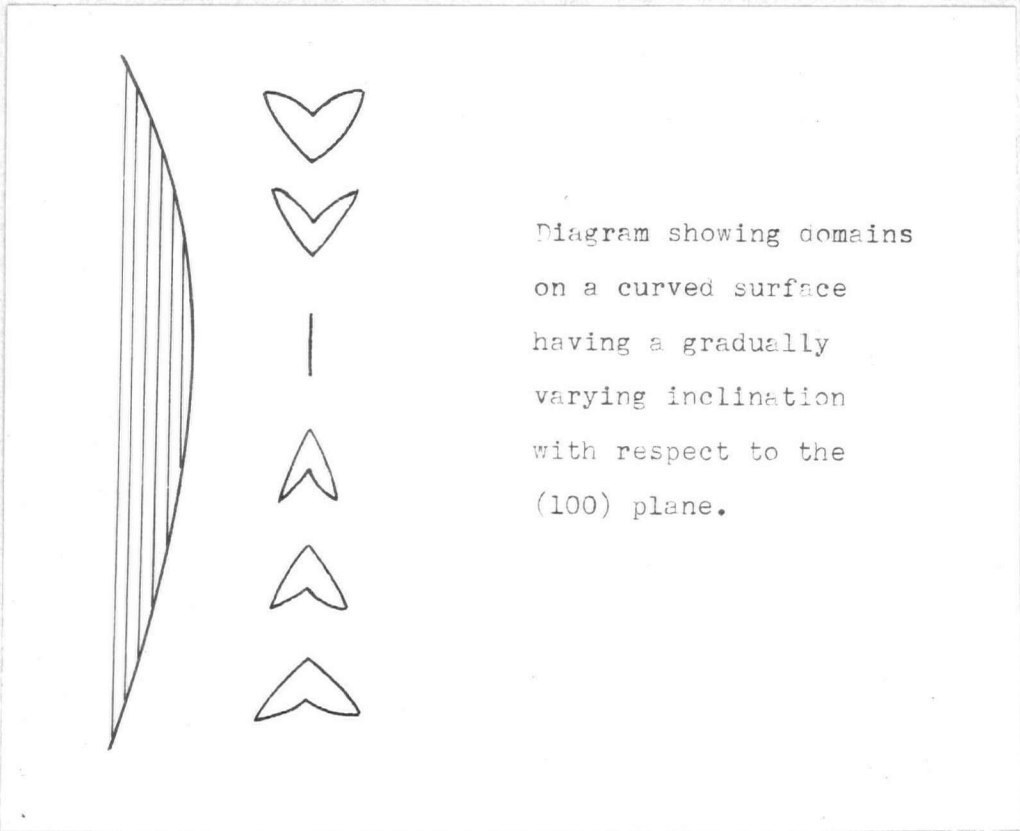


Fig. (42). Diagram of Domains on a Curved Surface.

working and surface flow caused by manual polishing. The bath was heated to 90°C and electrolysed with specimen as anode and copper rod as cathode. Polishing proceeded at 10 - 20 amperes per 1-2 square centimeters for about 5 minutes.

A colloidal suspension for the patterns was prepared. The suspension consisted of 2 grams hydrated ferrous chloride ($FeCl_2 \cdot 4H_2O$), 5.4 grams of hydrated ferric chloride ($FeCl_3 \cdot 6H_2O$), 300 ccs of hot water, 5 cc of NaOH solution added with stirring. The precipitate of Fe_3O_4 was washed and added to one litre of a 0.5% soap solution and the whole was boiled for a short time. A drop of the colloidal suspension was placed on the crystal surface and a thin microscope cover slide was placed on the drop. The iron specimen was then observed at 700 diameters.

This examination revealed that the (001) plane was very nearly (within 3 degrees) in the surface plane of the crystal. This result was fortuitous and enabled hardness tests to be made immediately since the specimen did not need to be cut and polished to get the (001) plane in the specimen surface.

The interpretation of these domain patterns is shown diagrammatically in figure (42). The straight line represents zero inclination to the specimen

plane. The pattern broadens as the inclination increases.

13. Knoop Hardness Variation with Crystal Orientation

This phase of the research is to show how the Knoop diamond hardness measured on one of the major crystallographic planes of a single crystal varies with the crystal orientation.

The Knoop diamond tests were made on the (001) plane of the specimen at various angles about a point, through 360 degrees. The hardness indentations were made with a Wilson Tukon tester equipped with a Knoop diamond indenter. A load of 300 grams was used throughout the tests. The diamond diagonal lengths were measured and the angle that the diagonal makes with one of the specimen edges was measured using the Leitz Metallograph microscope, calibrated stage, and ground glass in the camera. Figure (43) shows the diamond penetrations.

In order to index the indentation diagonal to the ‹110› direction, it was necessary to determine the ‹110› direction relative to the specimen edge. This was done by the etch-pit method outlined in Barrett.[44] The specimen was etched in 1:4 HNO_3(conc):H_2O solution for one minute. The specimen was examined under the binocular microscope at 80 power with oblique lighting. The ‹110› direction is at an angle of 45 degrees to the crystal

Fig. (43). Knoop Diamond Hardness Penetrations in Pure Iron Single Crystal. (magnification 115X)

TABLE IX.

KNOOP HARDNESS IN IRON SINGLE CRYSTAL.

TABLE IX.

Impression Number	Knoop Hardness	Angle θ from <110> Dir.
1	121.0	-11.3
2	121.0	+16.0
3	111.0	53.2
4	131.0	81.4
5	136.5	108.0
6	121.0	132.6
7	131.0	175.9
8	121.0	205.7
9	116.0	242.0
10	136.5	280.1
11	116.0	314.7

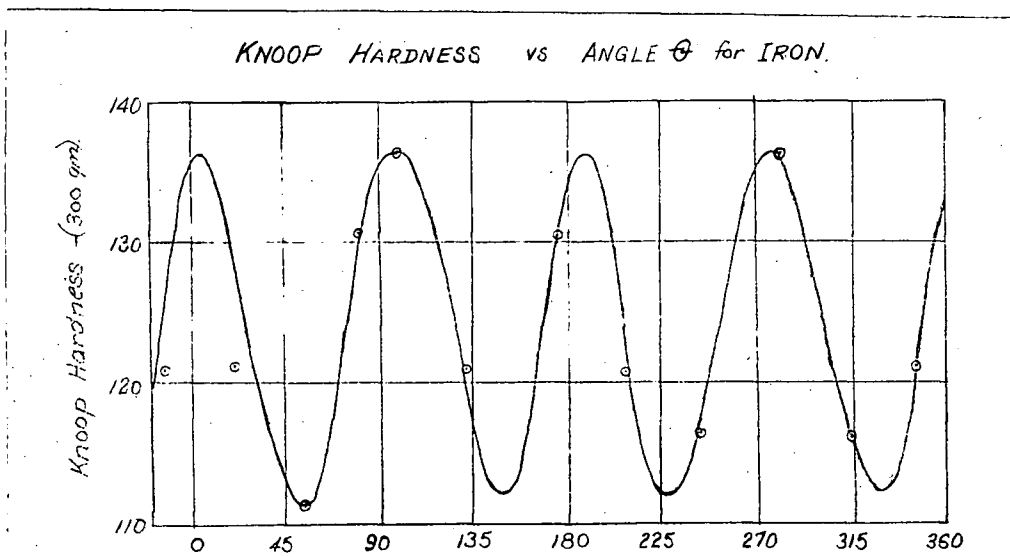


Fig. 44. θ - Angle between Diagonal & <110>.

Fig. (44). Angle θ vs Knoop Hardness.

edge.

The Knoop diamond hardness varies from 111 to 137 depending on the angular relation to the <110> direction. The results are given in Table (IX) and graphically in figure (44). These results show how the Knoop hardness of a single crystal of pure iron depends on the orientation of the crystal. The hardness has a 22 per cent variation and the hardness values repeat every 90 degrees in the {001} plane.

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