

THE α $\rightleftharpoons$ ϵ TRANSFORMATION IN COBALT WITH PARTICULAR
REFERENCE TO THE USE OF COBALT IN CEMENTED CARBIDES.

A thesis presented to the Faculty of Engineering,
University of the Witwatersrand,
in fulfilment of the requirements for the degree of
Doctor of Philosophy

by

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UNDERTAKING

I hereby certify that this is my own work, and
that it has not been submitted for the degree of
Doctor of Philosophy at any other University.

A handwritten signature in dark ink, appearing to read 'Rees', with a horizontal line drawn underneath it.

G.J. Rees

August 1972

ACKNOWLEDGMENTS.

Due acknowledgment is made to Dr. B. Young, Manager of Research, Boart and Hard Metal Products (S.A.) Limited, for permission to pursue the work concerned, during the course of employment at the Boart Research Laboratory. The author acknowledges the assistance offered to him by Mr. C.J. Guykers with respect to the chemical assays described, and the assistance of Mr. J. Miller, for the computer evaluation of the correlation coefficients described in Chapter 6. Thanks are due to the author's typist, Mrs. S. Troskie, and to Mr. C. Tavares, for the preparation of the line drawings. The author further wishes to record his sincere appreciation for the assistance and encouragement offered to him by his supervisor, Professor D.D. Howat, throughout the entire investigations.

SUMMARY

The $\alpha \rightleftharpoons \epsilon$ transformation in cobalt with particular reference to the use of cobalt in cemented carbides.

A study of the reduction of black cobalt oxide, using hydrogen as the reductant, showed that the temperature and time used for reduction exerted a profound influence on the proportions of face centred cubic (α) and hexagonal close packed (ϵ) cobalt allotropes obtained in the reduced metal powder. Reduction under certain conditions yielded a faulted hexagonal cobalt powder product which contained stacking faults.

The influence of oxygen and titanium on cobalt materials showed that these impurities did not stabilise the proportions of either the cubic or hexagonal phases under the conditions, which were used.

The grinding of cobalt powders from different sources showed different tendencies towards agglomeration, when acetone was used as the milling fluid. It was found that powders which contained an initially higher proportion of the hexagonal phase had a strong tendency towards agglomeration during the initial stages of grinding.

The importance of the different phases of cobalt present in the metal powders, and their different agglomeration tendencies on grinding, on the milling required for satisfactory densification of cobalt - tungsten carbide compacts has been shown; it was

found that hard metal alloys prepared using powders with an initially higher proportion of the hexagonal phase required less milling to achieve a given sintered density, than did mixtures prepared with other cobalt powders.

A correlation analysis between the properties of the milled hard metal powders and the properties of the sintered compacts was carried out; it was found that the most important correlation was between the specific surface area of the milled hard metal powder and the coercivity of the sintered product.

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CHAPTER 1.

Introduction and Literature Survey

1.1 Introduction:

Of the metals of the iron triad of the periodic table, cobalt has been found to be the most satisfactory binder metal for cemented carbide alloys. Several reasons have been advanced for this.⁽¹⁾ Iron and nickel have recently been used, and found to be suitable binders provided certain precautions are observed in the carbon content of the alloys,⁽²⁾ but only a small number of specialised alloys have been made using these binder metals. Thus although the major part of cobalt produced is used in the manufacture of high temperature steels and permanent magnet alloys, an important application of cobalt is its use, in powder form, for the fabrication of the technologically important hard metal alloys.⁽³⁾

In industry, it is well known that nominally identical batches of hard metal alloys do not behave in the same way during sintering.⁽¹⁾ An important variable of manufacture, which has not previously been thoroughly investigated, is the influence of different qualities of cobalt powder during the various processing stages. It has been found that the use of cobalt powders from different sources, with different characteristics, is an important consideration in this respect.

During the manufacture of hard metal alloys, a large number of powder properties and sintered compact properties are involved; a thorough mathematical

inter-relation between these properties has never been formulated.⁽⁴⁾ This has also been studied in the work described here.

The most important fabrication step in the production of cemented carbide alloys is the milling process where the cobalt and carbide powders are milled together under a protective fluid, in the presence of hard metal grinding balls.⁽⁵⁾ Therefore consideration of the characteristics of various cobalt metal powders and their behaviour during grinding is of importance.

The metal cobalt undergoes a martensitic transformation, from one close packed structure to another at 420°C.⁽⁶⁾:

i.e. hexagonal close packed (ϵ) structure $\xrightarrow[\text{cooling}]{\text{heating}}$ face centred cubic (α) structure.

It is generally recognised that the phase composition of any particular specimen of cobalt depends on its previous thermal and mechanical history, even in materials of 99.99% purity.⁽⁷⁾ This is a consequence of the low free energy change associated with the transformation; in addition the stacking fault energy, which is zero at the transformation temperature, is very low at room temperature.⁽⁸⁾ The free energy change associated with the transformation has been estimated⁽⁹⁾ to be about 100 cal./g. atom and the stacking fault energy about 20 ergs./cm². Thus stacking faults may easily occur in h.c.p. cobalt as a result of phase transformation and also plastic deformation.

Cold working can transform the face centred cubic allotrope of cobalt into the hexagonal close packed modification by shear;⁽¹⁰⁾ this phenomenon has been studied by many workers on massive cast and forged materials, and also on single crystals. However, in the case of cobalt powders, with particle sizes of 1-2 μ (with which this work is primarily concerned) some additional complicating factors can arise; for example cold work in the form of milling of the powders, can, in addition to causing transformation from the f.c.c. to h.c.p. structures, result in the agglomeration of the powder particles during the initial stages of grinding.

Another aspect of the low transformation energy is a consideration of the phases of cobalt produced by the hydrogen reduction of black cobalt oxide under various time and temperature conditions.

Therefore the main object of the work described here was to study the characteristics of cobalt metal powders produced under various conditions, and the behaviour of cobalt powders with different characteristics during wet grinding. The ultimate aim was to apply these findings to the milling and sintering processes involved in the fabrication of hard metal alloys. A fourth objective was to attempt to correlate the milled hard metal powder properties with those of the sintered compacts.

During the course of these investigations, a number of other topics of interest were found and briefly pursued:

- (a) In view of the importance of oxygen in all finely divided metal powders, the influence of adsorbed oxygen on finely divided hexagonal cobalt metal powder was studied.
- (b) Since titanium is the only metal (apart from cobalt) in the first transition series, which has a hexagonal close packed structure at room temperature, the influence of titanium on the phase structure of cobalt was briefly investigated.
- (c) A limited amount of work was carried out on the grinding of cobalt filings.

The experimental methods used for examining the reduced and ground powders were:

- (i) X-ray diffraction analysis (using a Philips PW 1060 Diffractometer).
- (ii) The preparation of carbon replicas suitable for examination on a Philips EM 200 Electron Microscope.
- (iii) Some powder samples were also examined directly on a Cambridge Stereoscan Electron Microscope.
- (iv) Various chemical assays of the powders.
- (v) Measurement of particle size parameters of the ground powders, in particular, the specific surface area, using a Perkin Elmer Sorptometer.

For the reduction studies, a Wild Barfield retort furnace was used. Some reductions were studied in a Stanton Mass Flow Thermobalance.

All grinding experiments were carried out using either 800 ml. stainless steel mills or 8 litre mills, which fitted a vibratory grinding machine.

1.2 Literature Survey:

1.2.1 Summary of work carried out on the Allotropic Transformation in pure cobalt.

Hull,⁽¹¹⁾ in 1921, first recognised that cobalt metal could exist in two allotropic forms, namely a face centred cubic form, and a hexagonal close packed modification. At this early stage it was reported that the transformation on heating occurred at 477°C and at 403°C on cooling. Cast cobalt was found to be completely hexagonal.

Wassermann⁽¹²⁾ further investigated the transformation using rolled cobalt sheet, which was impure containing 1.94% Ni, 1.84% Fe and 0.64% Mn. His findings may be summarised as follows:

- (1) X-ray examination of the rolled cobalt sheet showed that only the hexagonal modification was present.
- (2) The hexagonal cold rolled sheet assumed a cubic structure at 450°C , and on cooling this cubic form did not spontaneously change back to the hexagonal structure without renewed cold rolling.

Wassermann recognised that the transformation could occur by simple shearing without grain disintegration, and that because both the f.c.c. and h.c.p. forms are both geometric arrangements of the densest packing of spheres, both structures could therefore be converted into one another by displacements of atom layers parallel to the base plane. This work showed that the transformation could be caused by cold working.

At about the same time, work on the allotropic transformation was carried out by Hendricks, Jefferson

and Schultz,⁽¹³⁾ and Sykes.⁽¹⁴⁾

The former group of workers studied the hydrogen reduction of black cobalt oxide in the temperature range 300 - 1000°C. Below a reduction temperature of 400°C the pure hexagonal modification was obtained. Between 420° and 920° the face centred cubic only was obtained, while material prepared at 1020° appeared to comprise both forms. This suggested the existence of a second high temperature hexagonal modification. The existence of this has been propounded and contradicted by subsequent workers in this field. Where X-ray studies have been conducted with a high temperature camera, it is generally accepted that no second high temperature hexagonal modification exists.⁽¹⁵⁾

Sykes⁽¹⁴⁾ investigated the effects of the physical form of the cobalt on the phases present. He found:

- (i) Filings produced from massive material consisted of the hexagonal modification only. X-ray investigation showed that these same filings, when annealed at 600°C contained a mixture of both allotropes.
- (ii) A fine cobalt powder produced by hydrogen reduction of black cobalt oxide consisted predominantly of the cubic modification, with faint traces of the hexagonal modification.
- (iii) The third material was the filings (i) dissolved in sulphuric acid and plated from solution onto a cobalt cathode. This was found to be a mixture of both modifications.

(iv) An operation such as screening of the fine cobalt metal powder increased the proportion of the hexagonal modification in the undersize fraction.

It is now well known that pure hexagonal cobalt can be deposited electrolytically onto a suitable electrode provided the pH is greater than 5.⁽¹⁶⁾

Fundamental developments in the knowledge of the allotropic transformation of cobalt are due to Edwards and Lipson⁽¹⁷⁾ and Wilson.⁽¹⁸⁾ These authors recognised that the structure of any one specimen of cobalt depended on its previous history. They concluded that as was to be expected from the close packed nature of the hexagonal and cubic phases, the lattices would take up specific orientations with respect to one another; i.e. the close packed {111} planes of the cubic structure would be parallel to the {0001} planes of the hexagonal form, while the lines of closest packing, namely, (110) of the cubic would be parallel to the (10 $\bar{1}$ 0) directions of the hexagonal structure.

Another important finding by Edwards and Lipson,⁽¹⁷⁾ explained theoretically by Wilson,⁽¹⁸⁾ was that in a two phase mixture the X-ray diffraction lines common to both hexagonal and cubic modifications are sharp, whereas the remaining hexagonal lines are a mixture of the sharp and diffuse type. The sharp lines are those with integral values of $(h-k)/3$ and l zero. These effects could not be explained by small crystallite sizes, and the effect was interpreted to mean that the hexagonal structure can be

faulted and could contain stacking faults.

A face centred cubic lattice is made up by repeating the three planes ABCABC, the close packed planes being stacked so that an atom in one plane lies in the hollow formed by three atoms in the plane below.⁽¹⁹⁾ The atoms of the planes designated by the same letters of the alphabet lie vertically above one another.

The hexagonal close packed lattice, in contrast, has a repeat pattern ABAB. If the regular stacking order in an f.c.c. lattice is disturbed by removing a plane, a stacking fault occurs. Instead of the series ABCABC, the order is now ABCABABC. This therefore corresponds to a stacking fault in an f.c.c. lattice; correspondingly in a hexagonal close packed lattice the presence of a stacking fault would appear as ABABABCABAB. Thus a stacking fault in h.c.p. material corresponds to a platelet of the f.c.c. material. Different estimates for the concentration of stacking faults in different samples of cobalt have been given by various authors.⁽²⁰⁾

Two types of stacking faults are now considered⁽¹⁹⁾ to exist, namely growth and deformation faults. Single interruptions of the stacking law in h.c.p. crystals are known as growth faults; these are introduced by atomic growth processes. Clusters of two growth faults on successive atomic planes are known as deformation faults.

In terms of the notation described above, a growth fault would be described for an h.c.p. lattice as: ABABARACAB, and a deformation fault as ABABABACACAB. Stacking faults in metals and alloys have important

influences on mechanical properties e.g. yield strength and creep velocity.⁽⁸⁾ By means of stacking faults, the very close inter-relationship between h.c.p. and f.c.c. lattices can be visualised; a perfect h.c.p. lattice corresponds to a faulted f.c.c. lattice with a growth fault introduced at every atomic plane. Twin formation⁽²¹⁾ in f.c.c. crystals is closely related to the introduction of stacking faults; a deformation fault at every plane of an f.c.c. structure yields the f.c.c. twin crystal.

All diffraction lines of major intensity of the hexagonal and cubic structures of cobalt virtually coincide with two important exceptions; the (200) cubic line is well separated from any of the hexagonal lines, and the (10 $\bar{1}$ 1) hexagonal line is well separated from any cubic lines.⁽⁷⁾

As mentioned in 1.1 the difference in free energy between the two forms has been estimated to be about 100 cal./g. atom, and for a single crystal specimen the enthalpy change attendant on the transformation has been found to be 112 cal./g. atom, the exact value depending on the thermal history and microstructure of the specimen.⁽²²⁾

Over the past thirty years, numerous investigators have studied the phase transformation in pure cobalt using a variety of techniques. The early investigations are summarised in Table I.⁽²³⁾ Early investigators used rather impure materials. The more recent work has considered the crystallography and kinetics of the f.c.c. $\rightleftharpoons$ h.c.p. transformation in cobalt.⁽⁴³⁾

TABLE I.
Summary of Investigations into the Allotropic Transformation
in Cobalt (after 23)

Investigator	Method of Investigation	Transformation point °C
Maschumoto 1926	Electrical conductance, coefficient of thermal expansion, magnetic measurements, X-ray method.	422 - 477° when heating. 360 - 403° on cooling.
Umino 1925 - 27	Thermal measurements.	460° and 1150°C.
Schulze 1927	Variation of resistance with temperature, coefficient of thermal expansion.	400° - 500°. 452° when heating falling to 100° on cooling.
Schulze 1927	Thermal Electric temperature gradient.	465° - 470°.
Sekita 1927	X-ray method.	447°
Wevell, Maschumoto 1929	Dilatometric method.	465°.
Uffelman 1930	Optical interference.	450° when heating. 330° when cooling.
Schulze 1930	Electrical Resistance.	444° - 467° when heating. 350° - 400° when cooling.

TABLE I. (Cont.)

Investigator	Method of Investigation	Transformation point °C
Hendricks et al.) Wassermann) Sykes)	See Text.	
Sykes, Graff 1935	Thermal analysis.	420°.
Seyboldt et al. 1935	Solubility of O ₂ in Cobalt.	440° and 850°.
Von Steinwehr, Schulze	Heat transmission.	380° - 420°.
Marick 1936	Electro-resistance and X-ray method in high temperature chamber.	492°.
Meyer 1937	X-ray method in high temperature chamber.	No transformation up to 1187°
Newkirk, Geisler 1953	High temperature X-ray camera.	450° - 1223° cubic lattice.
Michel, Drain Bridelle 1954	Thermo-magnetic investigations.	498° vacuum heating. 441° on cooling. 447° on heating in hydrogen.

Because of the strong influence of source, history and the presence of stacking faults, the quoted lattice parameters for cobalt vary widely.⁽⁷⁾

Another consideration is that since cobalt is strongly ferromagnetic, some magnetostriction will always be present in the ferromagnetic domains. Such magnetostriction can give rise to local stresses, and thus the potential energy is never quite as low as possible, and this could be a feature, which could contribute to a faulted structure.⁽⁷⁾

Summarising,⁽²⁴⁾ therefore, the characteristics of the allotropic transformation in pure cobalt:

- (1) Massive cobalt on heating undergoes a phase transformation from the ϵ (hexagonal close packed) to the α (face centred cubic structure) at about 420°C .
- (2) The transformation is essentially athermal in nature, because it does not occur at a fixed temperature, and depends on the previous thermal and mechanical history of the specimen. ? — ? x
- (3) In a thermal cycle of cooling and reheating the transformation is reversible, with, however, hysteresis being observed in the transformation temperature. On cooling the transformation is at 390°C , and this is referred to as the M_s temperature.
- (4) The amount of ϵ which forms from the α on cooling is dependent on the purity and particle size of the

material. Impure cobalt and a fine grain size inhibit the reaction from going to completion. Subsequent deformation below 390° can drive the reaction to completion.

- (5) The above characteristics have led the reaction to be classified as being of the martensitic type.

In cobalt, the transformation is considered to be purely martensitic, thermally activated growth being impossible because of insufficient energy.⁽²⁵⁾ The following evidence rules out diffusion playing any part in the $\alpha \rightleftharpoons \epsilon$ transformation:

- (a) The transformation has been found to be independent of cooling velocity, and rates from 1° per second to $1,000^{\circ}$ per second have been used.⁽²⁶⁾
- (b) The fact that moderate deformation at room temperature or below causes transformation, also rules out the possibility of a diffusion controlled reaction because of the very low diffusion rates at room temperature.

In certain cases⁽²⁷⁾ (e.g. zirconium) a structural transformation of the nucleation and growth type occurs in the neighbourhood of the transition temperature; but the character of the transformation alters at temperatures sufficiently far removed from the transition temperature. All evidence suggests that the transformation in cobalt is of a simple martensitic type.

However, where impurity atoms in cobalt alloys are concerned, nucleation and growth mechanisms can occur under equilibrium conditions.⁽²⁴⁾

The evidence cited above concerning the unimportance of diffusion suggests that the transformation must occur by some form of shear.⁽²⁰⁾

1.2.2 Characteristics of Martensitic Transformations.

Martensitic reactions are only possible in the solid state and the product has the same composition as that of the parent.⁽²⁷⁾ Bilby and Christian⁽²⁸⁾ have suggested that the most convenient experimental feature to characterise a reaction as martensitic is a characteristic change of shape on a flat surface by tilting the region so transformed. The tilting implies that the movements are regular and co-ordinated, and supported by the conclusion that an ordered structure remains ordered.

It has been mentioned that a structural transformation can be classed as martensitic if the atoms on a primitive lattice defined by a selected unit cell of the parent structure move to positions on a primitive lattice defined by some unit cell of the product structure, in such a way that the displacements constitute a homogeneous deformation.⁽²⁹⁾ However, although lattice correspondence is a very convenient definition of martensitic relations it, as stated, embraces some reactions that are thermally activated. In addition there are a number of reactions that are intermediate in character between the nucleation and growth, and the martensitic type, as was discussed in 1.2.1.

A definition which covers all types of martensitic reactions is to consider that the following occurs:⁽³⁰⁾

- (a) A homogeneous strain (an invariant plane strain) is responsible for the observed change in shape. This usually does not convert the initial lattice into the final lattice. This homogeneous strain results in a small dilation.
- (b) - (a) is followed by another strain which is responsible for the product lattice in its observed orientation, without resulting in any further change in shape. On a macroscopic scale this strain is inhomogeneous, but on an atomic scale it is considered that it is homogeneous, but accompanied by localised displacements which counteract the change in shape accompanying the homogeneous displacement. These local displacements can only be slip in the lattices. Since there is no dilation accompanying the second homogeneous strain, and this is assumed to be an invariant plane strain, the homogeneous strain is a simple shear. In terms of this theory, phenomenological relations have been found for a number of martensitic reactions by Bowles and his co-workers ⁽³⁰⁾ which are in agreement with the observed experimental facts of these transformations, i.e. the predicted and observed habit planes agree. The final equation of these phenomenological relationships has the following form:

$$\underline{S} = \left\{ 1 + \left[\underline{S} y_1 - y_1 \right] \underline{P}_2' \underline{S}^{-1} / (\underline{P}_2' \underline{S}^{-1} y_1) \right\} \\ \times \left\{ 1 + \left[\underline{S} y_2 - y_2 \right] \underline{P}_1' / (\underline{P}_1' y_2) \right\}$$

where S is the strain in its matrix representation

y is the position vector with co-ordinates y_1, y_2, y_3

p is an invariant plane strain in its matrix representation

The following are essential characteristics of martensitic reactions: (29)

- (1) Many thousands of atoms are involved in a co-operative movement.
- (2) As discussed previously thermally activated processes cannot be responsible for the transformation.
- (3) The amount of transformation is characteristic of temperature, but is independent of time. The velocity of reaction is thought to be very rapid.
- (4) Coherency of parent and product phases is necessary.
- (5) The transformation on cooling begins at a temperature M_S which may depend on the previous thermal and mechanical history of the specimen. This temperature is independent of the cooling rate.
- (6) Plastic deformation or even the application of elastic stresses may induce the transformation above the M_S temperature. The highest temperature at which the transformation temperature may be stress induced is known as the M_d temperature.

Together with the transformation in iron-manganese alloys the f.c.c. $\rightarrow$ h.c.p. allotropic transformation in cobalt is thought to constitute the simplest martensitic

where S is the strain in its matrix representation

ψ is the position vector with co-ordinates ψ_1, ψ_2, ψ_3

p is an invariant plane strain in its matrix representation

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Together with the transformation in iron-manganese alloys the f.c.c. $\leftrightarrow$ h.c.p. allotropic transformation in cobalt is thought to constitute the simplest martensitic

reaction.⁽³¹⁾ An f.c.c. structure is converted into an h.c.p. structure with ideal axial ratio $(8/3)^{1/2}$ by a homogeneous shear of $|S| = \frac{1}{\sqrt{2}}$ in a $\langle 11\bar{2} \rangle$ direction on a (111) plane, this being half the twinning shear. If this shear is homogeneous, only half the atoms are in their correct positions in the h.c.p. lattice. However, the required movements are extremely simple if the atomic {111} planes are regarded as being locked together in pairs during the shear. On an atomic scale this means that the transformation is accomplished automatically if a Shockley partial dislocation of Burger's vector $a/6 \langle 11\bar{2} \rangle$ moves through alternate atomic planes of a parallel set of {111} planes.

There are three equivalent shear directions in each (111) plane, the net effect on the atomic arrangement of a displacement in any one of these three directions being the same. This means that if the alternate planes do not move relative to one another, in a common direction, but randomly in three equivalent $\langle 11\bar{2} \rangle$ directions, there will be no macroscopic shape deformation, and accompanying strain energy. If each lattice plane separately nucleated, the stresses due to any accumulating net shear would certainly ensure that the three directions are utilised at random, giving a transformation with zero shape deformation. The crystallographic relationships between the phases in cobalt are therefore (111) f.c.c. $\parallel \parallel (0001)$ h.c.p. and the relationships between the crystallographic directions are $\langle 110 \rangle$ f.c.c. $\parallel \parallel \langle 11\bar{2}0 \rangle$ h.c.p.

This involves a shear of $19^{\circ} 28'$ of $a/6$ (112) of every two atomic planes with respect to the plane beneath, thus changing the ABABAB stacking of the h.c.p. form to the ABCABC stacking of the f.c.c. form. There is a 3.6×10^{-3} % volume increase on heating and on cooling an identical volume decrease occurs.⁽³²⁾ However, as mentioned in 1.2.1 the hexagonal phase produced is often faulted; spontaneously transformed specimens contain growth faults whereas specimens transformed under stress contain deformation faults. Because of the volume decrease on forming the h.c.p. phase, there is an associated small contraction normal to the habit plane so that the Burger's vector is not identical with that of a Shockley partial dislocation, but has an additional component out of the habit plane.⁽³¹⁾

Thus although the general features of the martensitic transformation for cobalt are known, because of the importance of prior thermal history and deformation, cobalt materials from different sources can give widely differing proportions of the two structures.⁽⁷⁾

1.2.3 The Influence of Impurities on the allotropic transformation in cobalt.

Two factors must be borne in mind when classifying the effects of alloying additions on the phase transformation of cobalt:⁽²⁴⁾

- (1) The addition of alloying elements will always alter the temperature at which the martensitic transformation can occur; however, changes in the martensitic transformation temperature are also

altered by other variables such as the purity and grain sizes as mentioned earlier.

- (2) The addition of alloying elements will alter the temperature range of thermodynamic stability of the face centred cubic and hexagonal close packed forms. The alloying additions may result in an expansion or contraction of the α phase field. Strictly the temperatures of occurrence of the martensitic transformation should be represented on a metastable equilibrium diagram.

The varying effects of cobalt alloying additions on the martensitic transformation in cobalt are shown in Figure 1.1.⁽²⁴⁾ Only two possibilities exist for a cobalt rich binary system. These are shown in Figure 1.2. The lines in Figure 1.1 are shown dotted to emphasise that they are not true equilibrium diagrams, and they indicate the temperature at which the martensitic reaction can occur. It will be seen that the ϵ cobalt must be thermodynamically stable before it can be formed martensitically from the α form. This is so during milling.

The fact that some authors have given the martensitic lines of transformation in phase diagrams has, it has been suggested,⁽²⁴⁾ led to some confusion in the literature.

Koster,⁽³³⁾ on the basis of his extensive work has summarised the effects of all the elements of the Periodic Table on the cobalt phase composition in a cobalt rich binary alloy. His summary is shown in Table II, but it

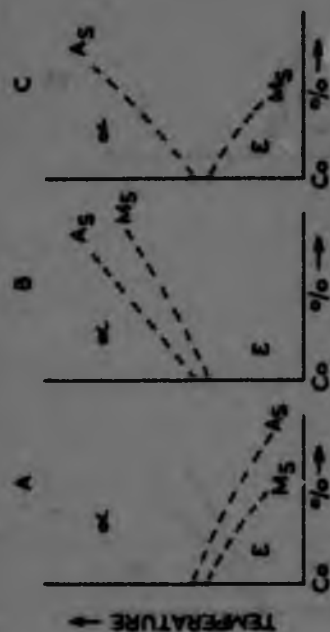


FIGURE 1.1:

VARIOUS POSSIBILITIES FOR THE EFFECTS OF ALLOYING ADDITIONS ON THE MARTENSITIC TRANSFORMATION TEMPERATURE OF COBALT ALLOYS

A: DECREASE OF BOTH M_s AND A_s TEMPERATURES

B: INCREASE OF BOTH M_s AND A_s TEMPERATURES

C: INCREASE OF A_s AND DECREASE OF M_s

IN A THERMAL CYCLE OF COOLING AND REHEATING THE CHANGE $\alpha \rightarrow E$ OCCURS AT THE M_s TEMPERATURE AND THE REVERSE CHANGE ON HEATING OCCURS AT THE A_s TEMPERATURE (AFTER NOSTER¹³ AND GIAMBI ET AL¹⁴)

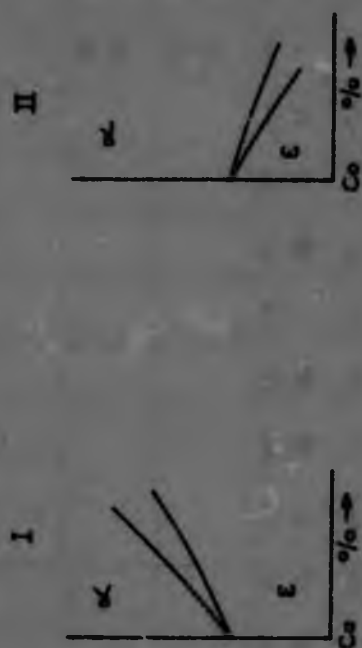


FIGURE 1.2:
THE ONLY TWO POSSIBILITIES FOR
THE EFFECTS OF ALLOYING ADDITIONS ON
THE COBALT ALLOY PHASE DIAGRAMS

TYPE I: CONSTRICTED α FIELD
TYPE II: ENLARGED α FIELD
(AFTER KOSTER¹³³ AND GIAMEI¹³⁴)

must be remembered that in many alloy systems, the effect of the added element on the temperature of the $\epsilon \rightleftharpoons \alpha$ transformation is often difficult to establish owing to the sluggishness of the transformation.

Solubility of the added elements in cobalt is governed by the size factor,⁽³⁴⁾ which is by definition:

$$\text{S.F.} = 100 \frac{(d_{\text{solute}} - d_{\text{solvent}})}{d_{\text{solvent}}}$$

where d_{solvent} and d_{solute} represent the closest distances of approach of atoms in the crystals of the respective elements; it has been generally found for cobalt that if the S.F. is $> \pm 15\%$ then appreciable solid solution formation is unlikely.⁽³⁴⁾ Elements with favourable size factors dissolve readily in cobalt forming solid solutions, and this is particularly the case for the transition metals, e.g. Mn, Fe, Ni, Rh, Ir and Pt form a complete series of solid solutions with α cobalt, whereas Ru, Os and Re form a complete series of solid solutions with ϵ cobalt.

In addition to Koster's work, Sage⁽³⁵⁾ has established that dissolved hydrogen stabilises the cubic form of cobalt, and in addition carbon and iron promote a stable cubic structure, and these elements may lead to the stabilisation of cubic material during the preparation of cobalt powders, by, for example:

- (1) The thermal reduction of cobalt chloride with hydrogen.
- (2) The thermal reduction of cobalt oxalate with hydrogen.
- (3) The reduction of an intimate mixture of cobalt

chloride with iron; 98% of the cubic structure was obtained when the material contained 7% iron.

Studies in catalysis⁽³⁶⁾ have revealed conflicting results on the phases of cobalt stabilised by carbon. Some work on the influence of oxygen is discussed in Chapter 3.

Field ion microscopy⁽³⁷⁾ studies have shown that the presence of impurities associated with the materials studied exerts a profound effect on the phases obtained. Wire from one source containing 1% nickel and 0.5% Mn transformed to the h.c.p. form during the field ion studies, while wire from another source which contained less than 0.1% impurities, but mostly iron, could not be transformed to the h.c.p. form. In both materials the grain size was estimated to be between 1 and 10 μ .

1.2.4 Previous Experimental Work on the cold working of cobalt.

The conversion of the cubic form of cobalt to the hexagonal form by cold working at room temperature or below, has been reported by many investigators. Even such operations as screening (as discussed by Sykes)⁽¹⁴⁾ or grinding cobalt powder in a mortar with a pestle⁽²⁸⁾ have been found to lead to a significant increase in the proportion of hexagonal close packed phase present.

The milling of cobalt powder has been previously studied by Exner and Fischmeister.⁽³⁸⁾ These workers milled a cobalt powder of 0.67 μ (Fisher Grain Size) under ethanol in a vibratory mill, and samples were removed after various milling periods. Their conclusions

may be summarised as follows:-

- (1) During milling the cobalt grain shape changed from originally elongated particles to particles with more rounded shapes.
- (2) Little change in grain size was discernible by electron microscopy.
- (3) Some evidence for agglomeration was, however, visible.
- (4) A rapid increase in powder coercivity occurred during the first stages of milling.
- (5) Excessive line broadening was observed in the X-ray diffraction patterns of the hexagonal phase formed during milling; this was attributed to the introduction of stacking faults, as had been suggested by Edwards and Lipson,⁽¹⁷⁾ and Wilson.⁽¹⁸⁾

Russian workers⁽³⁹⁾ have shown that tensile deformation (as a form of cold work) of quenched cobalt bars also increases the proportion of the hexagonal phase.

1.2.5 The selectivity of cobalt as binder metal for cemented carbides.

Dawihl⁽⁴⁰⁾ found that metal powders of the iron triad yielded a larger shrinkage when mixed with tungsten carbide powder than did other metal powders.

Since that time, cobalt has been found to be the most satisfactory binder metal; nickel and iron have been found to lead to more brittle sintered alloys, which have a strong tendency towards the formation of brittle double (carbon deficient) carbides of the M_6C or eta phase

(Co₃ W₃ C) type. A method has been proposed by which these tendencies may be overcome, and which yield alloys of strength superior to the conventional WC - Co type.⁽²⁾

An essential difference between cobalt, and iron and nickel as the binder metal is that the tungsten atoms scarcely dissolve in the binder phase in the case of iron and nickel, irrespective of the carbon level.⁽⁴¹⁾

The superior properties of cobalt as a binder metal are therefore ascribed to:⁽¹⁾

- (1) Wettability: Although the angle of contact of liquid cobalt on solid tungsten carbide cannot be measured properly because of dissolution, it has been determined that the angle of contact is infinitely small.⁽¹⁾ Wettability is an essential requirement for liquid phase sintering; it has been concluded that WC-Co constitutes a nearly ideal system for liquid phase sintering.
- (2) The relatively low melting point of the WC-Co eutectic.
- (3) The solubility of the carbide in the cobalt, both in the solid and liquid phase regions.
- (4) The small tendency of cobalt to form stable carbides.

The above observations constitute the reasons why cobalt is used almost exclusively as the binder metal for cemented carbides.

In sintered hard metal alloys the binder phase is usually in the f.c.c. form for the industrially important cobalt (3 - 20% binder) alloys.⁽⁴²⁾ The presence of any hexagonal phase in these alloys is considered to be

indicative of low quality and incorrectly sintered or annealed materials.

In hard metal alloys containing more than 30% binder, the hexagonal close packed modification starts to appear in the sintered material. In alloys containing more than 85% binder, the cobalt is entirely in the hexagonal form.⁽⁴²⁾

When external stresses are applied to hard metal alloys (e.g. grinding) particularly in alloys of high carbon content, transformation to the hexagonal form can occur at low temperatures.⁽⁴⁴⁾ This transformation in sintered alloys can affect the elastic and plastic behaviour of the material.

1.3 Conclusions:

Work carried out on the $\alpha \rightleftharpoons \epsilon$ transformation in cobalt has been reviewed: previous work on the phases present in reduced cobalt metal powder prepared by hydrogen reduction of cobalt oxide has been mentioned, together with results of cold work on the allotropic transformation. The selectivity of cobalt as the binder metal for cemented tungsten carbide^{See table 6.11.63} has been discussed.

The following chapters describe the characteristics of cobalt powders prepared under different reduction conditions, and the effects of milling cobalt under acetone on the ground powder properties. The application of these findings to tungsten carbide - cobalt alloy mixtures is shown.

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CHAPTER 2.

The investigation of the phases of cobalt produced by the hydrogen reduction of black cobalt oxide.

2.1 Introduction:

In some cases, as is shown in Chapter 5 for hard metal powders, hexagonal cobalt powder is of more importance than cubic cobalt powder. It was therefore decided to study the phases produced by the hydrogen reduction of black cobalt oxide using different reduction conditions.

Apart from the importance of cobalt in hard metal powder (Chapter 5), finely divided hexagonal cobalt is also of importance in permanent magnet manufacture. In this connection, methods of preparation of hexagonal cobalt have been reviewed by Mac Caig,⁽¹⁾ and the following have been considered:

- (i) The preparation of h.c.p. alloys in which a precipitate may be induced stabilising the hexagonal phase.
- (ii) Electrolysis onto a suitable cathode at high pH.
- (iii) Suitable chemical reduction of oxides.
- (iv) Evaporated films and whiskers.

Metallic cobalt in the hexagonal form has a very high magnetic crystalline anisotropy constant,⁽³³⁾ and for satisfactory magnetic properties, the powder must exist in finely divided form with a particle size less than 1μ .⁽²⁾ In addition the particles must be

magnetically aligned and closely packed. However, a magnet based on pure cobalt in the hexagonal form would have poor temperature stability, and would have to be used at room temperature or below, as the crystal anisotropy falls with increasing temperature.

The critical size for single domain particles may be derived from the following formula: ⁽¹⁾

$$d_s = \frac{9\sqrt{K}}{J_s} \sqrt{\frac{kT_c}{aJ_0^2}}$$

where J_s is the saturation magnetisation

K is the crystal anisotropy

k is the Boltzmann constant

T_c is the Curie temperature

a is the lattice constant

J_0 is the saturation magnetisation at 0°K

d_s is the critical particle size for single domain particles

(?) Substitution of values in this equation leads to a critical particle size of 0.2μ for hexagonal cobalt.

The most feasible method for the preparation of hexagonal cobalt for the purpose of milling appeared to be by the reduction of black cobalt oxide (Co_3O_4).

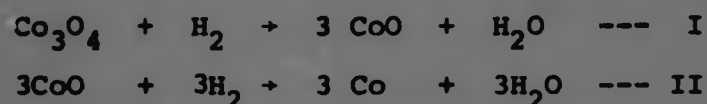
2.2 Previous work carried out on the reduction of black cobalt oxide by hydrogen.

Hydrogen reduction reactions of metal oxides usually consist of more than one process, ⁽²⁾ and in many cases it is extremely difficult to split the overall reaction into its constituent stages, and so obtain a

complete description of the overall process.

The variation of partial pressure of a reducing gas inside a piece of oxide depends on the rate of diffusion determined by the diffusion coefficient D' , and on the rate constant k .⁽³⁾ In general, it has been found that the type of reduction process which occurs depends upon the criterion $(\sqrt{k/D'})$, where a is the size of an oxide particle.⁽³⁾ A high value of the criterion implies a low rate of diffusion and vice versa. The value of the criterion therefore determines the shape of the reduction-time curve, at a fixed temperature.

According to Visnyovszky⁽²⁾ the hydrogen reduction of black cobalt oxide (Co_3O_4) to cobalt takes place in two reaction steps, viz.

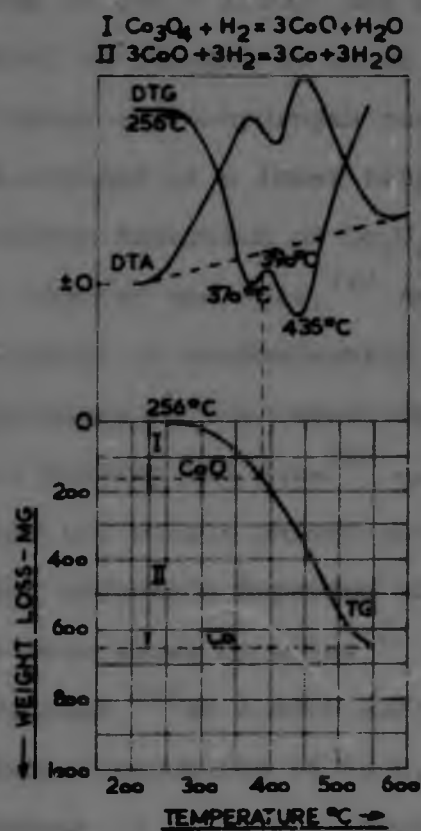


Visnyovszky's results are summarised in Figure 2.1; the D.T.A. and D.T.G. curves show unequivocally that two reactions are involved in the hydrogen reduction of Co_3O_4 . However, the two reactions overlap and the weight loss curve does not show any simple break into two parts. The D.T.G. curve shows that reaction I has a maximum speed at 370°C , and reaction II at 435°C . The reaction I begins at 256°C ; however, before this is complete, the second reaction has started.

Visnyovszky⁽²⁾ mentions the following characteristics in connection with reduction reactions:

FIGURE 2.1: SUMMARISED RESULTS OF VISNYOVSKY OBTAINED
WITH THE DERIVATOGRAPH ON BLACK COBALT OXIDE

HEATING RATE 14 °C/MINUTE SAMPLE WEIGHT 2.420 G.



- (1) The reduction of the highest oxide always begins at the lowest temperature and the lower oxide is reduced at a somewhat higher temperature.
- (2) When the difference in temperature for reduction reactions of two oxides is low, then both reactions can occur simultaneously.

This overlapping of the reduction reactions is not however evident when carbon is used as the reducing agent for Co_3O_4 .⁽²⁾ This reduction occurs in the temperature range of 600 - 1,200° and again the grey cobalt oxide (CoO) is thought to be an intermediate; in common with metal oxide-hydrogen reactions, the higher oxide is reduced at a lower temperature.

The hydrogen reduction of Co_3O_4 has also been studied by Nowotny and Juza,⁽⁴⁾ and it was shown that either hexagonal or predominantly cubic cobalt was produced depending on the reduction temperature. These results of Nowotny and Juza⁽⁴⁾ are summarised in Table I. That the cobalt phases obtained from Co_3O_4 by hydrogen reduction depended on the reduction temperature had been shown by Sykes⁽⁵⁾ and Hendricks, Jefferson and Schultz⁽⁶⁾ at a much earlier time.

The hydrogen reduction of Co_3O_4 has also been studied because of the great importance of finely divided cobalt as a hydrogenation catalyst. In this particular work⁽⁷⁾ where cobalt oxide - kieselguhr catalyst mixtures were mixed prior to reduction in hydrogen at 350 - 400°C, the reduced material yielded an unusual cobalt metal X-ray diffraction

TABLE I.

Summarised results of Nowotny and Juza⁽⁴⁾ on
the preparation of Cobalt Metal.

Starting Material	Reduction Temp. °C	Reduction Time hours	Phases found
Co ₃ O ₄	1,000°	2	Only cubic Co
Co ₃ O ₄	950°	2	Only cubic Co
Co ₃ O ₄	450°	2	Cubic and hexagonal
Co ₃ O ₄	350°	½	Hexagonal + cubic
Co ₃ O ₄	350°	½	Hexagonal + trace cubic
Co ₃ O ₄	350°	2	Only hexagonal cobalt

pattern which consisted of three major lines, which could be indexed either as the (111), (220) and (311) lines of face centred cubic cobalt (but with the (200) and (222) lines absent) or, alternatively, the three major lines could be indexed as the (11 $\bar{2}$ 0), (00 $\bar{0}$ 2), and (11 $\bar{2}$ 2) lines of hexagonal close packed cobalt but with the (10 $\bar{1}$ 1), (10 $\bar{1}$ 3) and (20 $\bar{2}$ 1) lines absent. It was thought that, but not confirmed in this catalytic work, that cobalt was combined in the form of a cobalt hydrosilicate with the kieselguhr.

Co_3O_4 is considered^{(8), (9), (10)} to have an analogous structure to that of Fe_3O_4 , which has been classified as an inversed spinel on the basis of its electronic conductivity. In a unit cell there are 8 Fe^{2+} ions, 16 Fe^{3+} and 32 O^{2-} ions.

Some Russian workers^{(11), (12)} have studied the reduction with carbon monoxide and hydrogen of a compound formed by heating cobalt grey oxide (CoO) in air at 250° to a constant weight. The structure of this compound was considered to be Co_3O_4 saturated with respect to oxygen i.e. $\text{Co}_3\text{O}_4 \cdot \text{O}_x$; these workers concluded from this work that the mechanism of reduction of Co_3O_4 to cobalt was the same as that of Visnyovszky,⁽²⁾ and that the grey cobalt oxide (CoO) was an intermediate product in the reduction process.

2.3 X-ray techniques used for the examination of reduced cobalt metal powder.

Sage and Guillaud⁽¹³⁾ have shown that in a

mixture of x g. cubic cobalt and $(1 - x)$ g. of hexagonal cobalt that:

$$\frac{x}{1-x} = 1.5 \left[\frac{I_{(200)}}{I_{(10\bar{1}1)}} \right]$$

where $I_{(200)}$ is the integrated intensity as represented by the area under the diffraction peak for the (200) cubic line and $I_{(10\bar{1}1)}$ is the integrated intensity as represented by the area under the diffraction peak for the $(10\bar{1}1)$ hexagonal line.

The above equation was verified by Sage and Guillaud⁽¹³⁾ by comparing the proportions obtained by X-ray data on powder samples prepared by mixing known proportions of the two allotropes under absolute ethanol. The above method is subject to the following errors:

- (1) the dimensions of the particles and internal strain.
- (2) the X-radiation normally used is not strictly monochromatic.

Thus the integrated intensities of the $I_{(200)}$ and $I_{(10\bar{1}1)}$ peaks in a diffraction pattern are a direct measure of the two allotropes of cobalt which are present. The method has a precision of about 5%, which can be improved by the use of crystal monochromators.

The values of 2θ corresponding to the peak maxima were calculated using the parabolic technique, first suggested by Ogilvie,⁽¹⁴⁾ which defines the peak position as the vertex of a vertical axis parabola fitted to the most intense portion of the diffraction peak:⁽¹⁵⁾

$$\text{i.e. } 2\theta_{\text{peak}} = 2\theta + \left| \frac{2\theta_1 - 2\theta_2}{2} \right| (3a + b)/(a + b)$$

where a and b are the differences in intensity between consecutive values of 2θ , $2\theta_1$ and $2\theta_2$ respectively; 2θ , $2\theta_1$ and $2\theta_2$ are points chosen on the curve which have intensities of at least 85% of the maximum intensity. In such instances a parabola is considered to be a good approximation to the shape of a diffraction peak in the region of maximum intensity.

For deformation and growth fault densities in hexagonal cobalt Rao, Lele and Anantharaman⁽¹³⁾ have shown that the compound fault probability $(\alpha + \alpha'/3)$ can be calculated from the formula:

$$(\alpha + \alpha'/3) = \frac{2c^2 \sin 2\theta}{3\lambda^2 L} \cdot \beta$$

where λ , L , c , α and α' are respectively the wave length of X-radiation, the hexagonal index, lattice parameter, deformation and growth fault densities. β is the integral breadth of the faulted profile, and $\beta = B - \frac{b^2}{B}$ where B and b are respectively the

integral breadths of the $(10\bar{1}1)$ and $(00\bar{5}2)$ hexagonal profiles. The above equation has been applied to samples of pure hexagonal cobalt metal powder.

All the cobalt powders prepared under different reduction conditions were examined in the 2θ angular range of $30 - 92^\circ$ using a Philips PW 1060 Diffractometer, with a scanning speed of $\frac{1}{2}^\circ$ per minute; $\text{Co } K_\alpha$ radiation was used with iron filters and entrance, exit and scatter slits of 1° , 0.1° and 1° respectively. One of the powders prepared was counted using the Geiger Counter on the Diffractometer, and certain others were examined using scanning speeds of $1/8$ and $1/4^\circ$ per minute. These are indicated in the text (Section 2.4.1.).

2.4 Experimental Work.

2.4.1 Reduction of Black Cobalt Oxide with hydrogen under Furnace Conditions.

The black cobalt oxide (Co_3O_4) used in this work was assayed and its specific surface area determined on a Perkin - Elmer Sorptometer.⁽³⁰⁾ The results are summarised in Table II. A measure of the oxygen content of the oxide was obtained by heating the powder in hydrogen at 950°C to constant weight. Assuming that the weight loss in hydrogen at 950° corresponds entirely to the oxygen present in the oxide, the calculated composition would be $\text{Co}_3\text{O}_{4.02}$. Another batch of black cobalt oxide made in the same way, as the batch investigated here, was

TABLE II.

Properties of Black Cobalt Oxide used for
reduction studies.

Analyses	Percent
Iron	0.026
Copper	0.003
Nickel	0.210
Sulphur	0.091
Silica	0.14
Alkaline Earths	0.03
Chloride	0.01
Sodium	0.001
Manganese	0.02
Loss in hydrogen at 950°C	26.68
Specific Surface Area	23.1 m ² /g.

found on heating in hydrogen at 950°C to have a weight loss of 26.58%, which corresponded to the formula $\text{Co}_3\text{O}_{4.00}$.

The major objective of this work was to prepare a finely divided hexagonal cobalt powder with a fine grain size, and all indications were, therefore, from previous work that a reduction temperature in hydrogen of about 400°C would be required. Further investigations, which are described in (2.4.2), showed that the pure hexagonal metal powder could be prepared by maintaining the black oxide for long periods at 260°C , and the theoretical weight loss could be obtained by heating at 190°C in hydrogen for long periods, but in this case the reduced material was pyrophoric on removal to the atmosphere, unless suitable precautions were taken.

50 g. quantities of the black oxide were, therefore, lightly packed into a stainless steel boat of dimensions 7" x 3" x 1" in height. The oxide powder was flattened into a very thin layer at the bottom of the boat. The powder was not packed on a mesh within the boat; in this case the hydrogen could have flowed beneath the powder bed. The oxide powder in the boat was heated to 400°C at a heating rate of $200^{\circ}/\text{hour}$ in a Wild Barfield retort furnace. The gas flow rate of hydrogen in this and all subsequent experiments was 20 cubic feet per hour. The dew point of the incoming hydrogen was in the range of -55 to -71°C . The powder

was maintained at 400°C for 30 minutes; the retort was then removed from the furnace and placed in a water cooled jacket for 30 minutes. Carbon dioxide gas was then passed through the furnace for 30 minutes to ensure stabilisation of the powder before exposure to the air. This stabilisation had been found to be necessary in previous reduction studies,⁽¹⁷⁾ and in one reduction experiment described below (350° - 30 minutes), the reduced powder was immediately reoxidised to Co_3O_4 , when this stabilisation treatment was inadvertently omitted.

It is likely that gas adsorption occurs on all surfaces,⁽¹⁸⁾ and it has been considered that finely divided metal particle surfaces might become deactivated by prestorage in inert atmospheres prior to exposure to air.⁽¹⁹⁾ It has been shown that the weight gain of finely divided pressed metal powder compacts on exposure to air is reduced if the powders have been previously inactivated by N_2 , argon or CO_2 .⁽¹⁹⁾ The stabilising action of CO_2 in reducing the pyrophoricity of cobalt metal powder can only be ascribed to the adsorption of gas on the highly reactive powder particles, preventing ignition when the powders are exposed to air. In some cases final quenching in water after reduction has been found to be necessary for cobalt powders to prevent pyrophoricity.⁽²⁰⁾

An X-ray diffraction pattern of the material prepared, as described above, was examined and it was found that some cubic cobalt was present, as well as some hexagonal cobalt.

It was then decided to study the cobalt metal phases produced by hydrogen reduction of Co_3O_4 as a function of the reduction time and temperature. In each case the temperatures were controlled to $\pm 5^\circ\text{C}$ by means of a Chromel Alumel thermocouple. Reduction of 50 g. quantities was carried out in the Wild Barfield retort furnace using the following temperature-time conditions:

300° 30 minutes, 1, 2, 3 and 4 hours
 350° 30 minutes.
 400° 30 minutes, 1, 2, 3 and 4 hours
 450° 30 minutes, 1, 2, 3 and 4 hours
 500° 30 minutes, 1, 2, 3 and 4 hours
 550° 30 minutes, 1 and 2 hours
 600° 30 minutes, 1, 2, 3 and 4 hours
 650° 30 minutes, 1, 2 and 4 hours
 700° 30 minutes, 1, 2, 3 and 4 hours
 750° 30 minutes, 1, 2, 3 and 4 hours
 800° 30 minutes, 1, 2 and 4 hours
 850° 30 minutes, and 1 hour

A heating rate of $200^\circ/\text{hour}$ to the reduction temperature was used in all cases. The one hour period (30 minutes in water cooled jacket and 30 minutes stabilisation with CO_2 before removal was adhered to in all cases. Thus strictly the material

was not quenched after the high temperature reduction; but in view of the pyrophoricity of the powders reduced at low temperature, it would not have been possible to immediately remove the powders without their reoxidising to Co_3O_4 . It was decided therefore to adhere to the above one hour period, before removal, in all cases.

The following tests were carried out on each sample of reduced cobalt metal powder:

- (1) An X-ray diffraction pattern was run at $2\theta = \frac{1}{2}^\circ$ /minute in the angular range of $30^\circ - 92^\circ$.
- (2) The specific surface area of each powder was measured on the Sorptometer.
- (3) The weight loss in hydrogen of a 5 g. sample was determined by heating in hydrogen at 950° in a nickel boat to constant weight, followed by re-weighing.

Prior to the above tests being carried out the reduced metal powders were lightly screened through a 100 mesh screen. No force or pressure was used here, because of the tendency for hexagonal cobalt to be formed during a screening operation.⁽⁵⁾ This screening treatment was merely to break up the small amount of lumps formed during the reduction process.

The above comments on screening only apply to the powders reduced at temperatures up to 700°C . The metal powders produced at 750° and 800° consisted of hard aggregates with a rounded shape. This is discussed further below.

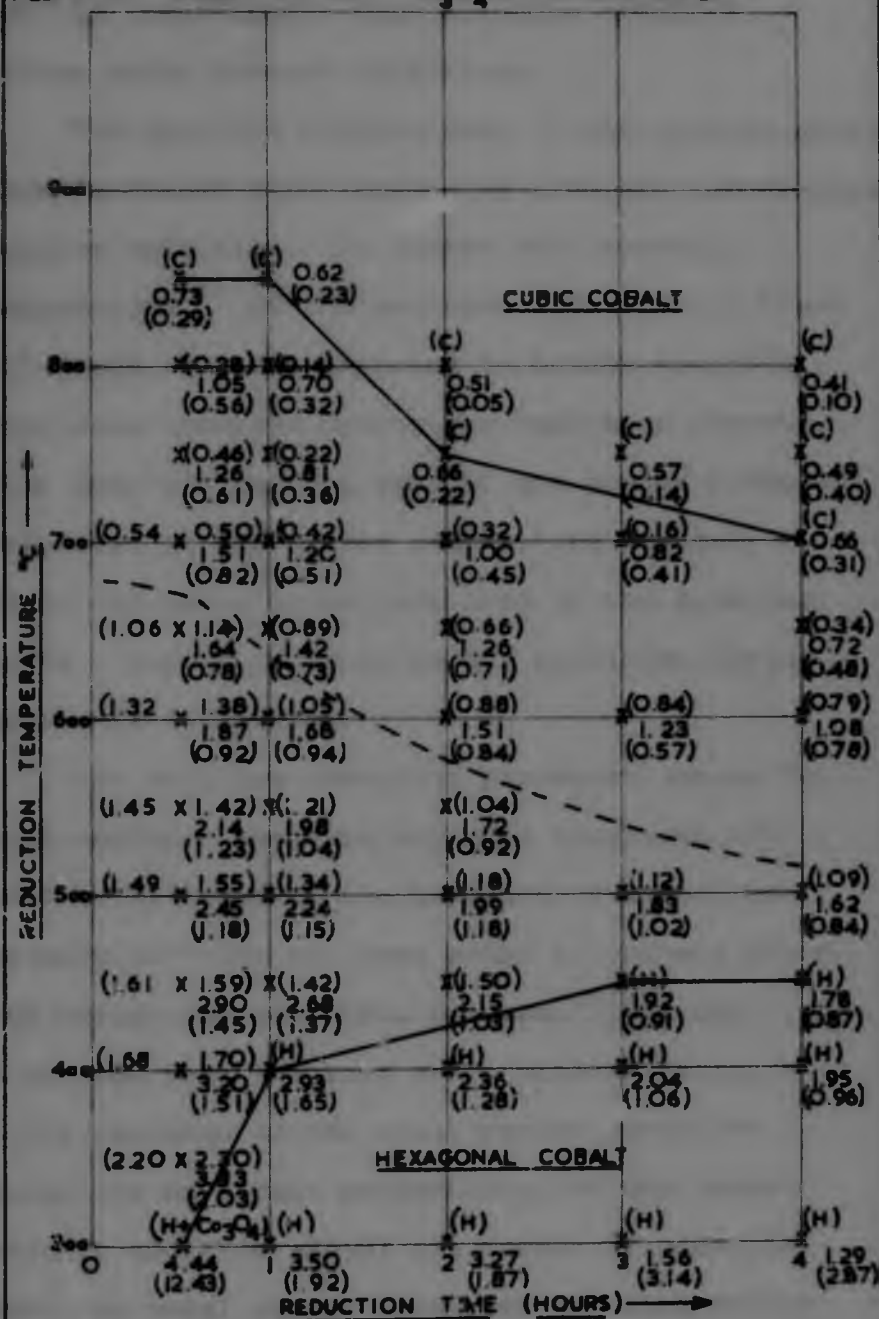
The specific surface area, weight loss in

hydrogen, and intensity ratios of the (10 $\bar{1}$ 1) hex. to (200) cubic X-ray diffraction lines for the powder samples are summarised in Figure 2.2. The X-ray data cannot be regarded as absolute, since no attempts were made to correct for line broadening effects with the fine powders reduced at the lower temperatures.

Some of the 30 minute X-ray diffraction patterns were re-run and yielded the duplicate sets of results shown in Figure 2.2. Thus from these results it is possible to see the conditions required for the preparation of the pure hexagonal and pure cubic allotrope powders. In general, the results show that a pure hexagonal powder may be obtained at any temperature below 400° with a reduction time in excess of one hour. A predominantly cubic cobalt powder is obtained at room temperature using any reduction temperature above 700°. Above 400°C the formation of an increased proportion of cubic material appears to be associated with increasing time and temperature of reduction. Generally therefore above the transition temperature for the $\epsilon \rightleftharpoons \alpha$ reaction, both hexagonal and cubic allotropes are obtained in the powders, and some hexagonal (low temperature phase) may exist at temperatures up to 800° provided short reduction times are used. The general findings of Nowotny and Juza⁽⁴⁾ are therefore confirmed.

The powder reduced at 300°C for 30 minutes

FIGURE 2.2 (1011)/(200) INTENSITY RATIO, SPECIFIC SURFACE AREA AND WEIGHT LOSS IN H_2 OF REDUCED POWDER AS FUNCTION OF REDUCTION CONDITIONS FOR Co_3O_4 WITH HYDROGEN



KEY

A CROSS (X) INDICATES A REDUCTION CONDITION STUDIED
THE THREE SETS OF NUMERALS ARE PHASE RATIO EG(0.79)
 S_g (M²/G) 1.06
LOSS IN H_2 (%) (0.78)

H = 100% HEXAGONAL

C = 100% CUBIC

THE DOTTED LINE INDICATES CONDITIONS WHERE THE
REDUCED POWDER CONTAINS APPROXIMATELY EQUAL
PROPORTIONS OF BOTH ALLOTROPE

was found on X-ray diffraction to be improperly reduced, and Co_3O_4 was evident in the powder. Thus 30 minutes at 300° is insufficient time to cause complete reduction under furnace conditions.

The specific surface area of the reduced metal powders decreased with increasing time and temperature of furnace reduction. In common with previous investigations⁽²⁰⁾ of the hydrogen reduction of black cobalt oxide, a large decrease in powder specific surface area occurred during the reduction process, and the specific surface area of the powder produced by reduction at the lowest temperature was only 19.2% of the specific surface area of the starting material. Growth of metal powder particles during reduction is well known.

For solution-reduction processes (where for example ammine - ammonium sulphate solutions are reduced by hydrogen in the presence of a catalyst), an organic additive has been added to prevent grain growth during the reduction process;⁽²¹⁾ it has been assumed that the long chain organic radicals coat the surfaces of the metal powder particles limiting (to an extent proportional to the amount of organic additive added) the number of contacts between the metal powder particles and thus reduce grain growth. However, different powder morphologies are often obtained by using different organic materials; this has been found to be so for nickel powders.⁽²²⁾ No additives were used in this work to

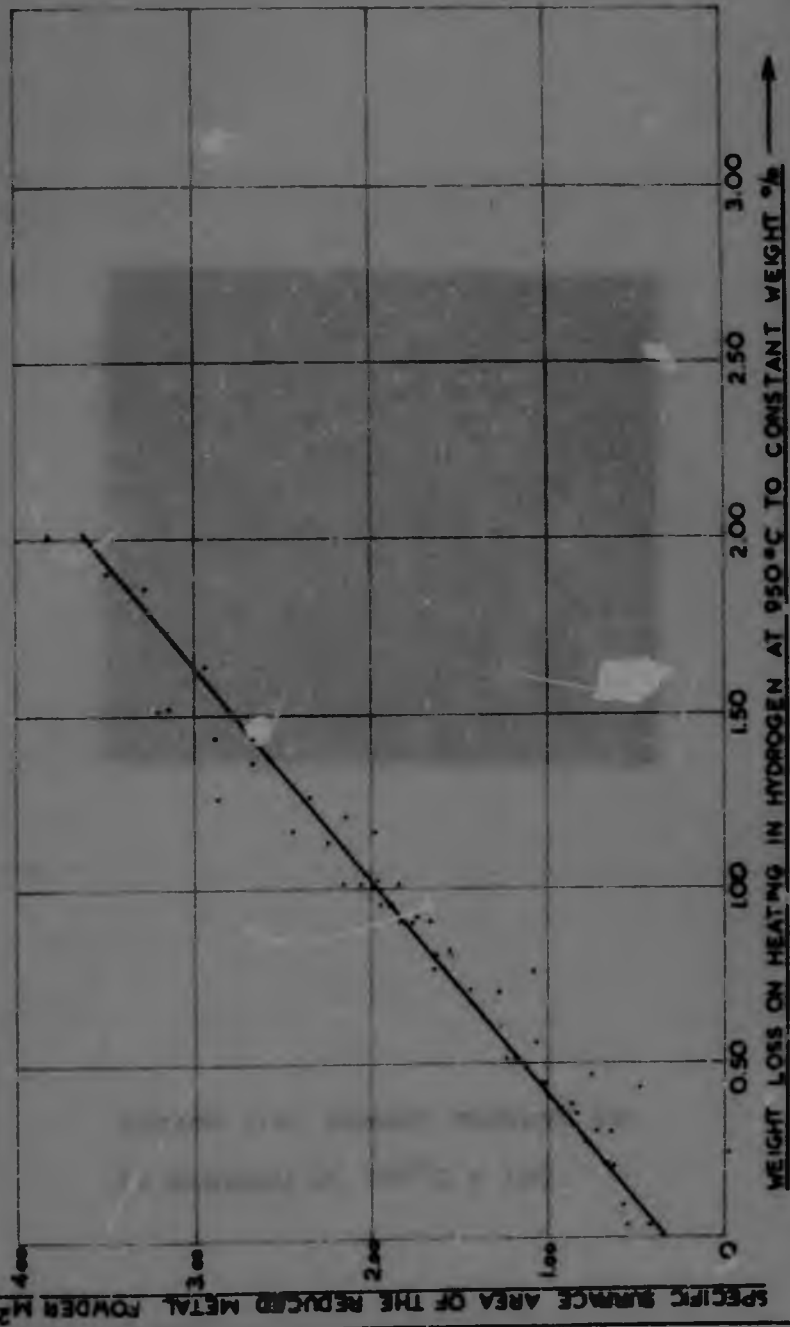
prevent agglomeration and grain growth. The presence of organic material might have an adverse effect on further powder metallurgical processing. This is discussed further in Chapter 5.

The relation between specific surface area and weight loss in hydrogen is shown in Figure 2.3. Although some scatter is evident, it would appear that the weight loss in hydrogen is linearly related to the specific surface area of the reduced metal powder. Indirectly this suggests that adsorption of the oxygen occurred after removal from the furnace, and was not necessarily associated with incomplete reduction.

Some of the reduced powders obtained were examined on a Cambridge Stereoscan Electron Microscope. The powder reduced at 400°C for 30 minutes is shown in Figure 2.4, and that reduced at 800°C for one hour in Figure 2.5. Powders prepared at low temperatures appeared to consist of fine filaments, whereas the powder reduced at 800°C can clearly be seen to consist of hard sintered aggregates. A single agglomerate of the latter powder is shown in Figure 2.6, and another example in Figure 2.7. Powder reduced at 500° for 4 hours also contains some aggregates, (Figure 2.8).

In order to prove unequivocally that pure hexagonal cobalt had been prepared in pure form with no traces of the cubic material, the powder reduced at 400° for 4 hours was selected and an analysis of the X-ray line shape was carried out on the $(10\bar{1}0)$, $(00\bar{0}2)$ and $(10\bar{1}1)$ hexagonal X-ray diffraction peaks.

FIGURE 2.3 VARIATION OF SPECIFIC SURFACE AREA AND WEIGHT LOSS IN HYDROGEN FOR COBALT POWDERS



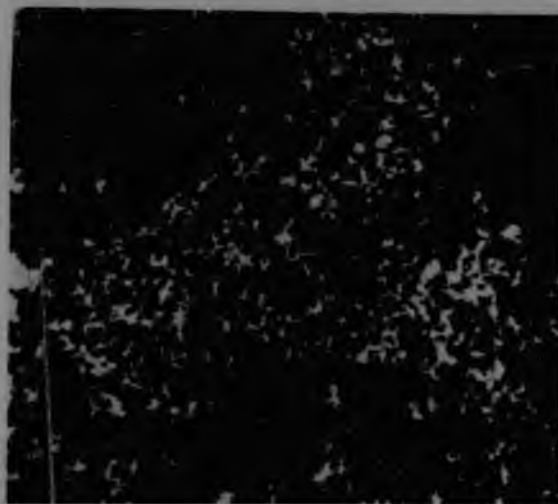


Figure 2.4: Powder reduced for
30 minutes at $400^{\circ}\text{C} \times 100$.



Figure 2.5: Powder reduced
at 800°C for 1 hour x 72.

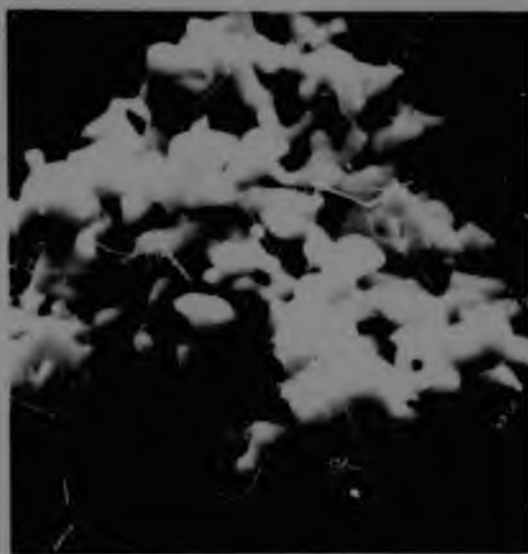


Figure 2.6: Fine Structure
of powder in Figure 2.5 x 10000.



Figure 2.7: Agglomerated Cobalt
prepared by reduction at $800^{\circ}\text{C} \times 2,400$.



Figure 2.8: Isolated aggregates in
powder reduced at 500°C x 10,000.

The powder was mixed with water glass to a pasty consistency and then mounted in the specimen holder.

A preset count period of 30 seconds was used and a scale factor of 1 x. Counting in the region of the (200) cubic peak was carried out, and this line was found to be absent with the count levels indistinguishable from the background. For the profiles, counting was carried out initially at 0.05° values of 2θ , and near the apices the counting interval was reduced to 0.01° values of 2θ .

The count results were plotted against 2θ , and the areas under the curves measured with a planimeter. Small particle sizes result in line broadening, but do not cause a shift of the peak maxima.⁽²³⁾ It was intended to compare the positions of the peak maxima with those previously published in the literature.⁽¹⁷⁾

The intensity values quoted in the literature are only visual estimates and did not consider line broadening due to small particle sizes. The diffractometer was run at operating conditions for 24 hours prior to counting being carried out, to ensure stabilisation of the equipment.

The positions of the peak maxima were calculated as described in Section 2.3.

Comparison of the d spacing values with those of Hofer and Peebles⁽¹⁷⁾ are summarised in Table III; good agreement of values is shown.

TABLE III.

Comparison of lattice parameter data with published
results for hexagonal cobalt powder prepared at 400°C
for 4 hours in hydrogen.

Line	d spacing obtained $\text{\AA}$	Results obtained by Hofer $(17) \text{\AA}$	Integrated Intensities cm^2
(10 $\bar{1}$ 0)	2.1611	2.1645 weak	14.61
(00 $\bar{2}$)	2.0288	2.0324 medium	31.01
(10 $\bar{1}$ 1)	1.9092	1.9104 v. strong	53.43

The results of the line shape analysis are shown in Figures 2.9, 2.10 and 2.11 for the $(10\bar{1}0)$, $(00\bar{0}2)$ and $(10\bar{1}1)$ peaks respectively.

As discussed in Chapter 1, the (200) and $(10\bar{1}1)$ peaks are the only well separated ones which can be used for the identification of cubic and hexagonal cobalt respectively. The only other lines obtainable with Fe filtered Co K_α radiation would be the $(11\bar{2}0)$ hexagonal line ($d = 1.2520^\circ\text{A}$) and the (220) cubic line ($d = 1.2532^\circ\text{A}$) but both these are of low intensity. Lines with smaller d spacing values (i.e. larger values of 2θ) could only be obtained with a molybdenum target X-ray tube which was not available.

Thus furnace procedures using a reduction temperature of lower than 400°C , and an adequate time for reduction can be used for the preparation of hexagonal cobalt, provided adequate precautions are taken against oxidation before exposure of the powder to air.

An interesting observation can be made from the examination of the data shown in Figures 2.9, 2.10 and 2.11. This concerns the breadth of the $(10\bar{1}1)$ profile, which in this instance is 2.86 times larger than that of the $(00\bar{0}2)$ profile. A calculation based on the equation of Rao, Lele and Anantharaman⁽¹⁶⁾ (given in 2.3) yielded the compound fault density $\left[(\alpha + \alpha'/3) \right]$ given in Table IV. In another case, a sample of reduced hexagonal cobalt

FIGURE 2.9: COUNT RESULTS ON THE $[10\bar{1}0]$ HEXAGONAL PEAK

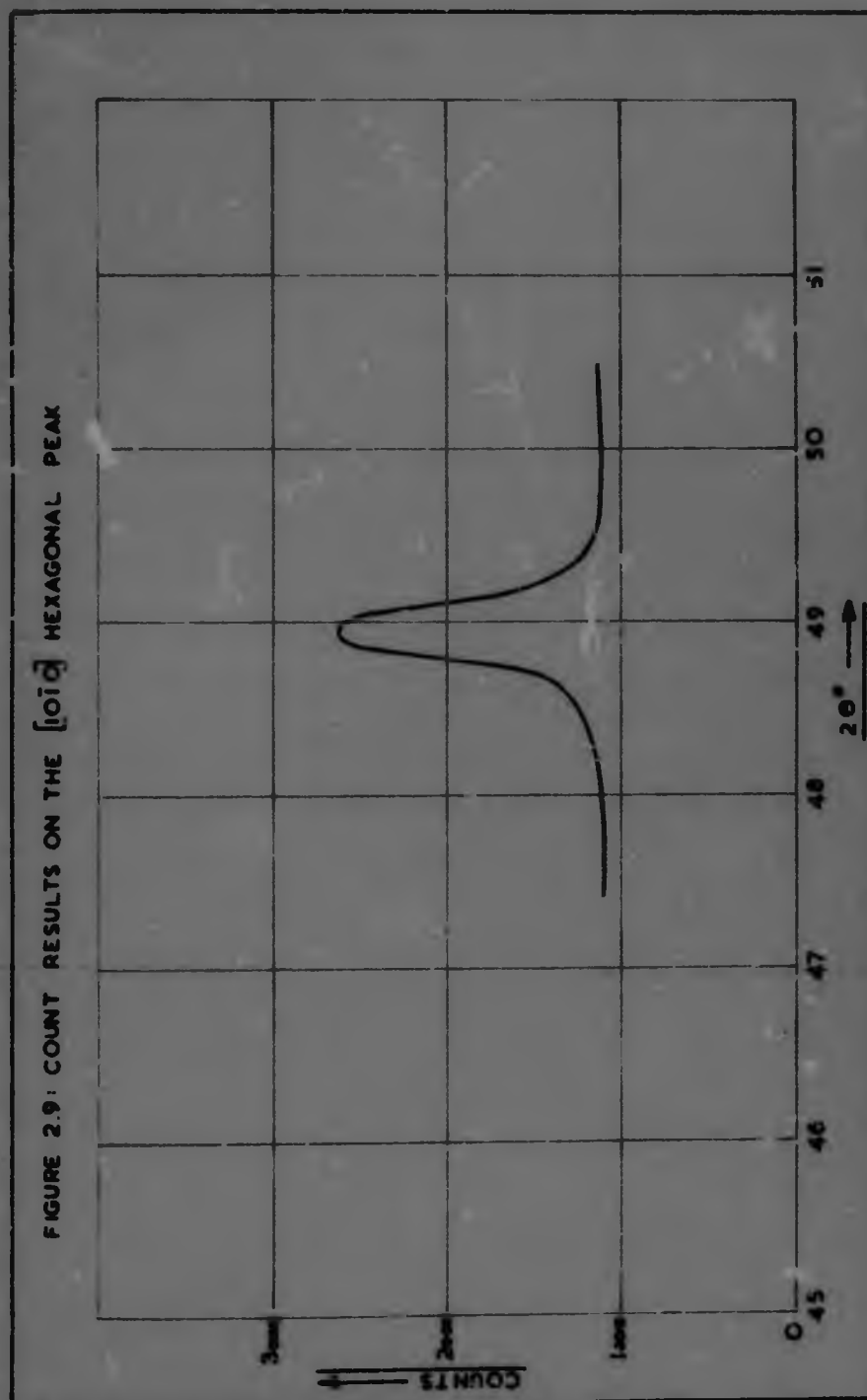


FIGURE 2.10: COUNT RESULTS ON THE $[00\bar{0}2]$ HEXAGONAL PEAK

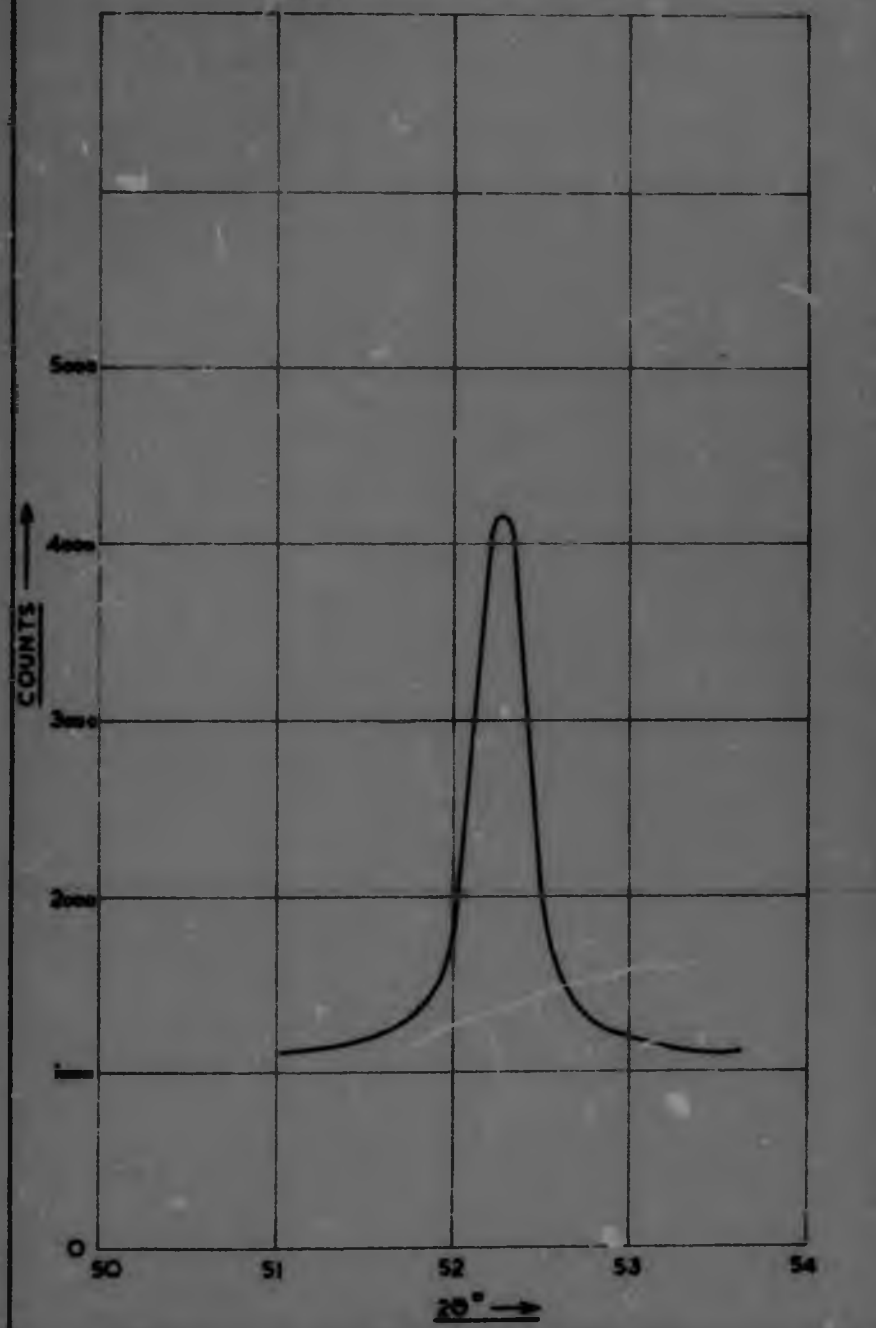


FIGURE 2.11: COUNT RESULTS ON THE $[10\bar{1}]$ HEXAGONAL PEAK

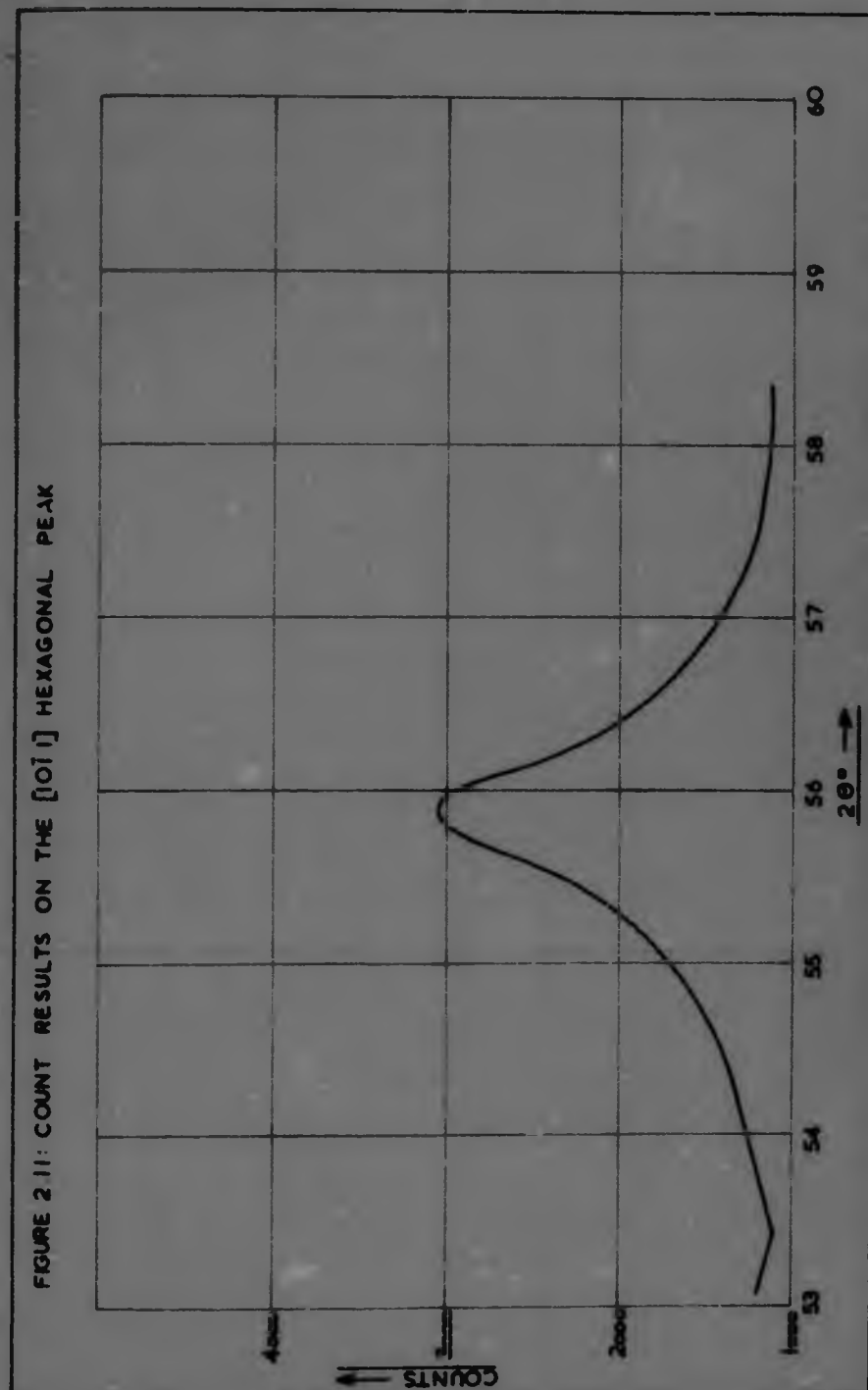


TABLE IV.

Comparison of Strain, Compound Fault Density, and domain size for different cobalt materials.

Sample	Work discussed here			(3) Results for Cobalt powder milled for 10 hours	(4) Results for $\alpha + \alpha/3$	(5) Results for ground cobalt		(6) Results for annealed cobalt powder				
	(1) $\alpha + \alpha/3$	(2) Mitra and Halder equation				D^0A	ϵ	D^0A	ϵ			
		D^0A	$3\alpha + \beta$									
Powder reduced at 400°C for four hours	0.00706	284	0.0028	0.0054	0.0152	614	0.0051	435	0.0054	1040	0.0014	-0.0005
Powder reduced at 360°C for four hours	0.00695	216	0.0026	0.0054	-	-	-	-	-	-	-	-

- 1) Using the equation of Rao, Lele and Anantharaman. (16)
 2) Equation of Mitra and Halder. Acta. Cryst. 17 817 (1964) (Ref. 24).
 3) Chapter 4 Table VI - Results on Milled Cobalt Powder using the Mitra and Halder (24) equation.
 4) Results of Rao et al. (17) for hexagonal cobalt powder
 (a) reduced at 460°C
 (b) reduced at 390°C
 (c) reduced at 300°C
 5) Results of Rama Rao and Anantharaman 2. Metallkunde 54 658 (1963).
 6) Annealed Cobalt - Chapter 4 Table VI - Equation of Mitra and Halder.

metal powder, prepared by hydrogen reduction at 360° was examined using the diffractometer at a scanning speed of $\frac{1}{4}^{\circ}$ per minute; here the breadth of the (10 $\bar{1}$ 1) profile was 2.82 times that of the (0002) profile. This powder yielded the value of compound fault density shown in Table IV. Various other values (due to previous workers) of strain, domain size, and fault densities for cold worked and reduced cobalt powders are shown in this Table; all these values were obtained by line breadth methods of analysis for the X-ray data.

The important conclusion from Table IV is that the reduced powder has twice the strain of a cobalt powder annealed at 300°C , and half the strain of a cobalt powder ground for 10 hours. The compound fault densities are approximately one third of the value obtained on a powder ground for 10 hours, and ten times the value obtained for an annealed powder.

Rao et al.⁽¹⁶⁾ concluded that their hexagonal cobalt obtained by hydrogen reduction of grey cobalt oxide contained approximately the same compound fault densities, and strain as cold worked materials. Thus the reduced hexagonal cobalt metal powders are strained and contain stacking faults.

Considerably reduced strains and compound fault densities were obtained⁽¹⁶⁾ on cobalt deposited electrolytically from solution. The large strains

found in the reduced powders were attributed to the large decrease in volume which occurs on reduction; this is confirmed by the large specific surface area decrease on reduction, which was referred to previously. The dominant type of faulting present in the reduced metal powders was thought by Rao et al.⁽¹⁶⁾ to be of the deformation type.

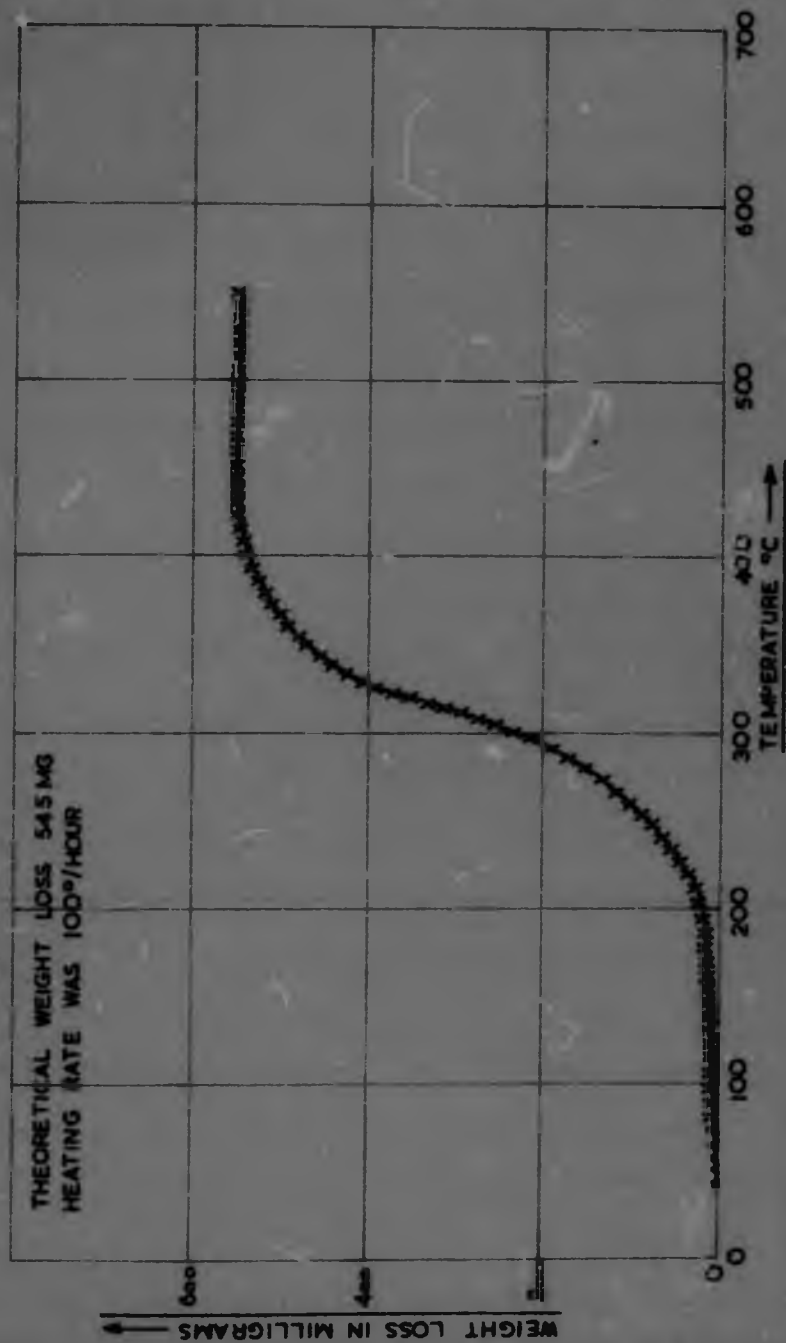
Another point which must be considered, is that the samples prepared here, were examined at room temperature; it would have been of great value to study the degree of faulting at the actual reduction temperature with the aid of a high temperature camera.

Comparison of the results shown in Table IV with those of Rao et al.⁽¹⁶⁾ shows that the compound fault density in the samples examined here was about half that of the values of the former workers; possibly this may be ascribed to the use of different starting materials, namely CoO , and Co_3O_4 , which was used here, or alternatively different grain sizes of the starting material.

2.4.2 Reduction of Black Cobalt Oxide with hydrogen in thermobalances.

A sample of the black cobalt oxide used for the furnace reduction studies was heated at $100^\circ/\text{hour}$ in an alumina crucible in a Stanton Mass Flow Thermobalance. The weight loss against temperature curve is shown in Figure 2.12. The hydrogen flow

FIGURE 2.12: WEIGHT LOSS ON HEATING BLACK COBALT OXIDE IN HYDROGEN IN A STANTON
THERMOBALANCE

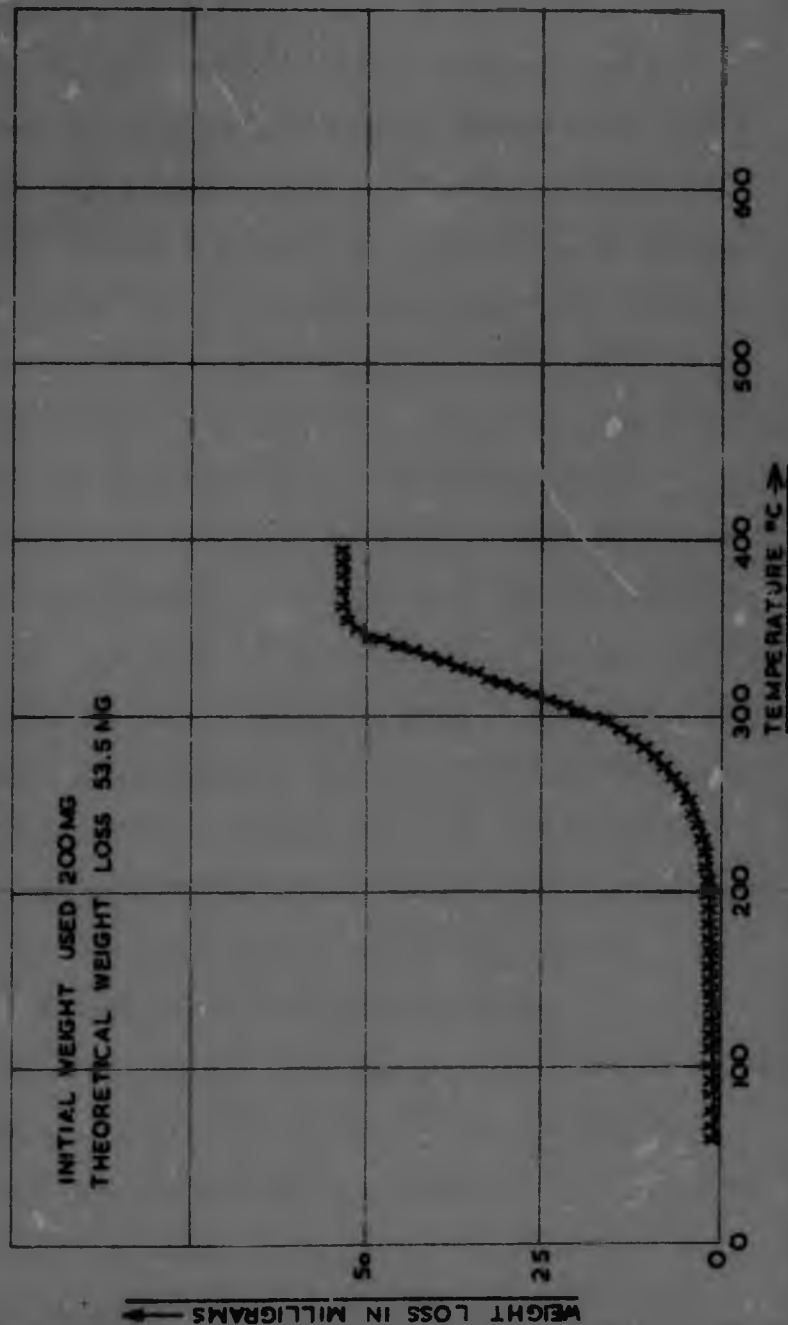


rate was 0.5 litres per minute. The reduced metal powder (which had been heated to 550° during the thermobalance reduction) was found to consist of a mixture of the hexagonal and cubic cobalt phases, which was in agreement with the data shown in Figure 2.2 (2.4.1).

However, when these results are compared with those of Visnyovszky,⁽²⁾ it is noteworthy that the entire weight loss had occurred by 410°C . The former author obtained a continuous weight loss up to temperatures of 550°C . That the Stanton Thermobalance results reported above were not in error was confirmed by carrying out a reduction in hydrogen of a 200 mg. sample in a Mettler thermobalance. This is shown in Figure 2.13 and in this case the reduction process was complete by 360°C . Visnyovszky's⁽²⁾ grain size of Co_3O_4 was not quoted, but presumably this difference in ease of reduction must be ascribed to a kinetic effect which might depend either on the grain size, the differences in heating rate, the differences in methods of packing the powder or on the gas flow. In agreement with Visnyovszky,⁽²⁾ however, the weight loss curve showed no distinct break into two parts, indicating that the two reduction reactions overlapped.

Isothermal reductions were therefore carried out at temperatures of 260° and 350° using $200^{\circ}/\text{hour}$ heating rates to temperature. The weight loss curves

FIGURE 2.13: REDUCTION OF Co_3O_4 IN HYDROGEN IN A METTLER THERMOBALANCE



are shown in Figures 2.14 and 2.15. Again no distinct breaks in the weight loss curves are evident. Thus it is not possible to consider the kinetics of the individual reactions constituting the overall process.

As Visnyovszky⁽²⁾ had indicated that the weight loss of Co_3O_4 in hydrogen commenced at 256°C , it was decided to ascertain if complete reduction could, in fact, be effected at a lower temperature. A sample of powder was therefore heated at rate of $200^\circ/\text{hour}$ to 190°C , and the weight loss recorded. The weight loss - time curve is shown in Figure 2.16, and indicates that reduction was complete in approximately 750 minutes at 190°C . However, this powder was pyrophoric, and was immediately reoxidised to Co_3O_4 on exposure to the air. Thus it was not possible to confirm whether in fact pure hexagonal cobalt had been prepared, thus confirming the trend of the data shown in Figure 2.2. A subsequent reduction at 190° confirmed that the theoretical weight loss was obtained at this temperature provided the time was sufficiently long.

In this second case the powder was stabilised before exposure to the atmosphere by passing CO_2 through the thermobalance for 2 hours after cooling. Furthermore, the air in the plastic container to which the reduced material was to be transferred from the alumina crucible was displaced by CO_2 before adding the powder.

FIGURE 2.14: REDUCTION OF Ce_2O_3 WITH H_2 IN A STANTON THERMOBALANCE-ISOETHERMAL AT 260°C

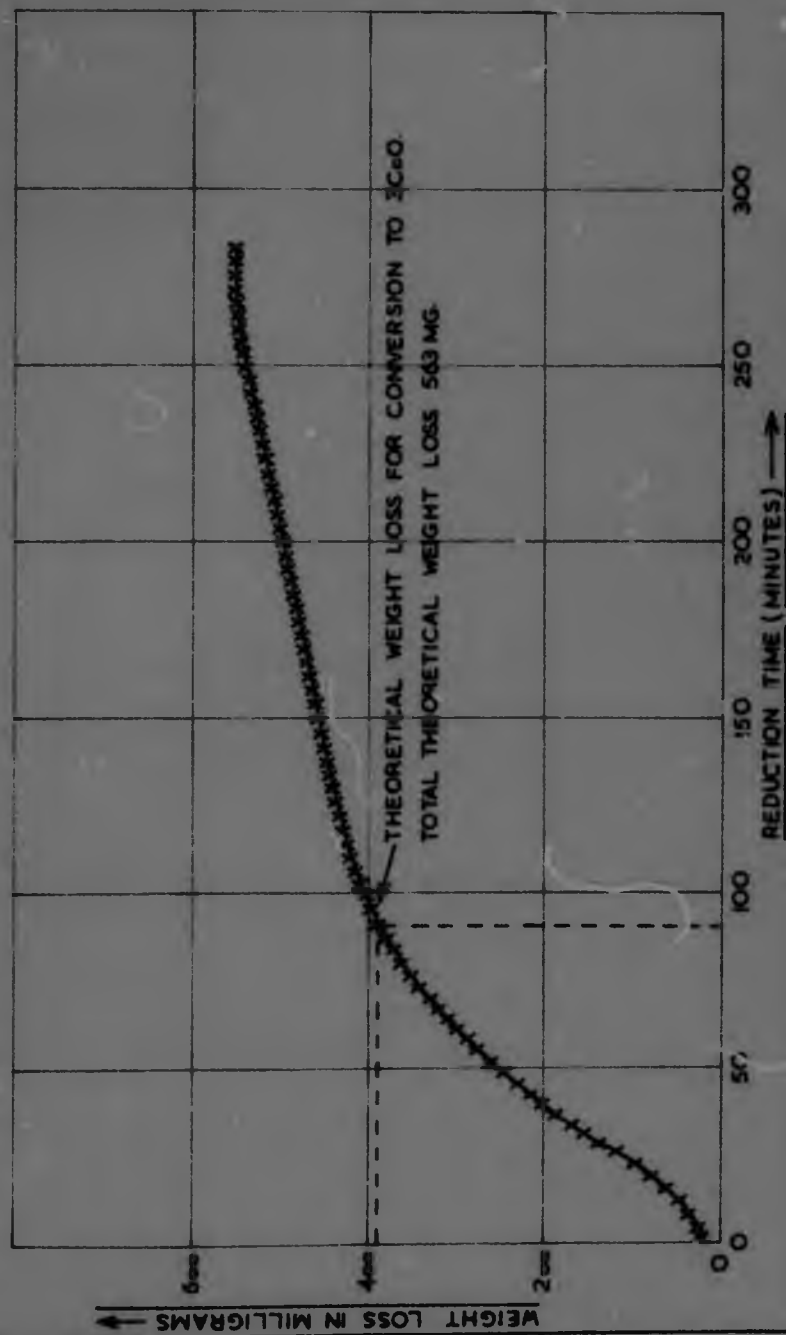


FIGURE 215 REDUCTION OF Co_3O_4 WITH HYDROGEN IN
A STANTON THERMOBALANCE-ISOTHERMAL AT 350°C

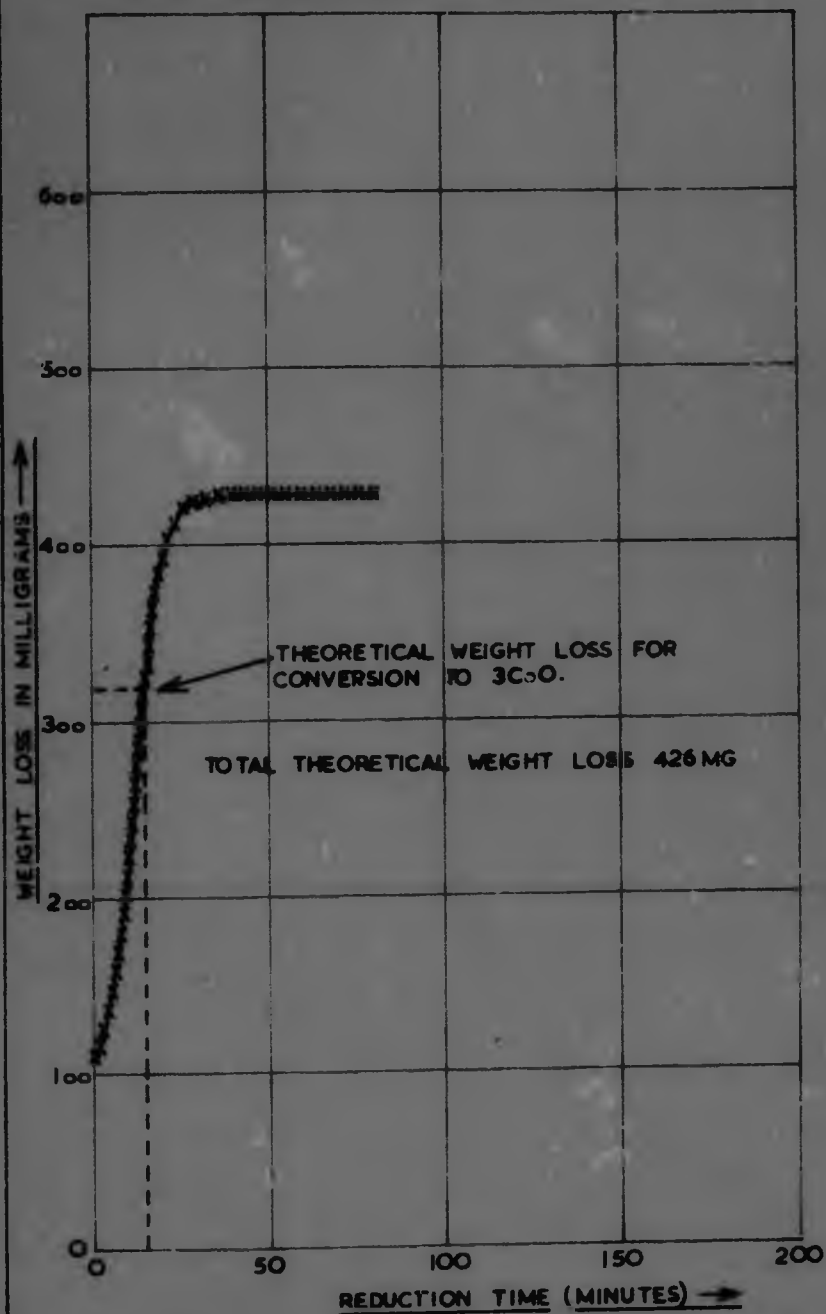
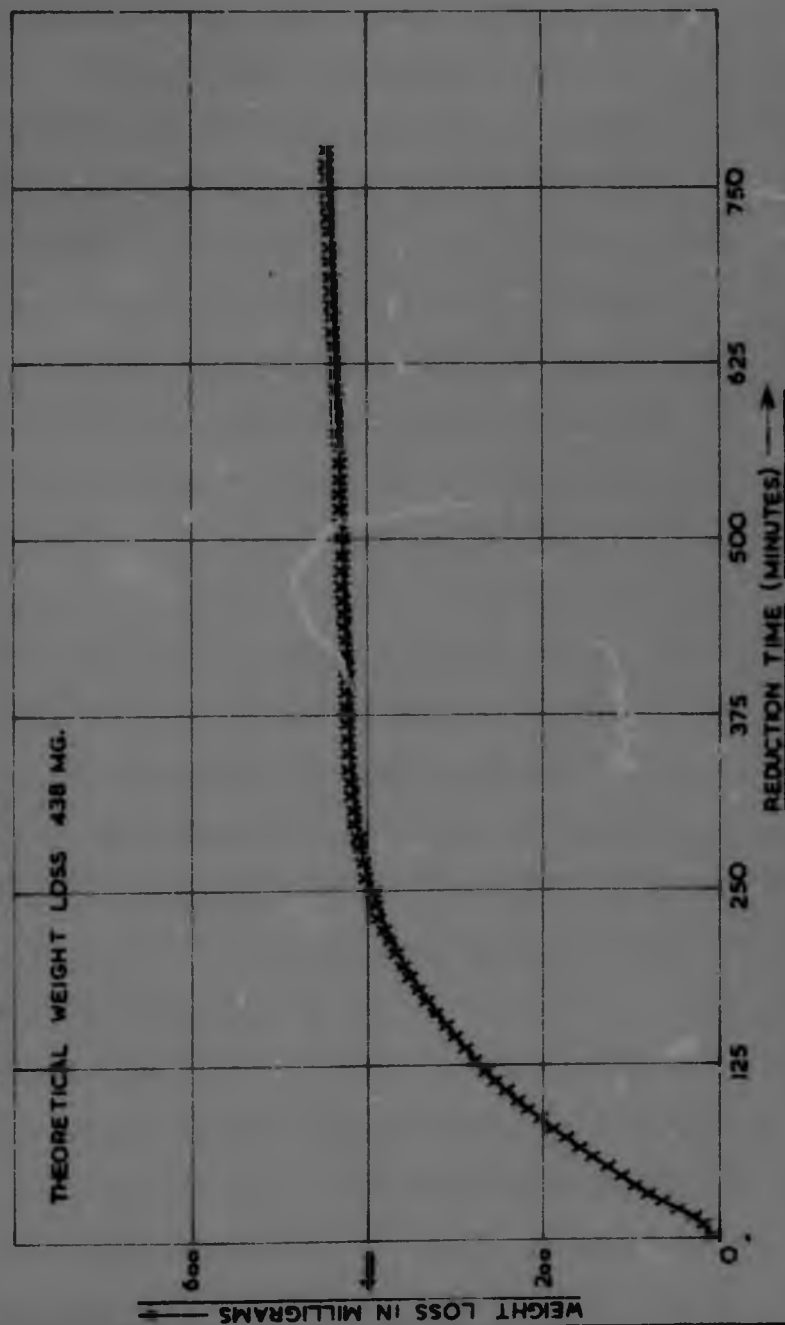


FIGURE 2.16: REDUCTION OF BLACK COBALT OXIDE IN HYDROGEN IN A STANTON THERMOBALANCE -
ISOTHERMAL AT 190°C



After this treatment, the powder was found to be not immediately pyrophoric, and it was possible to obtain the X-ray diffraction pattern. This material consisted of hexagonal cobalt with a faint peak from the strongest ($d = 2.43^{\circ}\text{\AA}$) Co_3O_4 line. The specific surface area was found to be $6.28 \text{ m}^2/\text{g}$, and the weight loss in hydrogen 2.52%. As figure 2.16 indicated that complete reduction had occurred at 190° , the presence of the oxide in the sample must be ascribed to reoxidation which occurred after removal from the thermobalance. It was noted with this powder that the peak maxima were displaced from their normal positions towards increased angles of 2θ on the $\{10\bar{1}0\}$, $\{00\bar{0}2\}$ and $\{10\bar{1}1\}$ planes, by approximately 0.5° in each case. A deviation from the normal lattice parameters has also been noted⁽²⁵⁾ for pyrophoric iron powder reduced at 350°C .

In all the other powders examined and described in this Chapter there were no deviations of the lattice parameters, i.e. the diffraction maxima occurred at 2θ values corresponding with those quoted in Table III.

Consideration was given to the possibility of a D.T.A. study of the hydrogen reduction of black cobalt oxide, but as this technique is dependent on a number of complex factors,⁽²⁶⁾ and a powdered solid system was involved, no attempt was made to confirm the previously reported findings.⁽²⁷⁾ In addition the grain size distribution of the solid under study is

a more important variable than the average grain size. This has been shown in another work for the $\alpha \rightarrow \beta$ transformation in quartz.⁽²⁷⁾

2.5 Other considerations of the reduction process.

There are several other aspects of the hydrogen reduction process of Co_3O_4 to produce cobalt metal powders which require investigation; among these may be cited:

- (a) the effects of flow rate of the reducing gas on the grain sizes of the reduced powder.
- (b) the thermodynamics of the hydrogen reduction of black cobalt oxide have been considered by Gulbransen and Andrew,⁽²⁸⁾ who have shown that the reduction of Co_3O_4 with hydrogen is thermodynamically feasible even in atmospheres containing large amounts of water vapour. However, the influence of the dew point of the incoming reducing gas on the grain size, phase ratio and oxygen content has to be considered.
- (c) the effects of packing e.g. the depth of the bed of powder used, and the mode of packing in the boats:
 - (i) whether the powder is merely packed at the bottom of a boat as was done here.
 - (ii) whether the powder is packed on wire mesh in a boat; in this way it would

be expected that more rapid diffusion of water vapour away from the powder bed would occur.

- (d) the effects of granulation (or state of agglomeration) of the cobalt oxide with a suitable organic binder prior to reduction, thus again ensuring a more rapid diffusion of water vapour away from the powder bed. If an organic binder were used, the effect of the resulting carbon on the allotropic ratio in the reduced cobalt metal powder would have to be considered.

2.6 Discussion:

The phases of cobalt produced in powder form by the hydrogen reduction of one batch of cobalt oxide under various conditions of time and temperature have been studied. The general trend, that as the time and temperature of reduction are increased above the $\epsilon \rightleftharpoons \alpha$ transition point, that an increased proportion of the cubic allotrope results, was confirmed by reducing a sample of black cobalt oxide at 600°C for 36 hours; the same heating, quenching, and cooling conditions, as those described above, were used. This powder was found to be entirely cubic in structure. On the other hand, reduction for long periods below the transition temperature results in an entirely hexagonal powder. A sample of powder was reduced in hydrogen for 24 hours at 375°C, and showed no traces of the (200)

cubic line profile.

The data in Figure 2.2 for the proportions of hexagonal and cubic cobalt produced under various reduction conditions, although in agreement with the findings of previous investigators cannot be thoroughly explained on the basis of previously published experimental evidence. The main facts which require explanation are:

- (a) That with short reduction times below the transformation temperature some cubic cobalt is always produced.
- (b) That with short reduction times above the transformation temperature some hexagonal cobalt is always produced.

Rao et al.⁽¹⁶⁾ have considered that above the transformation temperature of 420° , the metal powder is likely to be in the face centred cubic form, and that transformation to the hexagonal form could occur on cooling with the introduction of further growth faults. This could explain the presence of hexagonal cobalt in reduced powder metal samples where a short reduction time is used above the transition temperature. These authors concluded also that any hexagonal cobalt formed as a result of the reduction process would be expected to transform to the f.c.c. form in view of the large deformation arising from the decrease in volume of the particles occurring during reduction. Reversion to the hexagonal form could be expected

to occur on cooling. If this hypothesis is accepted, then the appearance of some cubic phase using short reduction times (30 minutes) below the transition temperature can be explained. Using longer reduction times below and above the transition temperature must enable the initially formed phase to assume its thermodynamic state.

There is some crystallographic evidence that on reduction, a cubic structure for the metal might be favoured initially. All previous investigations are in agreement that the grey cobalt oxide (CoO) is an intermediate product in the reduction of Co_3O_4 . CoO has a cubic (rock salt) structure⁽²⁹⁾ with a lattice parameter of 4.260°A . Cubic cobalt has a lattice parameter of 3.5447°A . Four rock salt unit cells would after reduction in volume and removal of the oxygen atoms correspond to a face centred cubic arrangement of metal atoms.

It has been reported that fine grain sizes inhibit the transformation from cubic to hexagonal cobalt on cooling, and in a fine cobalt powder, it has been considered that the face centred cubic structure is favoured.⁽³⁴⁾ However, the work reported here indicates that a fine powder (of surface area as high as $3 \text{ m}^2/\text{g.}$) can be prepared by hydrogen reduction of black cobalt oxide, which shows no traces of the cubic material, but which contains stacking faults.

Although Sage⁽³⁵⁾ has reported that hydrogen could be responsible for the cubic form of cobalt during reduction, the evidence here shows that hexagonal cobalt can be prepared in the presence of hydrogen. Rao et al.^{(16), (36)} maintained that occluded hydrogen could not be responsible for the large strains observed in their powders.

No investigations of the reduction process above 850°C were carried out because of the limitations of the Wild Barfield retort furnace winding. Thus the conditions claimed by Hendricks, Jefferson and Schultz,⁽⁶⁾ which they said led to a reappearance of a second high temperature hexagonal phase were not studied. The results of these workers⁽⁶⁾ are difficult to explain unless their phenomena may be ascribed to the fact that Co_3O_4 decomposes into CoO at temperatures of 850 - 900°C, and the hexagonal cobalt is in some way associated with the hydrogen reduction of CoO at a high temperature. In the experiments described in this work the material reduced at 850°C for 30 minutes and one hour consisted of entirely cubic material with no traces of the hexagonal phase.

2.7 Conclusions:

It has been shown that pure hexagonal cobalt may be prepared in finely divided powder form by the reduction of black cobalt oxide with hydrogen, provided the reduction conditions of time and temperature are correctly chosen. Under other

conditions a mixture of the two allotropes was found, and an attempt was made to assess the variations in the proportions of the two allotropes with reduction temperature and time. In general reduction at temperatures below 400° results in the formation of the pure hexagonal modification, whereas reduction at higher temperatures results in a powder consisting of a mixture of the two allotropes. Reduction at temperatures in excess of 800° results in a predominantly cubic cobalt powder. As the reduction temperature and time are increased, the specific surface area and weight loss in hydrogen content of the powder are reduced.

Careful stabilisation of the powder with carbon dioxide prior to removal to the air was found to be necessary, because the powders reduced at low temperatures tended to be pyrophoric.

The hexagonal cobalt powder produced by reduction at low temperature has a specific surface area of $3 \text{ m}^2/\text{g}$. and assuming that the particles are spherical (which is not strictly true) then calculation shows that the average particle size is 0.11μ . Thus it may be possible to prepare material suitable for low temperature magnets provided the particles can be satisfactorily pressed and aligned.

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CHAPTER 3.

The Influence of Oxygen and Titanium on Cobalt.

3.1 Oxygen.

3.1.1 Introduction.

It has been reported that oxygen⁽¹⁾ can stabilise the cubic modification of cobalt. In view of the decisive importance of oxygen in finely divided cobalt powder, as discussed later in Chapter 5, it was felt that this phenomenon required further investigation. In the reduction studies described in Chapter 2, it was shown that it was possible to prepare faulted hexagonal cobalt in finely divided powder form with a weight loss in hydrogen of 1.92% (300°C - one hour on temperature). However, some cubic cobalt was evident in the sample reduced at 350°C for 30 minutes; in this case the weight loss in hydrogen was, however, obtained after the material had been removed from the furnace, and as there was good correlation between the weight loss in hydrogen and the specific surface area it is difficult to ascribe the cubic cobalt found in this sample to the oxygen content of 2.03%. The presence of cubic cobalt in this sample was explained using the hypothesis of Rao et al..⁽²⁾

The oxidation of cobalt metal samples has been studied by several previous investigators: The following summarise the important findings:⁽³⁾

- (1) The kinetics of oxidation at low temperatures

have received little attention.

- (2) Between 400° and 700° the parabolic oxidation relationship is obeyed.
- (3) There are some deviations in the values of the activation energies for the oxidation processes in the various temperature ranges.
- (4) There is a sharp but unexplained increase in oxidation rate above $600 - 700^{\circ}\text{C}$.
- (5) At temperatures below 700° the cold worked (hexagonal) cobalt was found to oxidise faster than the cubic form.
- (6) The three oxides of cobalt, namely CoO , Co_3O_4 and Co_2O_3 have respectively cubic, inverse-spinel and hexagonal structures.
- (7) The proportions of CoO and Co_3O_4 obtained depend on the oxidation conditions used:
 - (i) Co_2O_3 is unstable above 300°C .
 - (ii) Co_3O_4 is unstable above $850 - 900^{\circ}\text{C}$.
 - (iii) The O/Co ratio in CoO can vary between 1.0098 and 1.0017 depending on the temperature and oxygen pressure used.
- (8) At high temperatures, Wagner's hypothesis holds, regarding the dependence of oxidation rate on the partial pressure of oxygen.
- (9) Various theories involving the mechanism of oxygen diffusion have been proposed for the oxidation process, but there is no general agreement between these.
- (10) The work reported in 1 - 9 above was mostly

carried out in atmospheres of pure oxygen at fixed pressures. However, Seybolt and Mathewson,⁽⁴⁾ in an early work, have shown that cobalt metal specimens heated in air to constant weight at 800°C contained the same amount of oxygen as samples heated in one atmosphere of oxygen at 800°C . It has also been shown that nitrogen is insoluble in solid cobalt.⁽⁴⁾

Thus there is considerable divergence of opinion as to the part played by oxygen on the structure of cobalt; attention has been focussed mainly on the nature and examination of the oxide films. Furthermore, little experimental work has been directed to the effects of oxygen at temperatures below 300°C , and the influence of oxygen on the structure of finely divided cobalt metal powder.

A recent work⁽⁵⁾ has shown that there are no differences in values of activation energy for oxidation of the two allotropes of cobalt, but anomalous behaviour in the region of the allotropic transformation temperature was found for the Arrhenius plot.

3.1.2 Experimental - Oxidation of Hexagonal Cobalt Metal Powders at 160°C .

A 500 g. quantity of hexagonal cobalt metal powder was prepared by reduction of black cobalt oxide at 400°C for one hour, using the procedures described in Chapter 2. X-ray diffraction tests of the material showed no traces of the cubic phase.

20 g. quantities of this powder were weighed into porcelain evaporating dishes, and placed in a temperature controlled oven at 160°C , for the time periods shown in Table I. After these periods an X-ray diffraction pattern of each powder was examined, and the weight loss in hydrogen determined on heating a sample to a constant weight at 950° . The X-ray diffraction results are summarised in Table I. In no cases was any cubic cobalt detected in the X-ray diffraction patterns. Samples stored in the oven for times in excess of one hour at 160°C were found to be completely oxidised, with no diffraction peaks due to the metal powder.

3.2 Titanium.

3.2.1 Introduction.

Koster⁽⁶⁾ has reported that titanium enlarges the face centred cubic field of cobalt, as was shown in Table II of Chapter 1. Nevertheless as shown in Figure 3.1, titanium is the only metal of the first transition series (apart from cobalt) which has a hexagonal close packed structure at room temperature. It was hoped that possibly, by the incorporation of this metal into cobalt, followed by cold working (filing) that it might be possible to prepare a pure hexagonal cobalt phase. This work was carried out before the reduction experiments of Co_3O_4 with hydrogen on the phases of cobalt produced, had been thoroughly investigated. As it was found possible to prepare pure hexagonal cobalt

TABLE I.

Summarised X-ray diffraction data and weight losses in hydrogen for
 hexagonal cobalt metal powder samples heated in an electric oven
 at 160°C for various time periods.

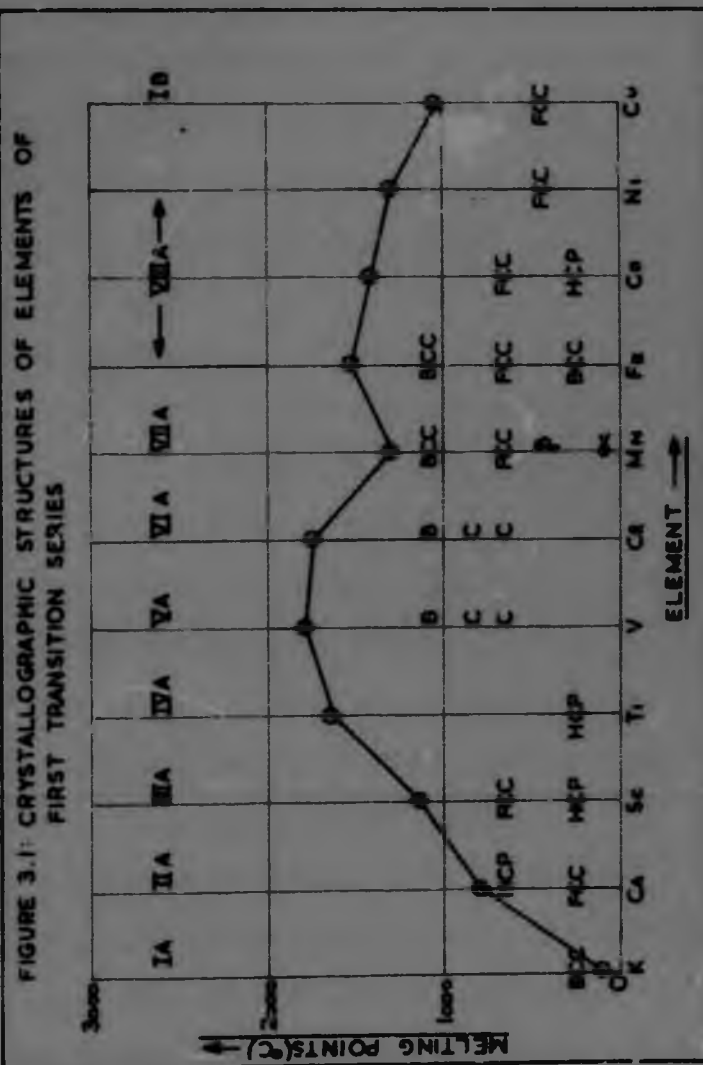
Time at 160°C	d spacing ⁰ A hexagonal cobalt			d spacing ⁰ A Co ₃ O ₄								Weight loss in H ₂ ⁽⁵⁾ %
	2.17	2.02	1.91	2.86	2.43	2.33	2.02	1.65	1.55	1.43	1.28	
5 mins.	P	P	P	A	A	A	P	A	A	A	A	2.5
8 "	P	P	P	P	P	P	P	A	A	A	A	7.5
10 "	P	P	P	P	P	P	P	P	P	P	P	12.5
15 "	A	P	A	P	P	P	P	P	P	P	P	22.9
30 "	A	P	A	P	P	P	P	P	P	P	P	23.0
45 "	A	P	A	P	P	P	P	P	P	P	P	22.5
1 hour	A	P	A	P	P	P	P	P	P	P	P	24.6
2 hours	A	P	A	P	P	P	P	P	P	P	P	23.4
5 "	A	P	A	P	P	P	P	P	P	P	P	20.8
10 "	A	P	A	P	P	P	P	P	P	P	P	26.0

TABLE I. (Cont.)

Time at 160°C	d spacing ^o A hexagonal cobalt			d spacing ^o A Co ₃ O ₄								Weight loss in H ₂ g (5)	
	2.17	2.02	1.91	2.86	2.43	2.33	2.02	1.65	1.55	1.43	1.28		
20 hours	A	P	A	P	P	P	P	P	P	P	P	P	25.4
1 day	A	P	A	P	P	P	P	P	P	P	P	P	26.1
2 days	A	P	A	P	P	P	P	P	P	P	P	P	28.0
3 "	A	P	A	P	P	P	P	P	P	P	P	P	25.6
5 "	A	P	A	P	P	P	P	P	P	P	P	P	19.2
6 "	A	P	A	P	P	P	P	P	P	P	P	P	24.9

Notes.

- (1) P $\equiv$ Present in Sample; A $\equiv$ Not present in Sample.
 (2) The spectra were run at $2\theta = 2^\circ$ per minute, in the range $30-90^\circ$.
 (3) Co_2O_3 was definitely not present because the (112) line $\left[\frac{I}{I_0} = 100 \text{ at } d = 1.78^\circ \text{A} \right]$ was absent.
 (4) CoO was definitely not present because the (200) line $\left[\frac{I}{I_0} = 100 \text{ at } d = 2.13^\circ \text{A} \right]$ was absent.
 (5) The weight loss in hydrogen values represent the loss in weight on heating the oxidised samples at 950°C in an atmosphere of hydrogen to constant weight; the weight loss in hydrogen therefore represents a measure of the oxygen content of the oxidised samples.



by suitable reduction techniques, the necessity for this work fell away, but it is reported for completeness.

The equilibrium diagram for the cobalt - titanium system (after Hansen and Anderko)⁽⁷⁾ is shown in Figure 3.2. A dispute has existed as to whether titanium raises or lowers the transformation temperature. An additional set of data for the phase equilibrium is shown in the inset diagram in Figure 3.2.

The influence of titanium was therefore investigated briefly.

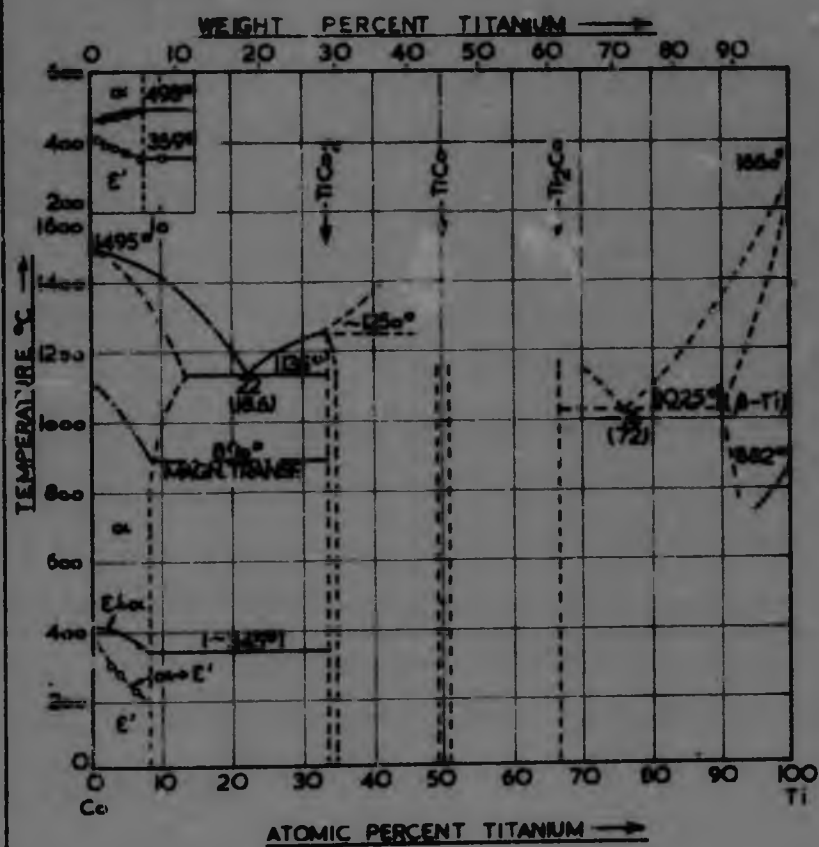
3.2.2 Experimental.

A 1 Kg. quantity of fine cobalt powder containing 3 atomic percent of titanium was milled in two charges in a 500 g. attrition mill for 9 hours under 300 ml. acetone. The initial specific surface area of the mixture was $1.25 \text{ m}^2/\text{g.}$, and after milling it was $1.53 \text{ m}^2/\text{g.}$ The titanium powder used was a chemically pure I.C.I. grade (- 325 mesh), containing 0.20% oxygen.

A similar mixture was made up using a coarser - 200 mesh powder which contained 0.16% oxygen. After mixing, both these mixtures were dried under vacuum to remove the acetone, and were pressed into compacts of 200 g. in a 1.300" diameter die at 10 tons/in². These compacts were packed in pure alumina and sintered in hydrogen at 1450°C.

The sintered compacts were filed with a

FIGURE 3.2 THE TITANIUM-COBALT EQUILIBRIUM DIAGRAM



coarse file, and an X-ray diffraction pattern of the filings examined.

The hexagonal to cubic phase ratios were 5.36 and 5.21 respectively for the coarse and fine titanium-cobalt compositions. In Chapter 4, filings prepared from pure cobalt powders are described, and the hexagonal to cubic phase ratio is shown to be 5.52. This indicated that the titanium had no significant effect on stabilising the hexagonal phase of cobalt.

These filings were then ground in 500 g. charges in an attrition mill, and milled for a further 9 hours, under 300 ml. acetone as milling fluid.

The iron contents of the milled filings were 2.65% and 2.95% respectively for the fine and coarse titanium-cobalt mixtures, before the additional milling. The milled filings were dried under vacuum to remove the acetone, and a sample of each re-examined by X-rays. The hexagonal to cubic phase ratios were found to have increased to 6.28 and 6.58 for the fine and coarse titanium-cobalt batches respectively. Small pieces of both sintered alloys were polished for micro-examination and found to be single phased.

3.3 Conclusions.

Hexagonal cobalt metal powder stored in air for various periods at 160°C showed no evidence of cubic cobalt; the surfaces of the metal powder samples stored for periods in excess of one hour were found to be completely oxidised with no evidence of metal powder structure.

Incorporating titanium in cobalt in small amounts appeared to have no advantages so far as the production of the hexagonal allotrope is concerned.

In any event, it was found possible to prepare the pure hexagonal modification in finely divided powder form by suitable reduction procedures as was described in Chapter 2.

REFERENCES FOR CHAPTER 3.

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- 2) C.V.S.H.N. Rao, S. Lele, and T.R. Anantharaman - *Trans. Indian Inst. Metals* 20 80 (1967)
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- 4) Seybolt and Mathewson - *Trans. AIME.* 117 156 (1935)
- 5) E. Chattopadhyay and J.C. Neasor - *J. Material Science* 4 457 (1969)
- 6) W. Koster and E. Wagner - *Z. Metallkunde* 29 230 (1937)
- 7) *Cobalt Monograph-Centre du Information du Cobalt* (1930) p 188

CHAPTER 4.

The Milling of Cobalt Powders and Filings.

4.1 Introduction:

The work previously described in Chapter 2 showed that the reduction conditions employed, exerted a profound influence on the proportions of the phases obtained and on the specific surface area of the reduced cobalt metal powder.

For powder metallurgical applications, cobalt powders from different sources are used, as is practised in the manufacture of hard metal alloys; the preparation of these materials involves a milling process where the cobalt and carbide powders are ground together. It was, therefore, decided to investigate how pure cobalt powders behave on wet grinding.

In the work reported here, commercial cobalt powders from different sources were vibratory ball milled under acetone, and the changes in powder properties (specific surface area, coercivity, and ratio of the two allotropes) were studied as a function of the milling time.

The properties of the cobalt powders used in these investigations are shown in Table I; the complete analyses on two of the powders used are also shown.

4.2 Previous Studies on the Milling of Cobalt Powder.

This was discussed in Section 1.2.4, and although certain phenomena pertaining to the milling

TABLE I.

Summarised Properties of Cobalt Powders used in
milling experiments.

Cobalt Source	Specific Surface Area of Initial powder m ² /g.	Intensity ratio of the (101) hex. to (200) cubic profiles	Analyses		
Hoboken ¹ Powder	1.53	0.70	C	0.07%	K 0.01%
			Fe	0.036%	Na 0.01%
			Mn	Nil	Ca Nil
			Cu	0.001%	Si 0.007%
			Ba	Nil	S 0.01%
			Sn	"	Ni 0.022%
			Zn	"	O ₂ 1.16%
			Al	"	
Hoboken ² pre-annealed powder	1.07	0.77	O ₂	0.62%	
CP-6 ³	1.25	0.38	O ₂	0.74%	
CP-6 ² pre-annealed powder	0.96	0.45	O ₂	0.41%	
CP-10 ³	1.32	0.22	C	0.03%	K 0.01%
			Fe	0.024%	Na 0.006%
			Mn	Nil	Ca 0.05%
			Cu	0.003%	Si 0.025%
			Ba	Nil	S 0.01%
			Sn	"	Ni 0.018%
			Zn	"	O ₂ 0.53%
			Al	"	
Pure hexagonal cobalt ⁴ powder	2.82	No cubic visible	Wt. loss in hydrogen 1.63%		

1. Supplied by Societe du Metallurgie du Hoboken - Belgium.
2. Pre-annealing conditions: Heating at 200°/hour to 600°C in hydrogen with 4 hours at 600°C. A 10°/hour cooling rate was used.
3. Cobalt powders supplied by Hard Metals Limited.
4. Prepared as described in the text.

of cobalt powders have been described, no complete picture of the complex processes occurring has emerged. Further work has been carried out by Hinnuber, Rudiger and Kinna,⁽¹⁾ and Kochanovska.⁽²⁾

The former workers milled a cobalt powder of 5 μ average particle size, under acetone, for a total period of 1,000 hours removing milled powder samples after various periods of time. After 100 hours, an increase in the proportion of hexagonal phase, present in their samples was evident, and after 800 hours these workers concluded that the powder was entirely hexagonal. The maximum oxygen content of the powders milled for 1,000 hours was 0.89%

Hinnuber et al.⁽¹⁾ obtained a continuous increase in the powder coercivity with milling times of up to 500 hours, after which the coercivity decreased slightly; these authors also studied the milling of a coarser cobalt powder of 15 μ particle size, and this displayed similar behaviour to their 5 μ powder in relation to the phase transformation, and also the increase in coercive force.

Kochanovska⁽²⁾ has also studied the milling of a fine cobalt powder, prepared from cobalt oxalate by hydrogen reduction, which initially had a cubic structure; on dry milling this powder, a partial transformation to the hexagonal modification occurred initially, but the cubic modification appeared again after 48 hours milling.

Kochanovska attributed the formation of the secondary cubic phase to a local rise in temperature occurring during the grinding process, and to an absorption of oxygen which made the transformation irreversible. Diffraction lines of cobalt oxide were evident in this work of Kochanovska.

Kochanovska's initial powder was, as mentioned above, prepared by the hydrogen reduction of cobalt oxalate at 550°C. Sage⁽¹⁷⁾ has shown that this reduction procedure leads to the formation of pure cubic phase, but which in his sample, contained 1.35% carbon.

4.3 The coercivity of ferromagnetic powders.

A marked increase in coercivity of fine ferromagnetic particles with decreasing particle size is well known. Some examples are shown in Figure 4.1.

Four major factors increase the coercive force of a ferromagnetic powder assembly:⁽¹²⁾

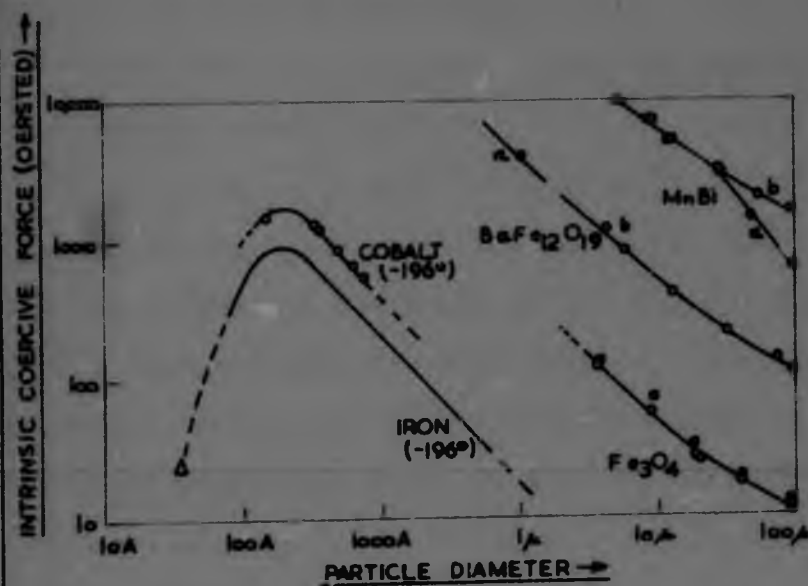
- (1) Crystal anisotropy.
- (2) Strain anisotropy.
- (3) Shape anisotropy.
- (4) Exchange anisotropy.

4.3.1 Crystal anisotropy.

The magnitude of this contribution to the coercivity is given by $2K/I_s$

where K is the crystalline anisotropy constant and I_s is the saturation magnetisation.

FIGURE 4.1: VARIATION IN COERCIVE FORCE WITH
PARTICLE SIZE FOR FERROMAGNETIC POWDER PARTICLES
(AFTER 12)



An expression for the energy of magnetisation in cubic crystals can be written as:

$$F_c = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2)$$

where F_c is the crystal energy of magnetisation
the K 's are the anisotropy constants
the α 's are the direction cosines of the magnetisation vector with respect to the principal crystal axes (100).

Some of the data for the anisotropy constants for f.c.c. cobalt are shown in Table II.⁽¹³⁾ At 1,000°C cobalt becomes magnetically anisotropic.

Similarly for hexagonal cobalt the expression for the crystal energy is:

$$F_c = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta$$

where θ is the angle which the magnetisation vector makes with the hexagonal axis. The relevant data⁽¹³⁾ determined at room temperature are also shown in Table II. From theoretical considerations, it has been concluded that the high crystalline anisotropy is a characteristic of the hexagonal lattice, and not of the element itself.⁽⁸⁾

4.3.2 Strain anisotropy.

An expression has been derived for the contribution of this to the coercivity, and its magnitude is given by:

$$\frac{3AT}{I_s}$$

TABLE II.

Crystal Anisotropy Constants for Cobalt.

Conditions of Measurement	Anisotropy Constants (10^5 ergs./cm ³)		
	K_0	K_1	L_2
h.c.p. room temp.	-	41	10
h.c.p. " "	400	39.8	19.8
h.c.p. " "	-	53	10
h.c.p. " "	-	43	12
f.c.c. 500°	-	- 2.30	- 4.31
f.c.c. 600°	-	- 1.09	- 3.21
f.c.c. 700°	-	- 0.60	- 1.91
f.c.c. 800°	-	- 0.23	- 1.03
f.c.c. 900°	-	- 0.09	- 0.57
f.c.c. 1,000°	-	0	0

where λ is the magnetostriction constant
and T is the stress in the material

4.3.3 Shape anisotropy.

The shape of fine ferromagnetic particles influences their coercive force, since the magnetisation of the particles for non-spherical particles varies with direction.

4.3.4 Exchange anisotropy.

This effect results from an exchange interaction coupling across an interface between a ferromagnetic particle and its coherent anti-ferromagnetic coating. An example of Co - CoO has been quoted in the literature.⁽¹²⁾ Thus oxidation of cobalt or cobalt-carbide compacts would influence the coercivity if some of the oxygen was present as CoO.

4.3.5.

In general, more than one of these effects is present in any one system, and theoretically it is necessary to consider the vectorial sum of the four exchange energy terms.

On the other hand, Zaikova and Shur⁽¹⁴⁾ have considered that the major reason for the increase in coercive force, when the size of ferromagnetic material is reduced, is due to an increase in stray magnetic fields on the surface, and the critical size below which the coercivity increases rapidly depends on the main characteristics of the ferromagnetic material.

namely the constants of crystalline anisotropy and the saturation magnetisation. According to these authors,⁽¹⁴⁾ stray fields on the surfaces of ferromagnetic materials will make the process of magnetisation more difficult, and thus increase the coercive force.

The coercivity is a structure dependent parameter and consequently depends on the degree of crystal perfection (i.e. the extent of cold working and the presence of faults) as well as on the proportions of the two phases present.

None of the theories derived to explain the coercive force of fine particle assemblies yields good agreement with experimentally measured values, and for powders the values obtained are always considerably less than those predicted by theory.⁽¹⁹⁾ Magnetic interactions between particles in assemblies are also of importance.⁽¹⁹⁾

4.4 Experimental Work.

The pure cobalt powders listed in Table III, were milled under the following conditions:

- (a) Cobalt powder charge 500 g. in all cases.
- (b) 800 ml. stainless steel mill used.
- (c) 300 ml. acetone as milling fluid.
- (d) Grinding media: 2 Kg. $\frac{1}{4}$ " Hard Metal Balls.

After milling for various time periods, small scoop samples containing approximately 8 g. cobalt powder were removed. These samples were

TABLE III.

Summary of Cobalt Powders studied.

(1)	CF-6
(2)	Hoboken (Repeated)
(3)	CF-10
(4)	A fine hexagonal cobalt powder prepared as described in the text
(5)	Hoboken annealed powder
(6)	CF-6 annealed powder

dried for three hours on a hot water bath under reduced pressure to remove the acetone present. Care was taken to ensure that, to prevent oxidation, the mills were cold before exposing the samples to the air. Understandably this drying procedure caused agglomeration of the powder samples, and the powders were therefore lightly crushed in a mortar with a pestle, prior to further measurements being carried out on the powders. It is not known what effects this slight extra cold working had on the state of the powders. No screening operations were carried out on the powders, as it was found to be extremely difficult to screen the ductile powders, and screening, as reported by Sykes, is known to enhance the proportion of the hexagonal modification. It has been reported⁽³⁾ that sedimentation analysis, in order to obtain the particle size distribution of the milled cobalt powders is of no value because of the tendency of the cobalt powder to agglomerate. Therefore, in order to characterise the size of the milled material, the specific surface area was measured on a Perkin Elmer 212D Sorptometer, and with the initial batch the Fisher sub sieve grain size was also measured.

X-ray diffraction patterns of the powder samples were examined on a Philips PW 1060 Diffractometer, using the following conditions:

Entrance, exit and scatter slits 1° , 0.1° and 1° respectively.

Cobalt K_{α} radiation-32Kv 10mA. Scanning speed -
 $2\theta = \frac{1}{4}^{\circ}$ /minute.

The intensities of the (200) cubic and (10 $\bar{1}$ 1) hexagonal peaks were measured with a Planimeter. As was discussed in Chapter 2, this enables the equation of Sage and Guillaud⁽¹⁶⁾ to be used, which has been shown to be a sound method for determining the proportions of the two allotropes of cobalt present.

The precision of the determination of the cobalt phase ratios, in hard metal powders, as determined by X-rays is discussed in Chapter 5.

Pronounced line broadening for the (10 $\bar{1}$ 1) hexagonal peak was evident as milling proceeded. An analysis of this phenomenon is considered later (4.7).

The coercivity measurements were made on the powders, mixed in equal proportions with Bakelite powder, and then pressed into compacts at 10 tons/in.² in a 0.475" ϕ die. This technique has been used before by Exner and Fischmeister,⁽³⁾ and although it is shown in Chapter 5, that the coefficient of variation with this technique is higher for hard metal powder compacts than for the pressed compacts, it was decided to adhere to it for the following reasons:

- (a) 8 g. powder, less the amounts used for the other studies, would give an insufficiently sized compact for coercivity measurements,

and more important,

- (b) As described in Section (4.9) the different cobalt phases present depend on the pressing pressure used, as does the coercivity.

The coercivities of all ferromagnetic powders are extremely sensitive to the packing conditions used. (9)

The Fisher grain size measurements (where they were carried out with the first batch examined) were made on 4 g. of the powder prior to pressing using the following formula to allow for the non-availability of the required 8.8 g.:

$$\text{Fisher grain size} = y \sqrt{\left(\frac{\rho_{av.}}{\rho_{av.} + x - 1} \right)^3}$$

where y is the apparent Fisher grain size measured with the instrument

$\rho_{av.}$ is the average porosity measured with the instrument

$$x = \frac{\text{the standard weight of powder}}{\text{the weight of powder used}} = \frac{8.8}{4.0}$$

The Fisher sub sieve sizer uses the principle of air permeability for particle size measurements; the resistance offered to a fluid passing through a porous plug of powder is governed by the pore structure of the plug. By making certain assumptions, the pore structure of the plug can be related to the specific surface area of the powder (and hence the

particle size). These assumptions are that the pressure difference is small, and that the plug is a uniform cylinder. The calculation of the surface area of the powder in a compressed plug using the air permeability technique was made by using the Kozeny-Carmen equation. This technique only measures the external surfaces of the powder particles, and the influences of blind channels and pores are ignored.⁽⁴⁾ Thus it is often the case that the surface area as determined by the nitrogen adsorption method is 5 - 10 times larger than that estimated by air permeability techniques.⁽⁴⁾

Attempts were made to examine the milled cobalt powder samples using electron microscope replica techniques, similar to those described in Chapter 5 for hard metal powder samples. However, although two examples shown in Figures 4.2 and 4.3 indicate that it is possible to examine cobalt powders using replica techniques, these techniques suffer from three main disadvantages:

- (a) the limited depth of field attainable with the replica technique.
- (b) there are certain inherent difficulties in replica work, where the replica has to be transferred to hydrochloric acid.
- (c) agglomeration of the powder particles can occur during the preparation of the replica.

The above difficulties were overcome when



Figure 4.2: Aggregate of Cobalt in CF-6
Powder milled for 20 hours; examined
using replica technique x 4500.

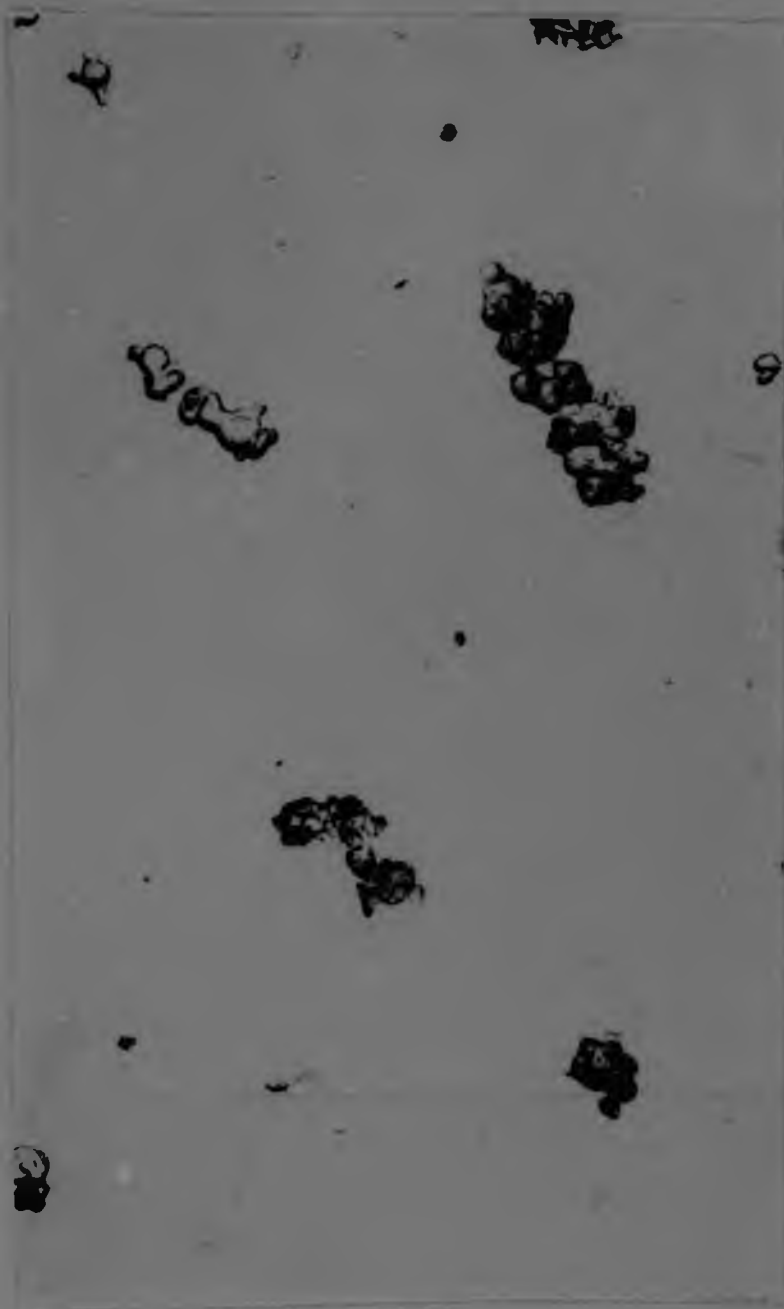


Figure 4.3: Individual Cobalt Particles
in CF-6 Cobalt Powder milled for 130 hours;
examined using replica technique x 4500.

the powders were examined (as is shown in the Figures below) on the Cambridge Stereoscan Microscope, where dispersion may be effected more easily. The advantages of a Stereoscan microscope for examining powders as compared with optical and replica microscopy have recently been fully reviewed.⁽²⁰⁾

4.5 Experimental Results.

4.5.1 CF-6 powder.

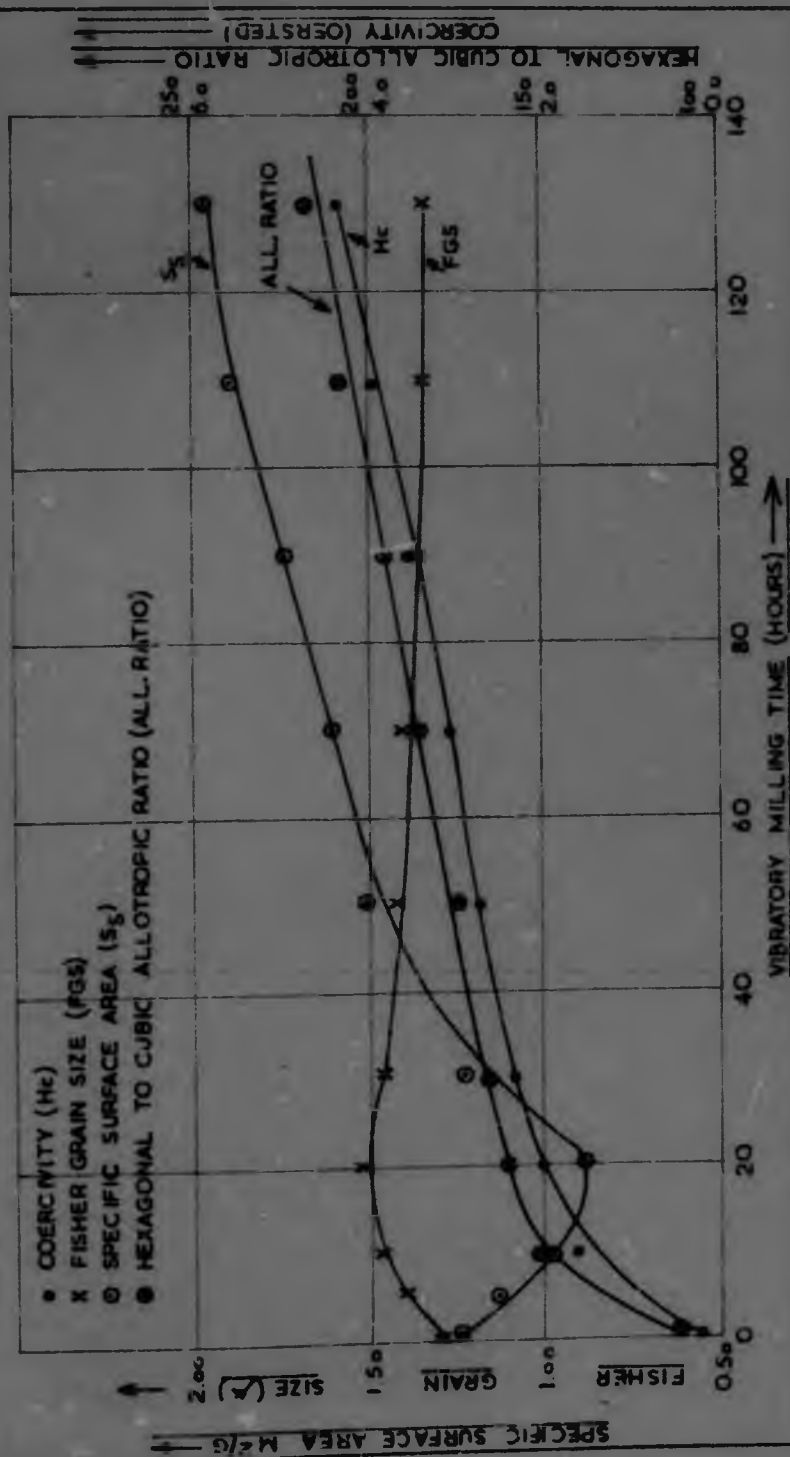
The measured property results of Fisher grain size, specific surface area, coercivity, and ratio of allotropes are plotted against the milling time in Figure 4.4. Figures 4.5 and 4.6 show the state of the powder after 20 hours milling showing the agglomeration. The initial powder is shown in Figure 4.7.

4.5.2 Hoboken cobalt powder.

Although the Fisher grain size variations with milling time for the CF-6 powder showed that some agglomeration had in fact occurred, it was decided to discontinue measurement of this parameter with the subsequent batches, because the total surface area was required as the parameter, not merely the external surfaces. Furthermore, only small sample weights were available for measurement of this property.

The Hoboken powder, in the initial condition, as examined on the Cambridge Stereoscan Electron Microscope is shown in Figure 4.8. This powder was much more filamentary and more agglomerated than CF-6.

FIGURE 4.4: VARIATION OF POWDER PROPERTIES WITH MILLING TIME FOR POWDER CP-6



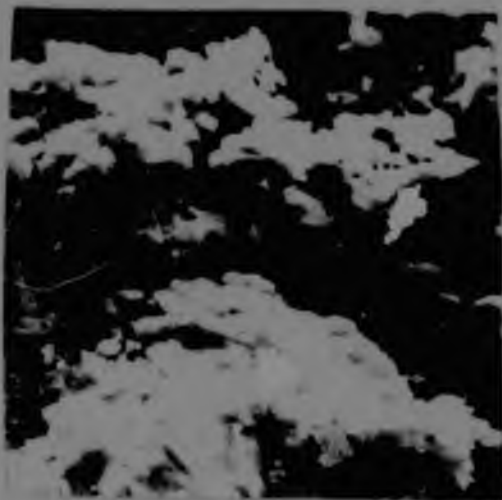


Figure 4.5: CF-6 Cobalt Powder
milled for 20 hours x 1,640.



Figure 4.6: CF-6 Cobalt Powder
milled for 20 hours x 3,300.

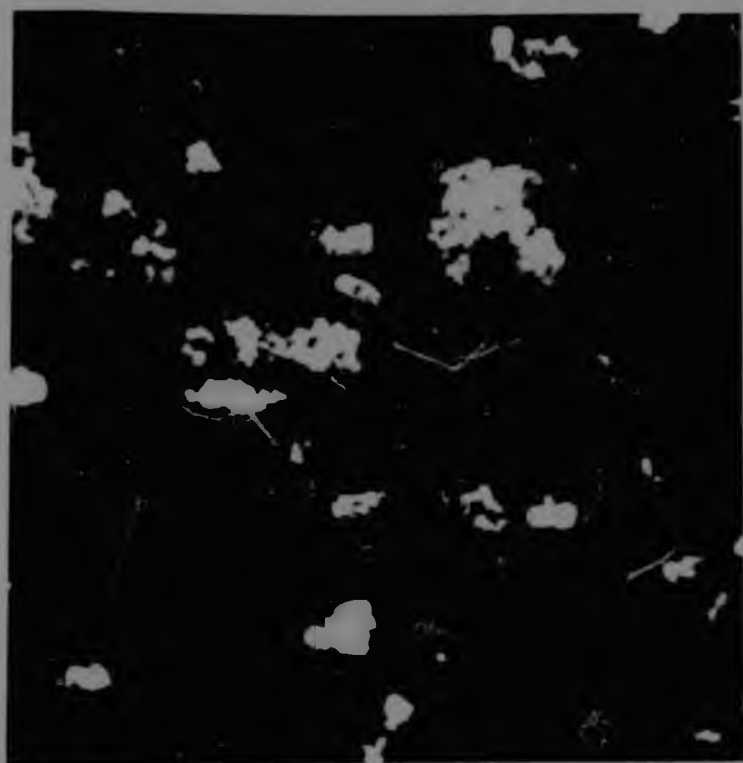


Figure 1. 100x (lower 20 microns)
magnification

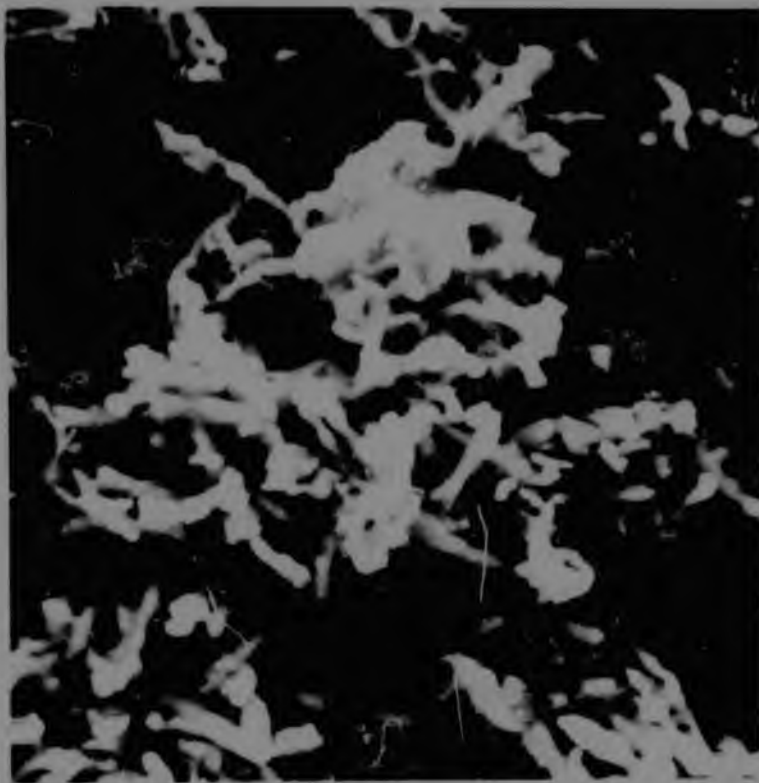


Figure 4.8: Hoboken Cohalt in
initial condition x 2400.

The variation in the various physical properties of the Hoboken cobalt powder, and the time of grinding are shown in Figure 4.9. Substantially similar data were obtained on the repeat batch (Figure 4.10).

4.5.3 CF-10 powder.

The same relationships between physical properties and milling time for powder CF-10 are shown in Figure 4.11. The initial powder is shown in Figure 4.12, and after 20, 50 and 70 hours of milling in Figure 4.13.

4.5.4 Extra fine hexagonal cobalt powder.

This powder was prepared in a manner described in Chapter 2 by reduction of black cobalt oxide at 400° for one hour.

The variations in powder properties with milling time are summarised in Table IV.

In this case there is a continuous decrease in powder specific surface area up to 90 hours of vibratory milling. This is in complete contrast to the coarser cobalt powders described above, which consisted of a mixture of both phases. The samples milled for 10, 20, 30 and 70 hours were examined by X-ray diffraction but no cubic cobalt, (the (200) line), was detected in any of these samples, neither were any diffraction peaks of cobalt oxide detected. The weight loss in hydrogen figures (determined by heating to a constant weight in hydrogen at 950°C) are also recorded in Table IV.

FIGURE 4.9: VARIATION IN POWDER PROPERTIES WITH MILLING TIME FOR HOBOKEN COBALT

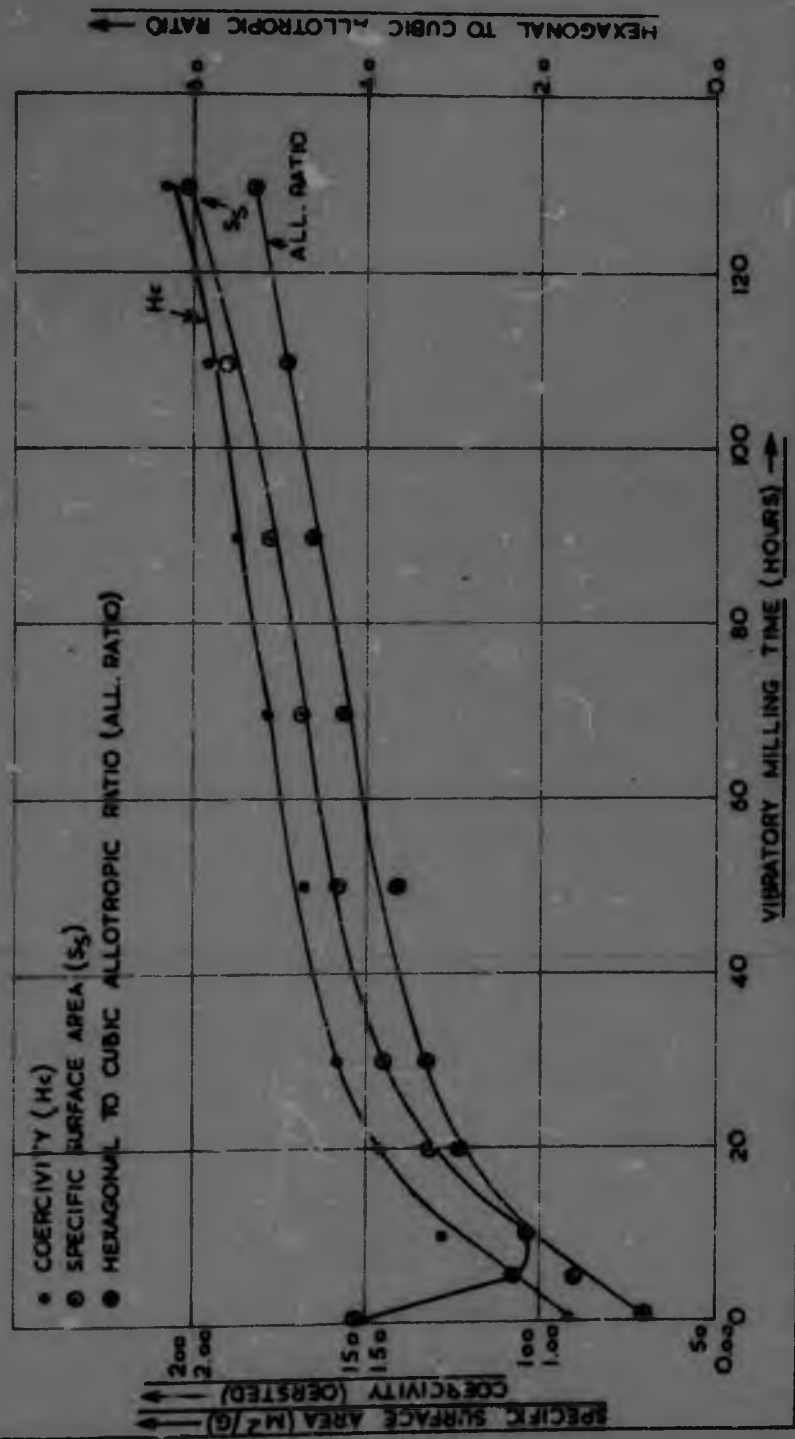


FIGURE 4.10: VARIATION IN POWDER PROPERTIES WITH MILLING TIME FOR HOBOKEN COBALT

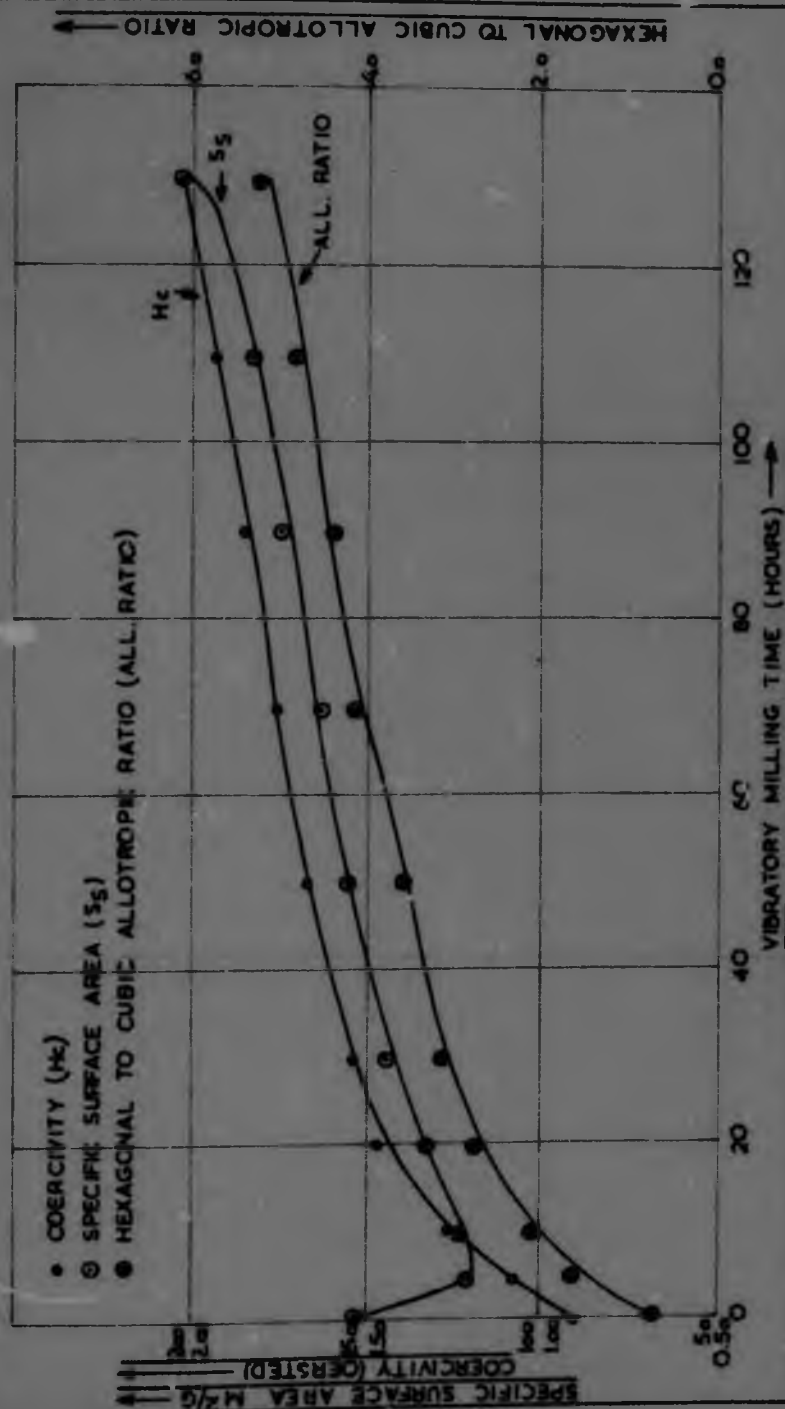


FIGURE 4.11: VARIATION OF POWDER PROPERTIES WITH MILLING TIME FOR CF-10 POWDER

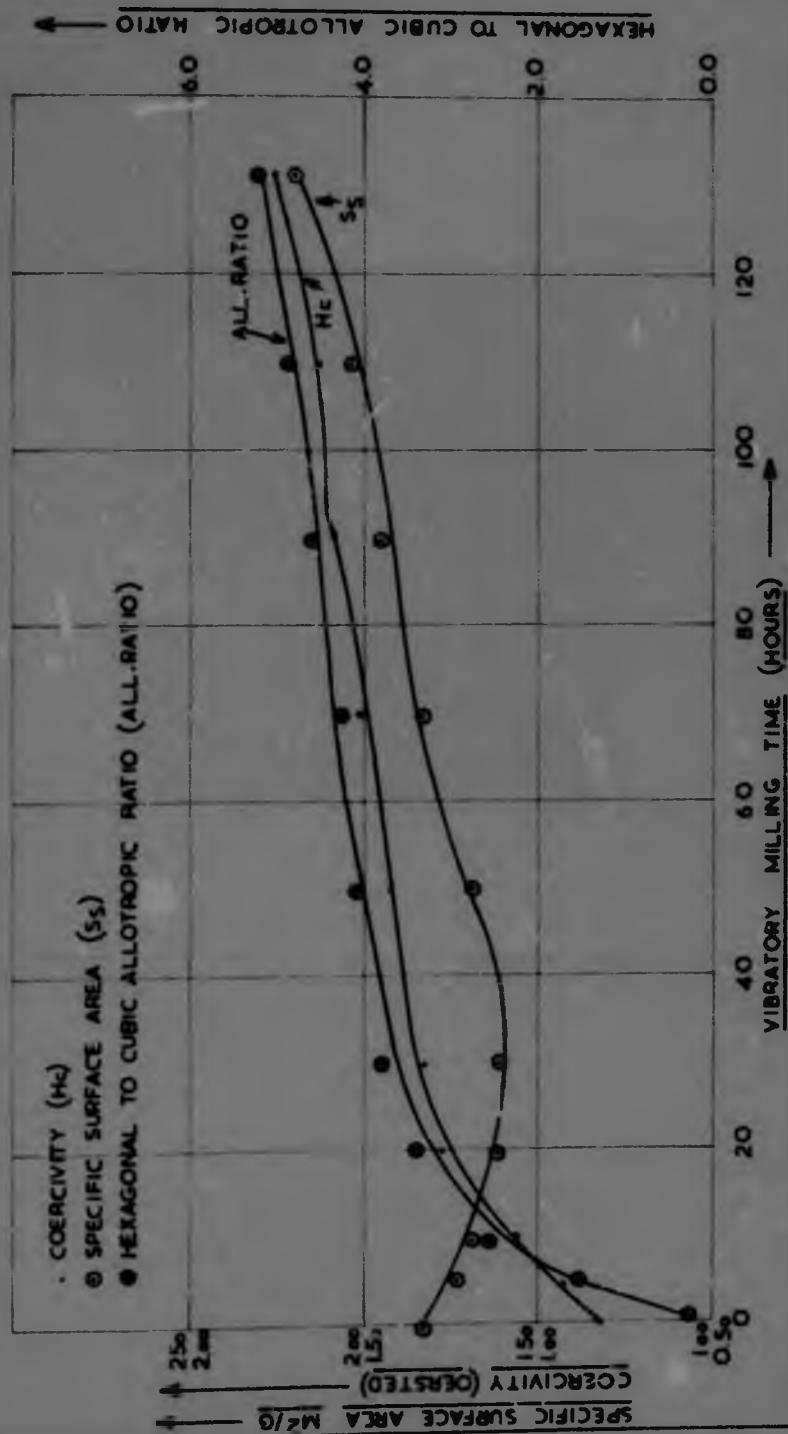
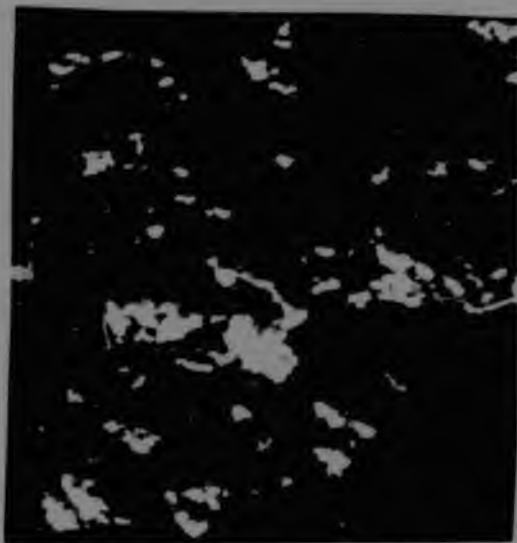
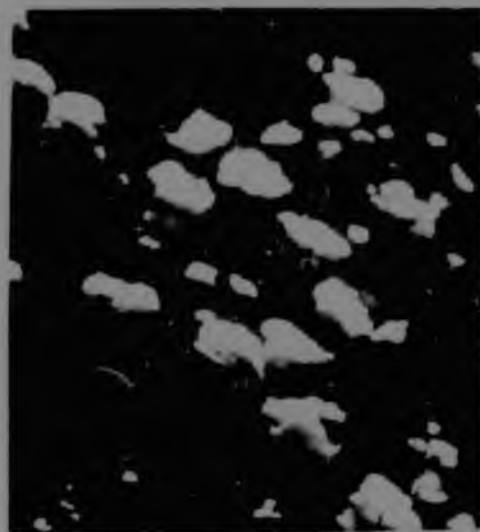




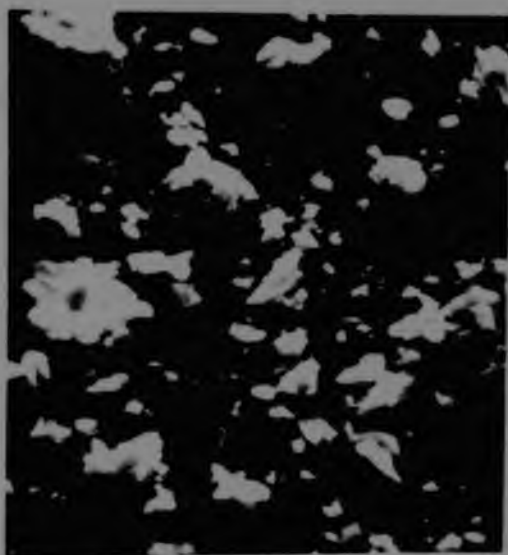
Figure 4.12: CF-10 powder in
initial condition x 1640.



20 hours



50 hours



70 hours

Figure 4.13: CF-10 Cobalt Powder after various milling times (all x 1,640).

TABLE IV.

Variations in milled hexagonal cobalt powder
properties.

Milling Time (hours)	$S_s \text{ m}^2/\text{g.}$	Coercivity (Oersted)	Wt. loss in H_2 %
0	2.82	245	1.63
10	2.45	246	2.12
20	2.37	252	-
30	1.94	255	3.55
50	1.39	257	3.47
70	1.24	262	3.82
90	0.97	261	4.15
110	1.05	258	3.98
130	1.22	265	3.72

Evidence that severe agglomeration occurred during milling is evident in the Stereoscan photomicrographs of the milled powders. (Figure 4.14).

In Chapter 5, the preparation of a hard metal batch using a similar fine hexagonal cobalt powder is described. This was found to require very little milling to achieve satisfactory densities on sintering. In view of the large disparity in size between the cobalt and carbide particles, it would have been expected that unless the cobalt particles had agglomerated together to form larger units, it would have been extremely difficult to prepare a hard metal powder, which would sinter satisfactorily.

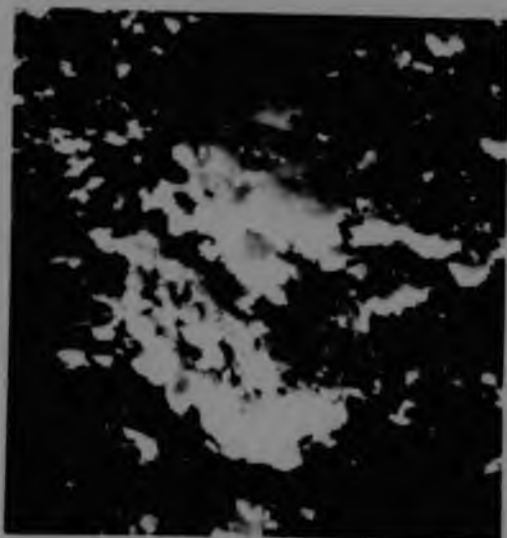
4.5.5 and 4.5.6.

Stereoscan photomicrographs of the annealed Hoboken and CF-6 powders prior to milling, are shown respectively in Figures 4.15 and 4.16.

The variation of milled powder properties with milling time for the annealed Hoboken cobalt is shown in Figure 4.17. The CF-6 powder showed results substantially similar to the Hoboken powder with no evidence of agglomeration during the initial stages of milling.

4.6 Interaction with the solvent during milling.

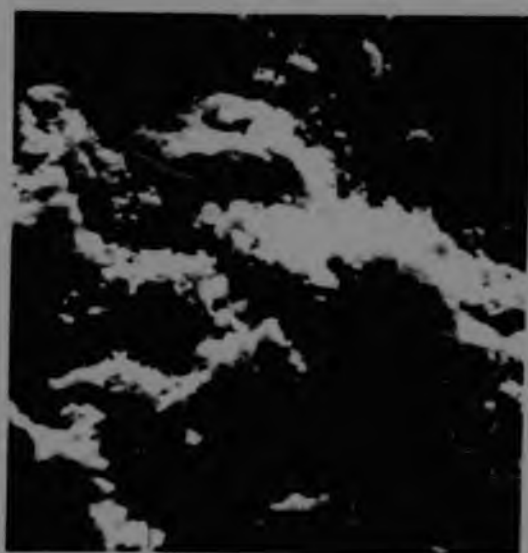
During the course of milling, it was found that the carbon content of the milled cobalt powder samples increased; one example where the carbon



10 hours.



20 hours.



30 hours.

Figure 4.14: Fine hexagonal cobalt powder
after various milling times (all $\times 1640$).

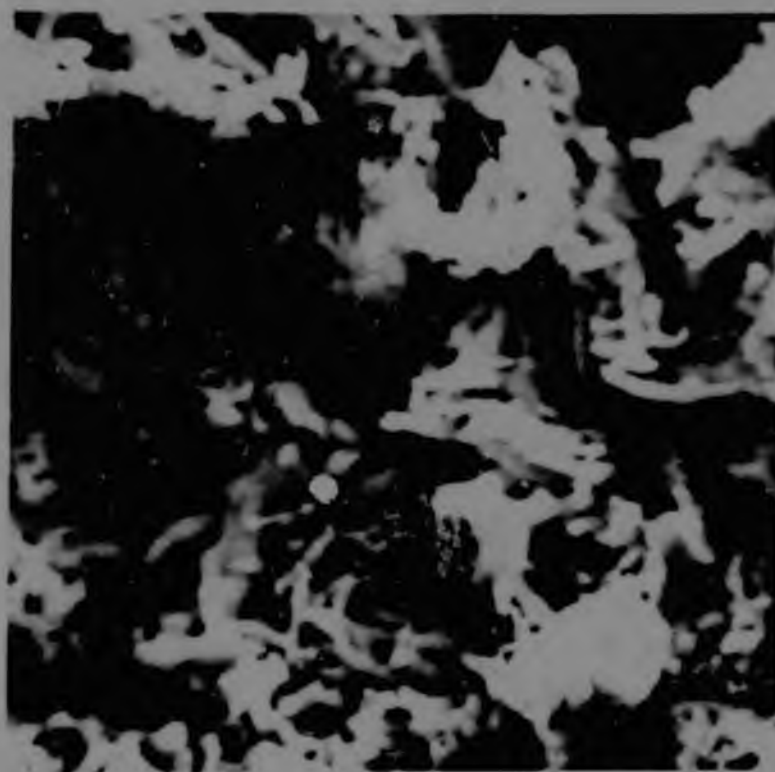


Figure 4.15: Annealed Hcboken Cobalt
in initial condition x 2400.

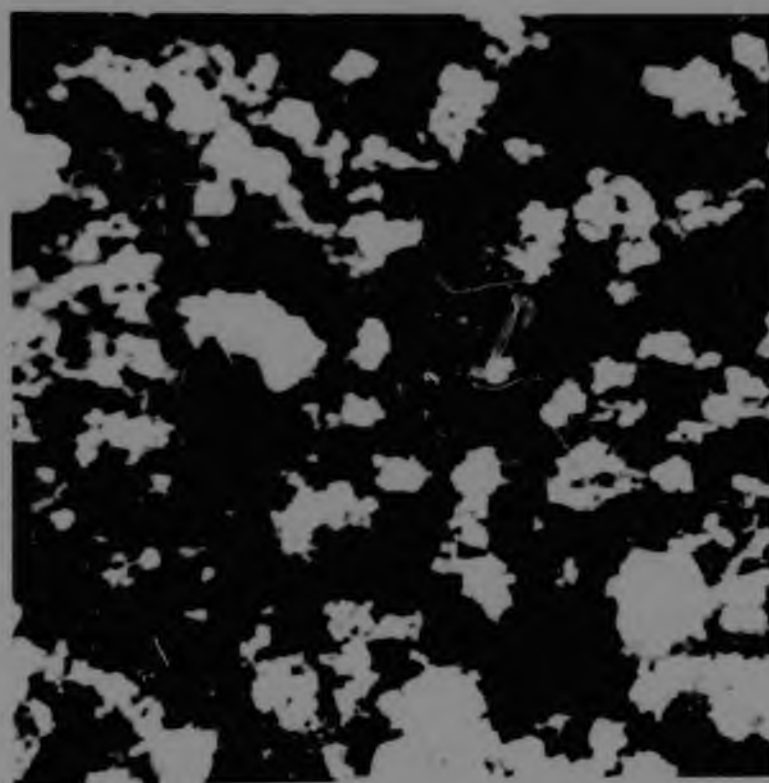
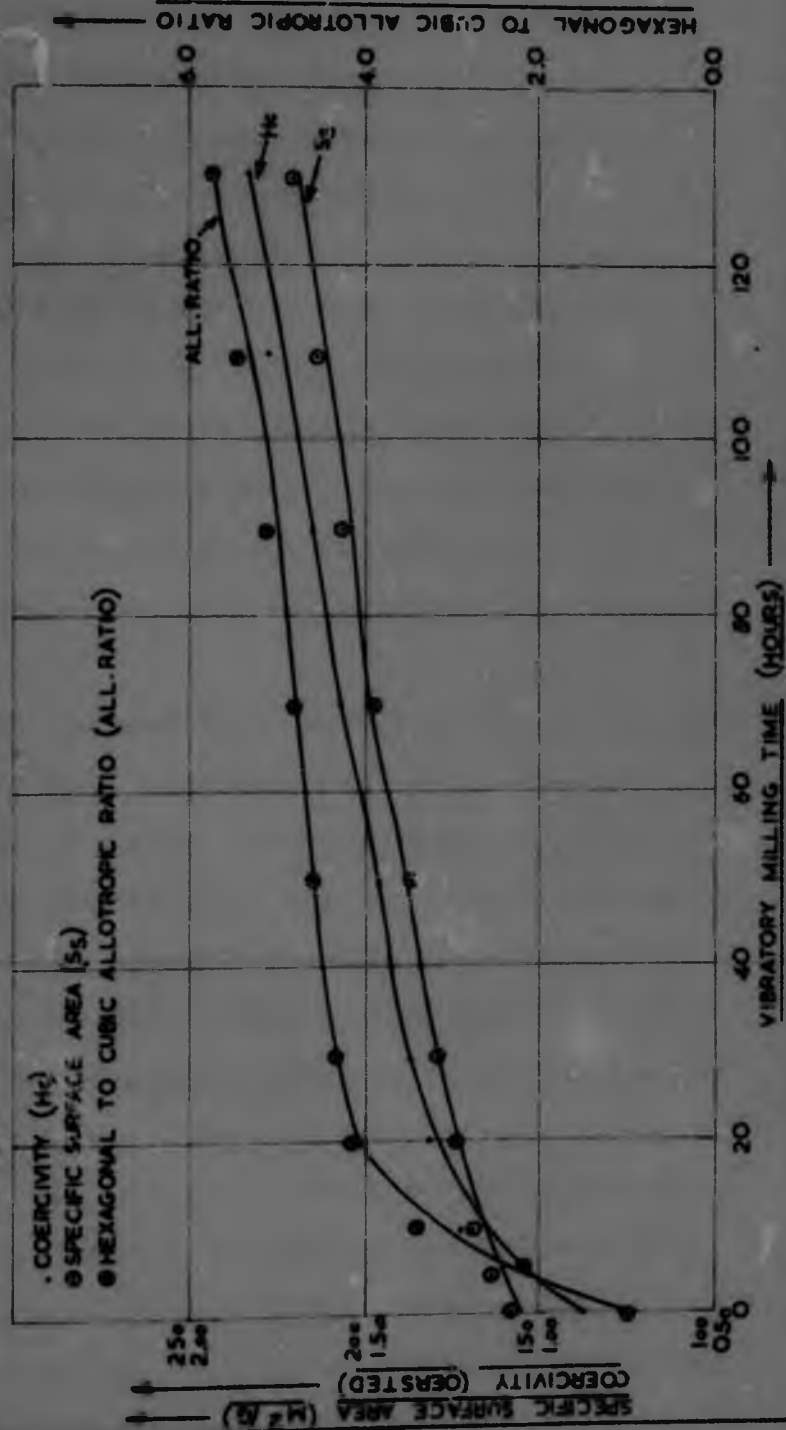


Figure 4.16: Annealed CF-6 powder in
initial condition x 2400.

FIGURE 4.17: VARIATION OF POWDER PROPERTIES WITH MILLING TIME FOR ANNEALED HOBOKEN COBALT POWDER



content was measured for all of the milled samples is shown in Table V. This problem was not specifically investigated, but it must be assumed that the carbon residue in the ground powders originated from an interaction of the metal powder with the acetone. When other ductile metal powders have been ground under a fluid, it has been suggested^{(5), (21)} that for extensive comminution of these to occur on grinding, they must react with the fluid. This problem is probably of more importance in the milling of hard metal powders, where carbon control is of critical importance. The work reported here did not reveal any effect of carbon as a cubic phase stabiliser, although this has been reported elsewhere.⁽¹⁷⁾

The solubility of carbon in cobalt has been studied at high temperatures,⁽¹⁰⁾ the weight percentage of carbon in solid solution increasing from 0.111% at 845°C to 0.861% at 1,285°C for face centred cubic cobalt. However, the carbon pick up occurring during grinding must be such that this element is physically entrained in some manner in the metal powder. This is shown below.

A further batch of CF-6 cobalt powder was vibratory milled under acetone for 60 hours in a manner similar to that described above. No samples were removed after any intermediate milling times. The milled cobalt powder was dried under vacuum to remove the acetone, exactly as described above.

TABLE V.

Carbon increase of milled cobalt powder with
milling time (CF-6 powder)

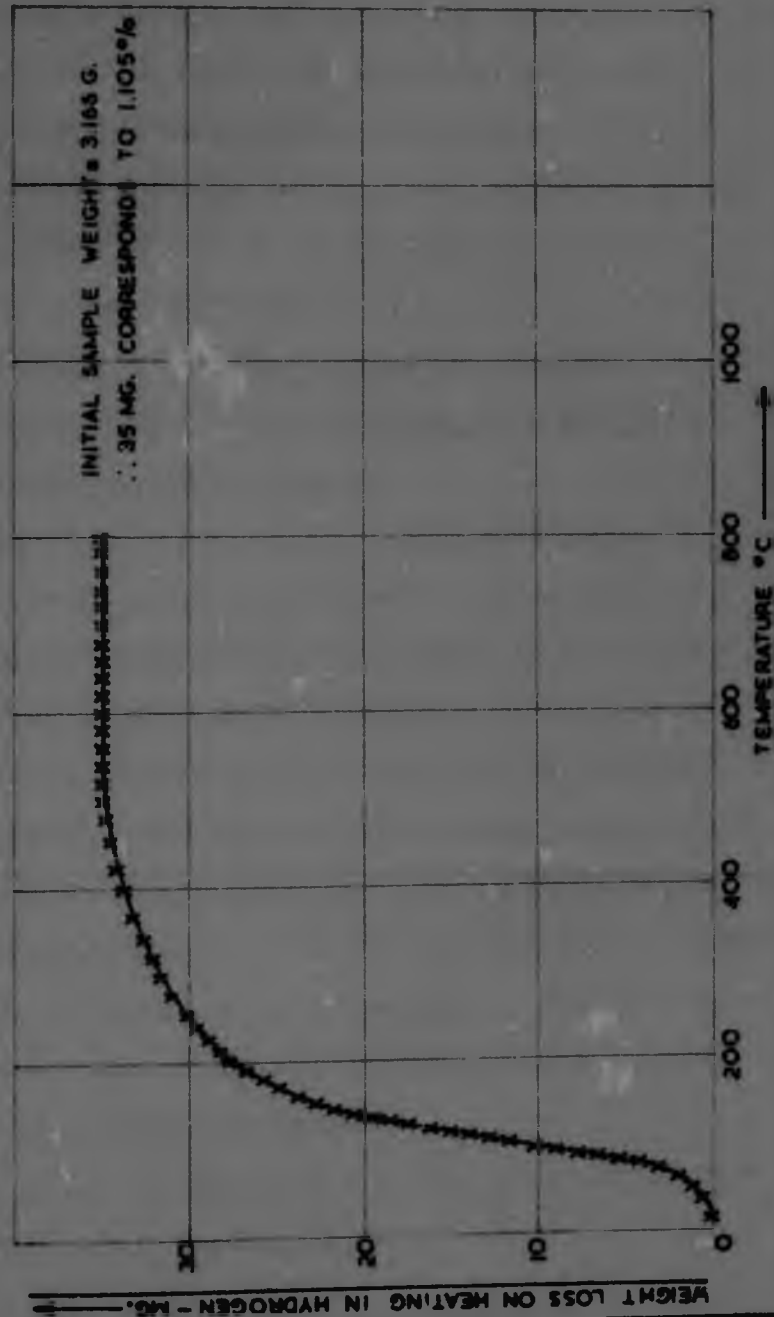
Milling Time Hours	Carbon Content %
Unmilled Powder	0.03
10	0.09
20	0.13
30	0.18
50	0.19
70	0.25
90	0.33
110	0.41
130	0.46

On assay the powder was found to contain 6.22% carbon and 0.83% oxygen. The carbon value obtained was in good agreement with the results reported in Table V.

A sample of this milled cobalt powder was heated in hydrogen in an alumina crucible in a Stanton Mass Flow thermobalance. The weight loss against temperature curve is shown in Figure 4.18. A 1°C per minute heating rate to a temperature of 200° was used; thereafter the heating rate was $200^{\circ}/\text{hour}$. The greater part of the weight loss was found to have occurred by a temperature of 200°C ; after 440°C no further weight loss occurred. In Chapter 2, it was shown that the reduction of cobalt oxide at 190°C was extremely slow, whereas in this experiment, the weight loss was particularly rapid, at temperatures well below 190°C ; this suggests that the weight loss was not due to the reduction of cobalt oxide. The major portion of the weight loss may possibly be ascribed to desorption both of oxygen and either free carbon in the form of a hydrocarbon with cobalt acting as a catalyst, or due to the desorption of physically entrained acetone.

Since the major portion of the weight loss was found to occur at desorption temperatures, it is unlikely that either carbon or oxygen were incorporated in the cobalt lattice during the milling process, and thus would not be expected to exert any

FIGURE 4.18: WEIGHT LOSS IN HYDROGEN OF A MILLED COBALT POWDER SAMPLE



influence on the phase structure of cobalt.

4.7 Further aspects of the $\alpha \rightleftharpoons \epsilon$ phase transformation arising from the milling of cobalt powder.

4.7.1 Introduction.

In Section 4.4, it was mentioned that considerable broadening of the (10 $\bar{1}$ 1) hexagonal line occurred as milling of the cobalt powders proceeded. In this section, consideration is given to results of a more detailed study of the X-ray diffraction patterns of the milled cobalt powders.

4.7.2 Theoretical aspects of X-ray analysis

associated with particle size, strain and stacking fault effects.

Although X-rays only penetrate a material to a depth of approximately $0.693/2 \mu$ cms. where μ is the linear absorption coefficient of the radiation in the metal, X-ray methods provide more information about phases, particle sizes, strain and stacking fault effects, than do optical microscope studies.⁽⁸⁾ Optical microscope studies provide little information about deformed cobalt. For Co K_{α} radiation on cobalt material, the depth of penetration is about 7.6μ .

Three quantitative measurements may be made on an X-ray diffraction peak:

- (a) the angle corresponding to the position of the maximum peak intensity.
- (b) the area under the curve.
- (c) the shape of the diffraction peak.

The data obtained may be analysed either by line breadth analysis or by the methods of Fourier analysis.

X-ray diffraction work is normally carried out using doublets consisting of two wavelengths (the α_1 and the α_2) close together. An annealed material normally shows two well defined peaks, but cold working often results in a broad asymmetric peak. Correction for the separation of the $\alpha_1 - \alpha_2$ doublet may be applied using the methods suggested by Rachinger.⁽¹¹⁾

A further difficulty is whether the particle size and strain effects give rise to Cauchy or Gaussian line profiles, and whether they act separately or interact with one another. In most cases studied it has been found that the measured profiles lie somewhere between these two extremes. The differences between these two cases arise as follows:-

If I is the X-ray intensity at any point at distance x from the peak position, and if the intensity I is of the form

$$I = I_0 / (1 + k^2 x^2) \text{ then}$$

$$\beta = B - b$$

where B is the breadth of a particular peak for a sample showing line broadening

b is the breadth of a particular peak for an annealed sample.

If, alternatively, I has the form $I = I_0 \exp. (-k^2 x^2)$

then the relation $\beta^2 = \beta'^2 - b^2$ holds. The first case corresponds to a Cauchy profile where the integral breadths are additive, and the second to a Gaussian profile, where the squares of the integral breadths are additive.

The interpretation of line broadening for cold worked metals may be summarised as follows:-

- (1) In all cold worked metals a variation in strain from point to point of the irradiated area causes line broadening.
- (2) In cold worked metals fragmentation has occurred giving rise to crystallites of a size small enough to cause line broadening.
- (3) Lattice defects such as stacking faults, dislocation vacancies and other imperfections also give rise to line broadening.

The simplest case of line broadening in a poly-crystalline material is that arising from particle size. If the mean crystallite size is less than about 10μ the diffraction peaks are broadened symmetrically by a measurable amount with no movement of the peak maxima. Thus the interpretation of line breadths where particle size effects only are present are generally simpler; on the other hand, lattice defects such as stacking faults cause a movement in position of the diffraction maxima as well as line broadening. This has been shown to be the case for several cold worked metals. ⁽⁵⁾

There are certain difficulties associated with the measurement of the breadth of X-ray diffraction peaks:

(a) The Background Count Rate:

After an accurate and systematic record has been obtained of the intensity diffracted by a specimen containing either small particles, strain or stacking faults, a correction must be applied for the background. Visual estimates are likely to be higher than the true background especially at low and medium 2θ angles.⁽¹⁵⁾

Generally the background level is subtracted from each value on the experimental profile, and a new profile constructed.

(b) Instrumental Broadening.

For all breadth methods, a correction must be applied for the broadening associated with the Instrument. In the Fourier method, the correction is implicit. It is usual to compare the broadened profile with one for which it is assumed that diffraction broadening is negligible. Any polycrystalline sample having lines near those of the defect specimen under consideration can be used as a standard provided it does not introduce diffraction or different instrumental broadening. It is desirable to use a sample of the same material as the test specimen, but with large particles,

and with the sample well annealed. If the particle size is larger than about 10 μ small particle broadening will be negligible.⁽¹⁵⁾

Wagner⁽²⁶⁾ has suggested the following relation for estimating the instrumental broadening:

$$\beta_S^* = \beta_T^* - \frac{\beta_I^{*2}}{\beta_T^*}$$

where β_S^* is the broadening due to the specimen

β_T^* is the measured total broadening

β_I^* is the instrumental broadening.

where $\beta^* = (\beta \cos \theta / \lambda)$ and β is the integral breadth of the line in radians.

Before attempting the elaborate analysis of breadths, it is often of assistance to assess the problem using an extension of the method suggested by Mazur,⁽¹⁸⁾ for studying the integral breadths of assumed Cauchy profiles. This involves plotting the product of some measure of the breadth and $\cos \theta$ against $\sin \theta$ for several values of (hkl) . Mazur⁽¹⁸⁾ has interpreted the types of defect(s) present in terms of the slopes of the resulting lines. However, this technique could not be used with milled cobalt, for particle size, strain and lattice defect effects are known to be present.

The defects present in various specimens of cobalt have been studied by many previous investigators.⁽²²⁾ The purpose of the work described here was to study the incidence of faulting in the hexagonal cobalt produced by wet milling of fine grained cobalt powder predominantly cubic in structure, using the line breadth method of analysis.

Samples of cobalt powder produced from the filing of cobalt have been studied using the line breadth method by Mitra and Halder.⁽²²⁾ The particle size and strain broadening may be obtained from the fault free reflections e.g. the $(10\bar{1}0)$ line, and the total breadth of a faulted hexagonal reflection e.g. $(10\bar{1}1)$ can be written as

$$B_i = K_1 / \cos \theta + K_2 \tan \theta + B_i^F$$

where B_i is the integral width where all three effects are present and B_i^F is the contribution to the broadening produced by faulting. The first and second terms in the above equation take account of the particle size and strain broadening respectively. Mitra and Halder⁽²²⁾ have separated the particle size and strain broadening for the (100) , (110) , (200) , (002) and (004) reflections where it was shown that there was slight anisotropy in K_1 and K_2 . Although hexagonal cobalt is anisotropic, Halder⁽²³⁾ has shown that the anisotropy factor in the case of deformed and annealed cobalt is not very large, the deviation from the mean strain being about 6%, and from the mean particle size, the deviation is negligible.

Thus K_1 and K_2 may be determined and K_1 has been shown to be equal to λ/D and $K_2 = 2\epsilon$.

where λ is the wavelength of the radiation used

D is the particle size.

ϵ is the mean strain.

The probability of faulting for an (hkl) reflection,

where l is an odd number is given by

$$B_i^F(2\theta) = 180/\pi \tan \theta |l| (d/c)^2 (3\alpha + \beta)$$

where d is the (0002) lattice spacing

and $c = 2d$

α is the deformation fault probability

β is the growth fault probability

Thus the line broadening relations employed by Mitra and Halder⁽²²⁾ were used in this work to find the particle size, strain and stacking fault probability, consisting of both deformation and growth faults.

The examination of the faulting probability in the h.c.p. phase of a mixture of both h.c.p. and f.c.c. cobalt is extremely difficult to carry out, because of the overlapping of the (111) cubic and (0002) hexagonal lines, and therefore it is not possible to split the probability of faulting into the growth and deformation contributions. However, as has been done by Halder the $(10\bar{1}0)$ line may be used to obtain the particle size and strain effects in hexagonal cobalt, and this combined with the data from the (200) cubic line can be used to

evaluate particle size and strain separately.

4.7.3 Experimental.

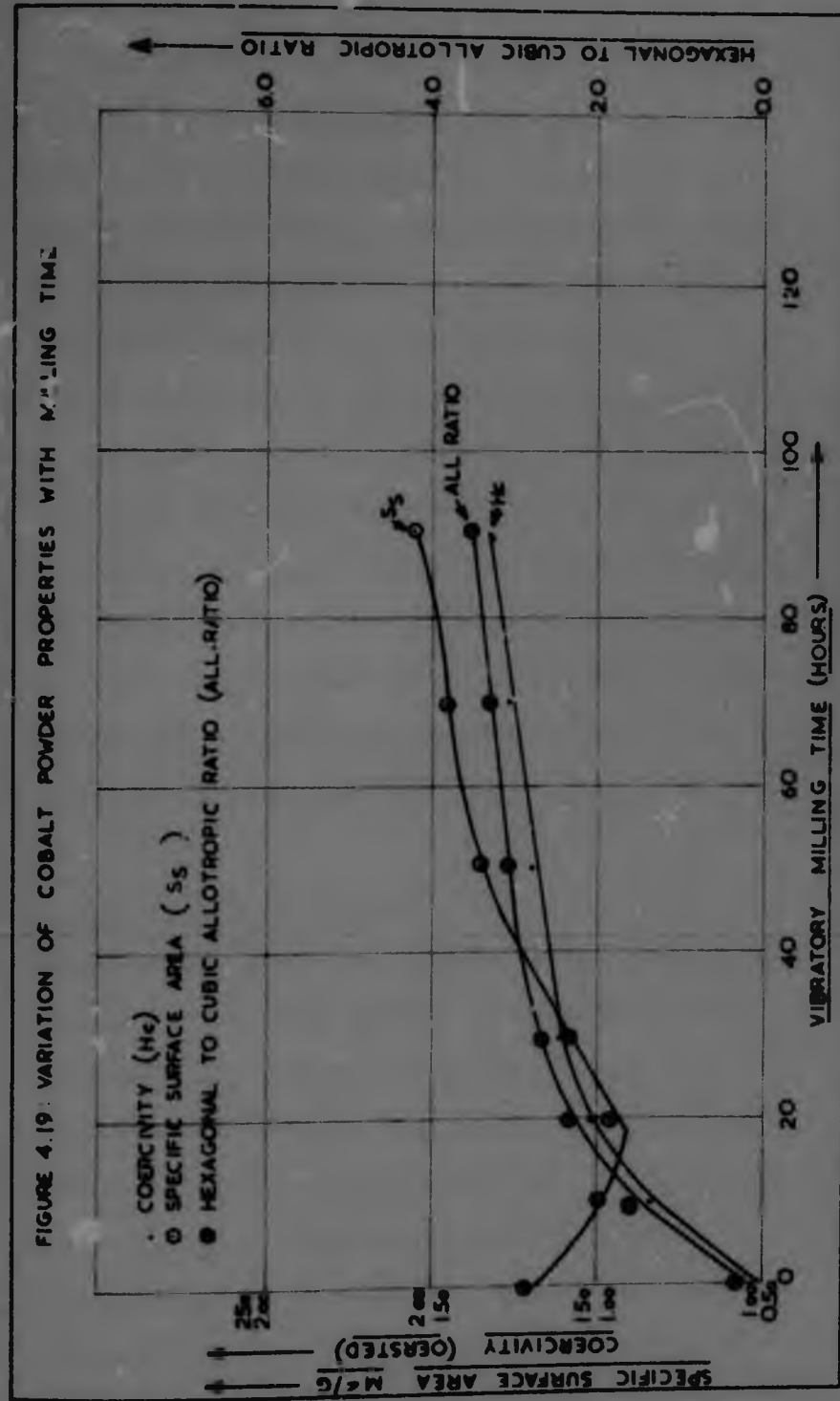
A cobalt powder prepared by the hydrogen reduction of black cobalt oxide at 750°C was vibratory wet milled under acetone, exactly as described for the batches in 4.4. Samples were removed from the mill after 10, 20, 30, 50, 70 and 90 hours of vibratory milling. These samples were dried and the specific surface area measured. Compacts of the powders mixed with bakelite were prepared for coercivity measurement. The specific surface area and coercivity measurements are summarised in Figure 4.19.

The milled powder samples were mixed to a pasty consistency with water glass and mounted in the X-ray specimen holder. The $(10\bar{1}0)$, $(10\bar{1}1)$ and (200) profiles were counted on a Philips Diffractometer using intervals of 0.01° , and a fixed time period of 300 seconds.

A sample of the same cobalt powder was annealed at 300°C for 12 hours and similarly examined by X-ray diffraction. The same procedures were applied to a sample of the unmilled cobalt powder.

A disc of cobalt prepared initially by sintering pressed cobalt powder in hydrogen at $1,200^{\circ}\text{C}$, (and subsequently annealed for 24 hours) was used as the reference sample. It was assumed that this sample was strain free. The cobalt grain size in this specimen was greater than $10\ \mu$ as determined microscopically. The $(10\bar{1}0)$, $(10\bar{1}1)$

FIGURE 4.19: VARIATION OF COBALT POWDER PROPERTIES WITH MILLING TIME



and (200) peaks in this specimen were also examined. This sample was used for determination of the instrument broadening.

Only in this disc were the peaks resolved into the α_1 and α_2 doublets. Some indications of resolution were obtained with the other specimens, but it was not distinct. The peaks were therefore replotted using the graphical correction method of Rachinger.⁽¹¹⁾ The integral breadth of the α_1 component was used for all subsequent calculations.

The particle size and strain contributions to broadening were calculated from the (200) and (10 $\bar{1}$ 0) lines, and using this data the contributions to line broadening due to stacking faults on the {10 $\bar{1}$ 1} planes were calculated. The three effects are summarised in Table VI together with the values of $(3\alpha + \beta)$ derived from the equation of Mitra and Halder.^(5,2)

4.7.4 Discussion of Results.

- (1) The results shown in Table VI show that on milling of cobalt powder an initially rapid increase in stress occurs during the first stages of milling. The values obtained for the crystallite size variations with milling time indicate that no crystallite growth occurs during the first stages of milling. The surface area results do however show an agglomeration, but as shown in 4.4 the initial particles have very rough surfaces, and as

TABLE VI.

Summarised particle size, strain and stacking
fault effects for milled cobalt powder.

Milling Time (hours)	$D^{\circ}A$	ϵ	$(3\alpha + \beta)$	$\Delta 2\theta^{\circ}_{\text{peak}}$ (1011)
Annealed Powder	1040	0.0014	- 0.0005	0.00
No milling	849	0.0023	0.0048	- 0.02
10	614	0.0051	0.0152	- 0.06
20	518	0.0078	0.0117	- 0.05
30	448	0.0113	0.00919	- 0.05
50	342	0.0146	0.00785	- 0.04
70	287	0.0122	0.00485	- 0.02
90	196	0.0138	0.00322	- 0.02

milling proceeds the particle surfaces become smoother. The initial agglomeration referred to as cold welding by Exner and Fischmeister⁽³⁾ must be a physical agglomeration of the particles, which break down in size as milling proceeds further.

- (2) The results for the powder annealed at 300°, suggested that the stacking faults had been removed by this heat treatment. On fine filings annealed for 2 hours at 300°C Houska, Averbach and Cohen⁽²⁵⁾ found a stacking fault contribution to broadening; however, it has been mentioned that stacking faults can be removed on heat treatment at temperatures of 500°C - the reduction in coercivity of cobalt being evidence for this.⁽⁵¹⁾ In an experiment where cobalt powder was annealed at 300°C for one hour in hydrogen, the decrease in coercivity was from 92 to 65 Oe, and the corresponding decrease in surface area from 1.19 m²/g to 1.13 m²/g. In the powder annealed for 12 hours at 300°C in hydrogen the decrease in specific surface area was from 1.32 m²/g to 1.24 m²/g. Mitra and Halder⁽²²⁾ found some evidence for stacking faults in filings annealed for 24 hours at 300°C. On the other hand Rao and Anantharaman⁽²⁹⁾ found that material annealed at 375°C for a few weeks was practically devoid of stacking faults in the hexagonal phase.

- (3) The strain in the unmilled cobalt powder was slightly higher than that of the annealed material possibly due to the screening operation, which is carried out after the reduction process during manufacture.
- (4) The probability of faulting ($3\alpha + \beta$) for the $\{10\bar{1}1\}$ planes was found to be greatest after 10 hours of milling, i.e. there is a high probability of faulting in the hexagonal material initially produced; thereafter the stacking fault probability decreases. This finding is difficult to explain for new particle surfaces are being generated, as milling proceeds; it is unlikely that the temperature rise occurring during grinding is such that the faulting can be removed by annealing, although Kochanovska⁽²⁾ attributed the formation of cubic phase during grinding to local rises in temperature produced by the grinding balls (and an absorption of oxygen).
- (5) The degree of faulting ($3\alpha + \beta$) was lower than that found by Mitra and Halder⁽²²⁾ for their cobalt filings. This may possibly be ascribed to the inefficiency of milling as a working process. Variations in the extents of line broadening produced by different forms of cold working are well known⁽²⁴⁾ in the case of deformed metals.

4.8 The Milling of Cobalt Filings.

Fine cobalt powder (specific surface area $1.25 \text{ m}^2/\text{g}$) was cold pressed without further lubrication into compacts $1.300''$ in diameter and $2''$ long in a single acting steel die at 10 tons/in^2 . The compacts were sintered in hydrogen at $1,100^\circ\text{C}$ packed in a pure alumina packing to avoid carbon pick up during sintering. On average these compacts had attained 85% of their theoretical density after this treatment.

A coarse file was used to convert the sintered compacts into filings (which had an initial iron content of 2.42%).

A 500 g. quantity of this material was annealed under vacuum for two hours at 800°C , in a porcelain dish, in a Balzers 10V6 High Frequency Vacuum Furnace using a graphite susceptor. Temperature measurements were made by means of a tungsten - tungsten 26% rhenium thermocouple. The minimum pressure obtained during this treatment was 1.2×10^{-5} mm of mercury. Cooling to room temperature was effected under vacuum over a 16 hour period. Nitrogen gas was admitted to the furnace after it had cooled to room temperature, and the annealed filings were not exposed to air for a further two hours. From the appearance of the filings some slight sintering of the material had occurred during this annealing period.

An X-ray diffraction pattern of the annealed filings was obtained, and their specific surface area was measured on the Sorptometer. The measured specific surface area was $0.06 \text{ m}^2/\text{g}$, which is at the lower end of the range of this instrument. However, after 5 hours of milling, the specific surface areas were within the reported accuracy range of the Sorptometer.⁽³⁵⁾

The filings were milled under acetone, exactly as reported above for the cobalt powders; samples were removed after various milling periods, and specific surface area, X-ray and coercivity measurements carried out.

From visual observation, the cobalt filings milled for periods up to 30 hours contained particles with a very wide range of sizes. Great care was therefore necessary in packing the powder in the specimen holder so that satisfactory X-ray patterns were obtained.

The physical property results for this first batch of filings are summarised in Figure 4.20. After 5 hours milling it was found that the cubic modification of cobalt started to increase, and the coercivity started to decrease. After 70 hours the amount of cubic phase started to decrease, and the coercivity to increase.

The agglomeration previously observed with the fine powders, was again obtained with the crushed filings, when the specific surface area reached about

FIGURE 420: VARIATION OF PROPERTIES OF ANNEALED COBALT

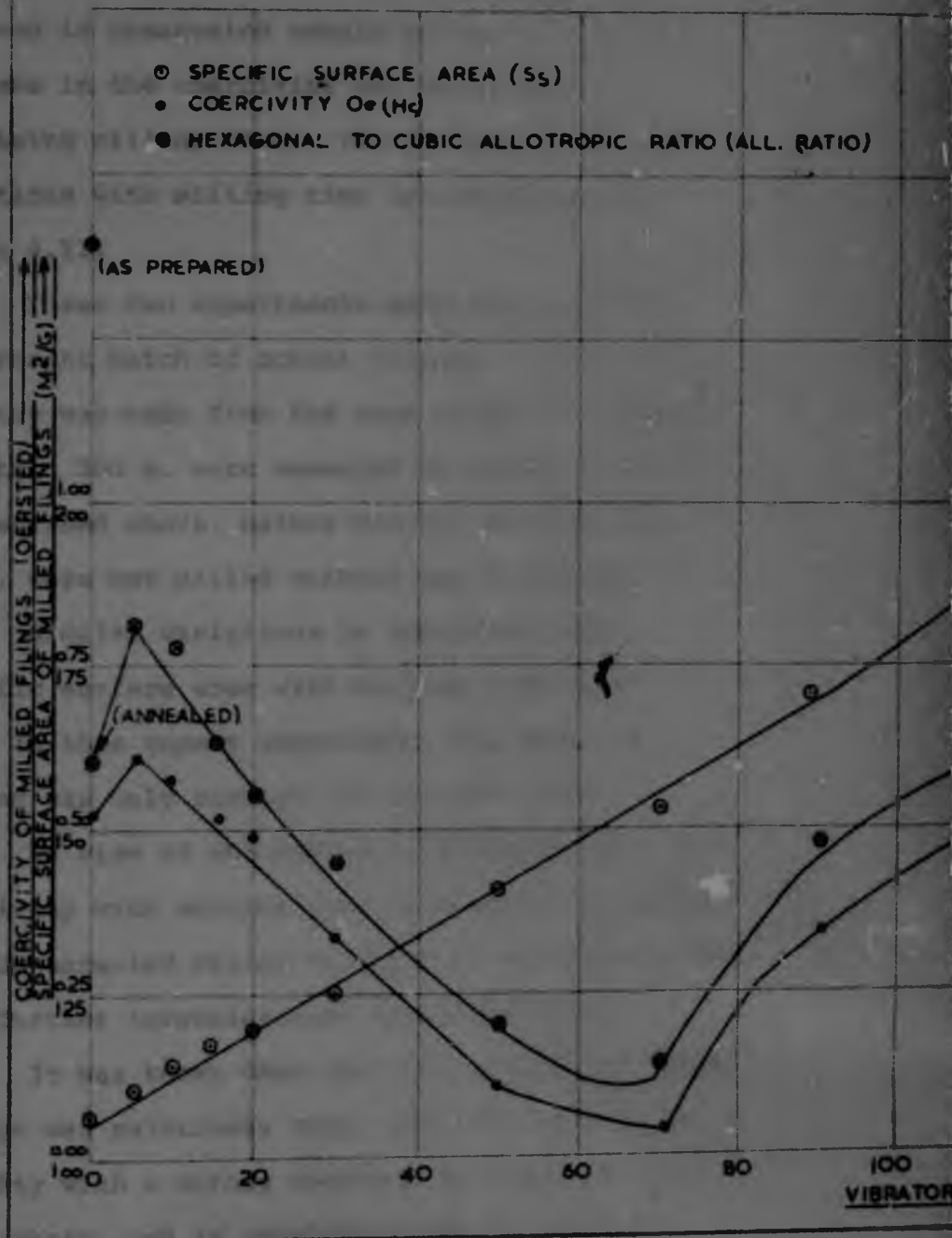


FIGURE 420: VARIATION OF PROPERTIES OF ANNEALED COBALT FILM

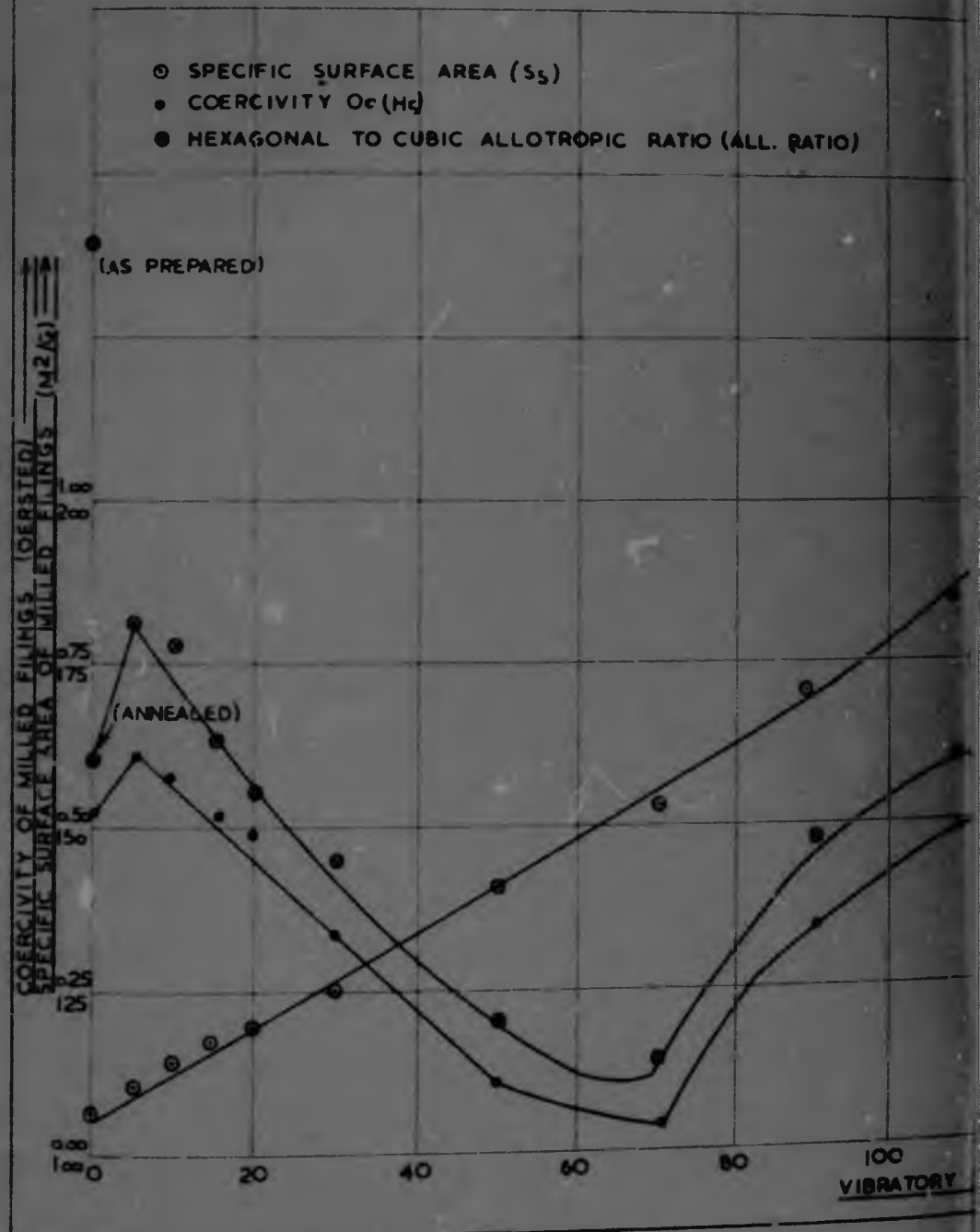
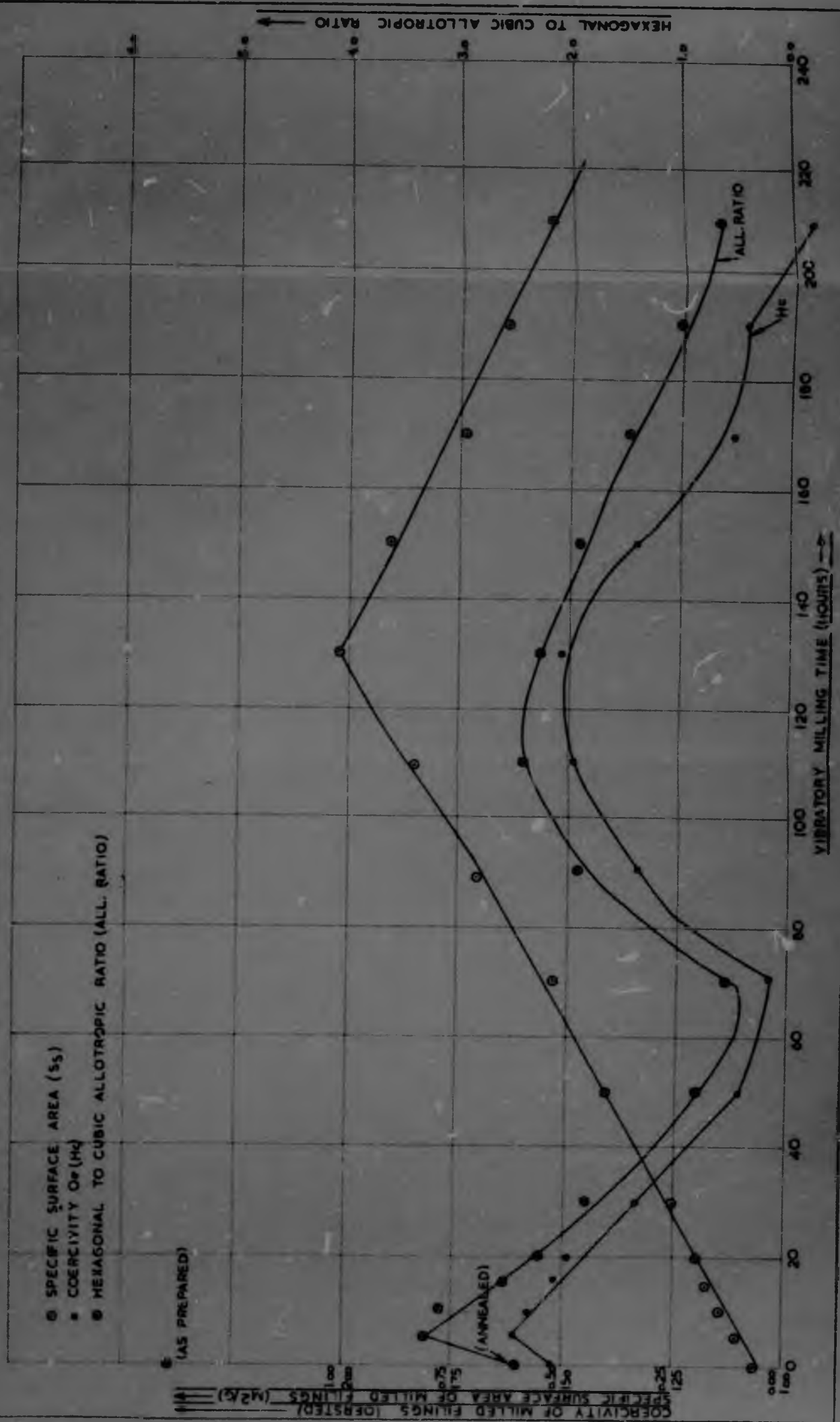


FIGURE 420: VARIATION OF PROPERTIES OF ANNEALED COBALT FILINGS WITH MILLING TIME



$1 \text{ m}^2/\text{g}.$

Different behaviour was observed when the filings were not annealed before milling. Here the behaviour of the phase change was similar to that observed in unannealed cobalt powders. A gradual increase in the coercivity was observed with increasing milling time. The measured parameter variations with milling time are summarised in Figure 4.21.

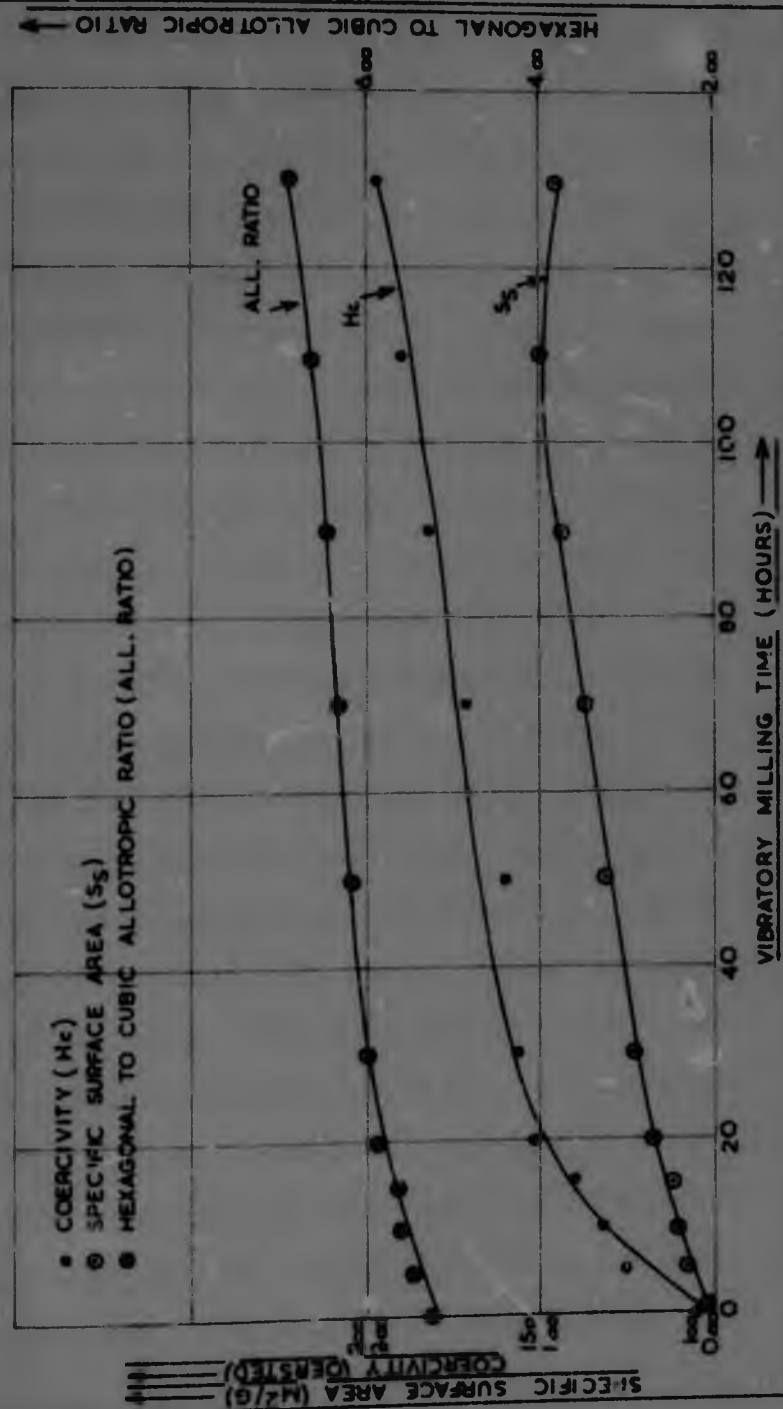
These two experiments were repeated with a different batch of cobalt filings. A one kilo quantity was made from the same batch of sintered pellets. 500 g. were annealed in vacuum at 800°C , as described above, before the wet milling, and 500 g. were wet milled without any annealing.

Similar variations in coercivity and specific surface area with milling time were found in this repeat experiment, but here the milling was only carried out for 130 hours.

In view of the marked differences in coercivity with milling time between the annealed and non-annealed milled filings, it was considered that further investigations were necessary.

It was known that the iron content of these filings was relatively high, and that iron is an impurity with a strong tendency to stabilise the cubic phase, and is sometimes used in complex cobalt alloys to suppress the formation of any hexagonal phase. (27) Attempts were therefore made

FIGURE 4.21: VARIATION IN PROPERTIES OF UNANNEALED COBALT FILINGS WITH MILLING TIME



to try to separate the iron and cobalt in these filed and milled samples.

In order to do this, some preliminary trials were carried out using a mixture of 90 g. fine cobalt powder, and 10 g. fine carbonyl iron powder, which had been thoroughly mixed in a mortar for 10 minutes. 50g. of this mixture was treated with a solution of 400 ml. 10% sulphuric acid and 400 ml. cobaltous sulphate solution, saturated with respect to this salt. This solution was allowed to react with the mixed metal powders for one hour. The mixture was centrifuged for 30 minutes, and distilled water repeatedly added, followed by further centrifuging until the supernatant liquor was neutral to litmus. The powder was then dried and screened to break up lumps; the iron content on assay was found to be 0.27%, but 47.2% of the initial weight of the powder had been lost by dissolution. The above procedures were repeated in duplicate, but allowing the mixed solutions to react with the metal powders for only 30 minutes. The iron contents were 0.22 and 0.26%, and the corresponding weight losses 34.8 and 37.6%. A third treatment of the powder with the acid - cobaltous sulphate solution in contact with the powder for only 15 minutes, yielded a product containing 0.25% iron, with a resulting weight loss of 24.6%.

This treatment was therefore applied to some of the milled filing samples, one batch of which had

been annealed before milling, and the other unannealed. The iron assay results on the milled filings treated with acid - cobaltous sulphate solution are summarised in Table VII.

Immediately apparent from this table is the ease with which the iron content of the non annealed but milled filings could be reduced compared with the annealed filings when using the same leaching treatment.

This particular treatment of the milled filings with acid - cobalt sulphate solution must be regarded as being rather crude, but nevertheless the iron contents of the annealed and milled materials were considerably greater than those of the non annealed and milled samples after the same treatment.

This indicates that some of the iron produced during the filing may have diffused into the cobalt lattices during the vacuum annealing treatment. It is thought that the solid solubility of iron in cubic cobalt may reach 10%.⁽³⁰⁾ In the unannealed material any iron could not be in the cubic lattice, and furthermore the unannealed filings had a ratio of I_{1011}/I_{200} of 5.52.

Apart from the references to the influence of iron on the stabilisation of the cubic phase quoted above, Sage's work⁽¹⁷⁾ has also shown that iron exerts a tendency to stabilise the cubic phase: when cobalt chloride was mixed with iron

TABLE VII.

Comparison of Iron Contents of Annealed and milled,
non annealed and milled, filings before and after
treatment with 10% H_2SO_4 - $CoSO_4$ saturated solution.

A. Annealed and Milled Filings.

Milling Time Hours	Fe Content after milling %	Fe Content after milling and leaching %
10	7.06	1.04
30	5.14	0.79
50	3.80	0.78
70	5.89	1.31
110	4.39	1.38

B. Non Annealed and Milled Filings.

Milling Time Hours	Fe Content after milling %	Fe Content after milling and leaching %
10	5.21	0.32
30	6.29	0.40
50	6.08	0.36
70	4.20	0.62
90	4.18	0.68
110	4.24	0.37

and reduced in hydrogen, 7% of iron resulted in the formation of 90% of the cubic modification in the reduced mixture. No iron, resulted in the formation of 20% of the cubic modification.

4.9 The influence of pressure on the allotropic transformation in cobalt.

Another way in which the martensitic transformation from cubic to hexagonal cobalt may be caused, is by the application of pressure to a powder sample. An applied pressure of 8 tons/in.² on a cobalt compact heat treated at 800°C, and consisting entirely of the cubic modification has been reported⁽²⁸⁾ to cause partial transformation to the hexagonal phase; the application of 20 tons/in.² to a similar sample resulted in complete transformation to the hexagonal structure, and also considerable visible deformation of the sample. In another work⁽²⁵⁾ the application of pressure to fine cobalt filings obtained from a cobalt rod has also exhibited a hexagonal structure on X-ray analysis.

These observations are of definite interest since they confirm indirectly that a shear mechanism is responsible for the transformation.⁽²⁸⁾

In the work described here, it was also observed that pressure promotes the transformation; 10 g. quantities of a powder which on X-ray diffraction showed no traces of hexagonal cobalt were pressed in a 1.300" die using pressures of 5, 10, 12, 15, 20, 25

and 30 tons/in.². X-ray diffraction patterns were taken of the surfaces of the compressed discs. It was found that it was not necessary to add a lubricant to the powder prior to pressing as perfectly sound compacts could be obtained by pressing the powder neat. Using pressures of up to 12 tons/in.² only cubic phase diffraction peaks were evident in the specimens. At 15, 20 and 25 tons/in.² both cubic and hexagonal diffraction peaks were evident, the intensity of the hexagonal peaks increasing as the pressure increased. At 30 tons/in.² only hexagonal cobalt was present, and the (200) cubic diffraction peak was absent.

The application of different compacting pressures to various cobalt powders also exerts a profound influence on the coercivity of the pressed specimens as is shown in Table VIII; and thus the method of measurement of powder coercivity for cobalt and hard metal powder compacts is of critical importance.

It has been suggested that the application of different pressures to a series of cobalt compacts could be used to evaluate the enthalpy of the transformation,⁽²⁸⁾ and also the energy of activation for the transformation. However, the applied pressure also is used to overcome die wall friction, and it is difficult to eliminate this contribution from the calculation.

TABLE VIII.

The Effect of Compacting Pressure on the Coercivity
of Pure Cobalt Powder Compacts.

Compacting Pressure	Coercivity (Oersted)	
	Batch 1	Batch 2
5 tons/in. ²	85.6	87.2
10 tons/in. ²	94.4	109.6
20 tons/in. ²	129.0	130.2
30 tons/in. ²	162.0	162.0

The powders used for Batch 1 and Batch 2 were two fine commercial cobalt powders.

4.10 Discussion and Conclusions.

4.10.1 The Milling of Cobalt Powders.

The following conclusions were drawn from these studies on the milling of cobalt powder:

- (1) Cold work due to the milling operation converted a significant proportion of the cobalt initially in the cubic allotrope to the hexagonal modification.
- (2) Evidence that agglomeration occurred during the milling of the cobalt powders was obtained, both by specific surface area measurements, and by means of the observations of powders on the Cambridge Stereoscan Electron Microscope.
- (3) An increase in coercivity of the milled cobalt powders occurred as milling proceeded. For the reasons described in 4.3 the coercivity can at best be regarded as an empirical parameter, relating to the proportions of the two allotropes of cobalt, the strain, and the proportion of stacking faults. These three factors vary during the course of milling, and thus it is difficult to assess the reasons for the exact significance of the increase in coercivity as milling proceeds.
- (4) The relations of coercivity to milling time and hexagonal to cubic phase ratio to milling time reported in the present work are similar to the findings of Exner and Fischmeister,⁽³⁾

namely, a very rapid rise in coercivity (or hexagonal to cubic phase ratio) during the initial stages of milling followed by a much reduced increase of coercivity (or hexagonal to cubic phase ratio) as milling proceeded further.

- (5) Of considerable significance is the ease with which the various cobalt powders started to agglomerate after milling commenced. The Hoboken cobalt powder (Figures 4.9 and 4.10) was fully agglomerated after 5 hours of milling, whereas the CF-6 powder reached a minimum surface area after 20 hours of milling, and the CF-10 after 30 hours of milling.

Huttig⁽⁷⁾ has suggested that the milling of a ductile metal powder consists of both comminution and welding processes, this also having been discussed by Arias.⁽⁵⁾ In cobalt metal powder milling the surface area measurements gave no evidence for a "milling equilibrium" having been established after the state of maximum agglomeration had been reached. It would have been expected however that the fine metal particle surfaces produced by fragmentation of the larger aggregates would have had a tendency to cold weld to one another. This was not observed. Thus possibly, as postulated by Arias,^{(5), (21)} the acetone aided comminution by preventing particle welding.

4.10.2 The Milling of Cobalt Filings.

The differences in allotropic ratios obtained on milling annealed and non annealed filings was ascribed to the known effects of iron on the stabilisation of the cubic phase.

4.10.3 The Application of Pressure to Powders.

Application of pressure to cobalt powder samples is another form of cold working which causes a transformation from the cubic to the hexagonal phase.

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CHAPTER 5.

The Fabrication and Sintering of hard metal powder compositions showing the importance of initial cobalt powder characteristics.

5.1 Introduction:

In Chapter 4, consideration was given to the behaviour of cobalt powders from different sources, on grinding; it was shown that when acetone was used as the milling fluid, certain cobalt powders agglomerated during the initial stages of milling more readily than other cobalt powders.

In the work reported in this Chapter, the finding of different agglomeration characteristics of different cobalt powders has been extended to hard metal powders, prepared by milling together cobalt and tungsten carbide powders. These powder mixtures are subsequently pressed and sintered. The importance of the hard metal milling on the sintering characteristics of the alloy is considered.

The powder mixtures, which contain the cobalt powders showing the maximum agglomeration on milling on their own, require less milling to achieve satisfactory densification on sintering than do the hard metal powder mixtures, which contain a cobalt powder with a reduced tendency to agglomerate on milling.

It is shown, therefore, that these agglomeration characteristics of the initial cobalt powder are an important consideration in relation to the subsequent processing of hard metal alloys.

5.2 The Processing of hard metal alloys.

Cemented carbides may be divided into two broad categories: ⁽¹⁾

- (1) The straight tungsten carbide - cobalt alloys; this work being concerned with alloys of this type.
- (2) The W - C - Co - TaC/NbC - TiC alloys which are mainly used for machining applications.

Hard metal powders are prepared by the intimate milling of cobalt and carbide powders under a milling fluid in stainless steel mills, using hard metal balls as the grinding media. Rotary, vibratory, attrition, and other high energy mills have been used. ⁽⁶⁷⁾

Vibratory ball mills require about 1/6th of the time required for rotary ball mills for satisfactory milling of hard metal powders. ⁽²⁾ Attrition mills led to greater efficiency compared with vibratory mills. ⁽³²⁾ Several other advantages have been claimed for vibratory mills compared with the older rotary mills. ⁽²⁾

For hard metal alloys, one of the few conclusions that can be drawn is that the carbide grain size in the sintered structure is closely related to the carbide grain size in the milled powder, ⁽³⁾ but the same close correlation has not been predicted between many of the other properties of the milled powders and sintered compacts. It has, however, been possible in practice to develop conditions which give an optimum product.

Differences in sintering characteristics between different commercial batches of the same composition are well known in hard metal technology.⁽⁴⁾

Usually, stainless steel or in some cases hard metal lined mills are used, and in the former case the pick up of iron does not exceed 0.2%.^{(2), (32)} Other impurities from the stainless steel are also found in the hard metal powder, e.g. Ni and Cr. Contamination from the grinding balls also occurs.⁽⁵⁾

Great care is necessary in making up a hard metal composition, especially in choosing constituents of the correct carbon level, because the final physical and mechanical properties are especially sensitive to the carbon content.⁽⁶⁾ A carbon level that is too low or too high can cause a non uniform grain size in the sintered product, and the transverse rupture strength decreases rapidly if there is too much carbon (with the resulting appearance of free carbon in the sintered microstructure) or too little carbon (which results in the formation of eta phase). Eta phase is a solid phase of probable composition $\text{Co}_3\text{W}_3\text{C}$, which decomposes at $1,700^\circ$ into other compounds which have not been thoroughly investigated.⁽⁷⁾ Eta phase can interfere with the normal liquid phase sintering process. The narrow two phase (WC + Co) region is clearly evident in the high temperature ternary equilibrium diagram of Rautala and Norton.⁽⁸⁴⁾

The variation in transverse rupture strength with carbon content has been investigated by Suzuki et al. ^{(8), (70)} for a 10% cobalt hard metal composition.

The carbide powder must be properly crushed and free flowing prior to the milling process, otherwise large carbide aggregates may float to the top of the ball layer, and remain intact during milling. ⁽²⁾

The dependence of the transverse rupture strength, hardness and wear resistance on the carbon content of sintered alloys is shown in Figure 5.1, due to Foster. ⁽⁶⁾

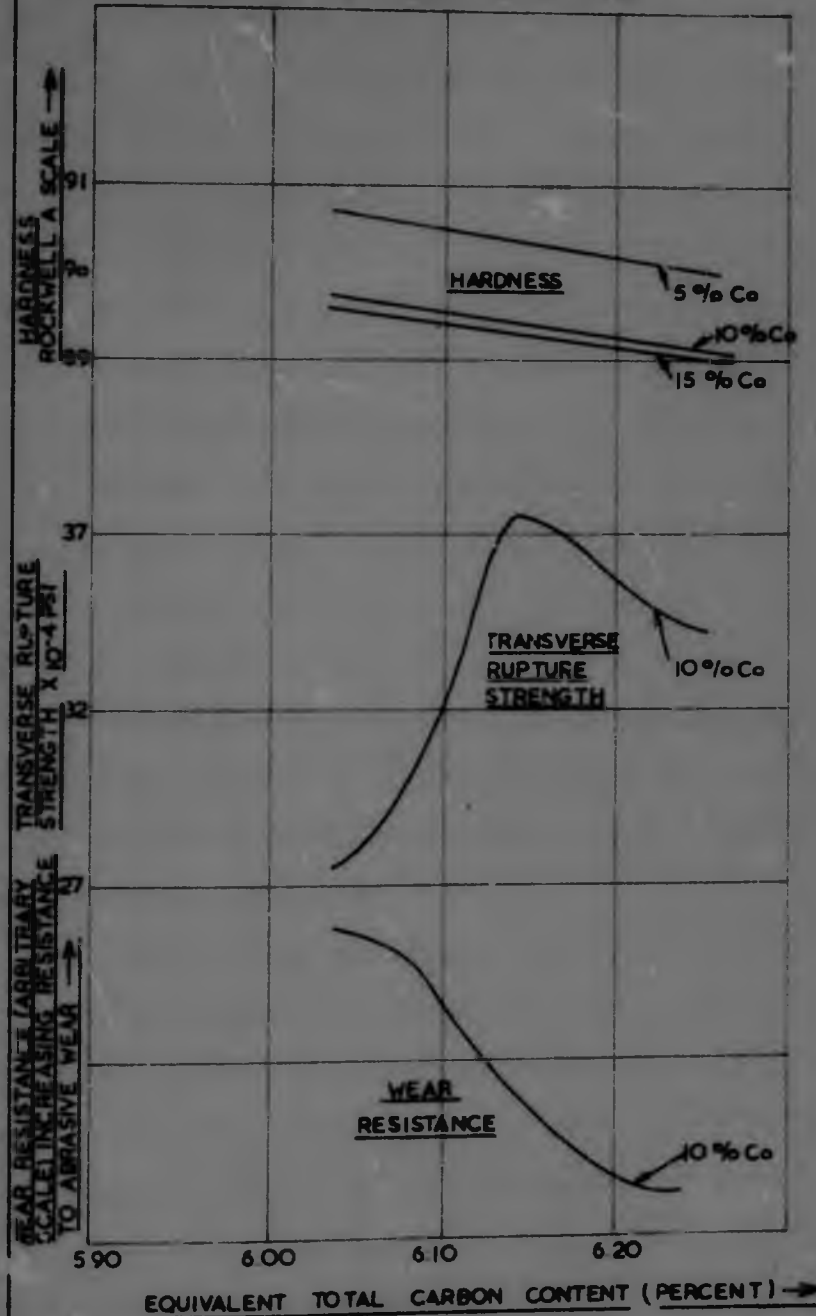
Furthermore at the mill make up stage, allowance must be made for the loss or gain of carbon, which can for example occur during the subsequent preheating, storage or sintering operation.

After milling the hard metal powder is dried under vacuum to remove the milling fluid and screened; special attention must be directed to this drying procedure, otherwise unsatisfactory sintering characteristics will result, presumably due to incomplete removal of films of organic material, which interfere with the sintering process.

Interference by organic matter with the sintering of metal powders has been observed by Gessinger, Ansell and Lenel, ⁽⁹⁾ during studies on the sintering of silver spheres.

Since hard metal powder has no great tendency to deform plastically, the cavities can

FIGURE 5.1 EFFECT OF EQUIVALENT TOTAL CARBON CONTENT OF SINTERED ALLOYS ON HARDNESS, TRANSVERSE RUPTURE STRENGTH, AND WEAR RESISTANCE OF CEMENTED CARBIDES



only be filled during pressing by mechanical sliding together of the grains; the pressing process can be made easier, and the pressing stresses required can be reduced, if a suitable lubricant is added to the powder prior to pressing.⁽¹⁰⁾ A lubricant dissolved in a suitable solvent (such as 1 - 1½ weight percent of paraffin wax in trichloroethylene, or camphor dissolved in diethyl ether) is usually added to the powder at this stage to assist in the pressing operation. The solvent is evaporated after dispersion of the binder. The hard metal powder is pressed into components using either hydrostatic or die pressing. Various shaped dies may be used depending on the intended final shape of the sintered component.⁽¹⁾

The next operation is preheating where the binder is removed under a protective atmosphere (usually hydrogen or vacuum) at about 800°C. This process also imparts sufficient mechanical strength to the compact before final machining, but reduces the sintering reactivity.

Any process of heating hard metal powder above 500°C reduces the coercivity not only due to coarsening of the cobalt grains,⁽¹¹⁾ but also due to the elimination of stacking faults. That the sintering reactivity is reduced by heat treatment of hard metal powder at 500°C has been demonstrated in the case of the sintered densities of high pressure anvils.⁽¹²⁾

The final sintering operation may be carried out either in hydrogen or in vacuum, and various precautions are necessary for both techniques. Sintering temperatures in the range 1,350 - 1,500°C are used depending on the composition.

According to Schwarzkopf and Kieffer,⁽¹³⁾ at 1,450°C a 5% cobalt alloy would contain approximately 15 volume percent of liquid, and at 1,350°C a 20% cobalt specimen would contain approximately 44 volume percent of liquid. A 2% cobalt alloy at 1,340°C contains approximately 5 volume percent of liquid.

The prolonged milling operation necessary for the manufacture of cemented carbides is probably unique in metal powder processing, but that such milling times are necessary, has been shown by many investigators.⁽²⁾

Dawihl and Mal⁽¹⁴⁾ have classified two phase alloys as consisting of two extreme types:

- (1) Where the principal phase forms a skeleton.
- (2) Where the auxiliary phase surrounds the individual grains of the principal phase on all sides; (hard metal alloys have a structure which is intermediate between these two extremes).⁽¹⁴⁾

For the second structure type, complete wetting must occur during the liquid phase sintering process. If the auxiliary metal is not thoroughly dispersed before the sintering process, then there is no guarantee that it will (in spite of increased mobility on heating) penetrate contiguous carbide

grains, which thereby become welded to one another during the sintering process.

The milling time normally used depends on the particular application of the sintered alloy, and has a marked effect on the final characteristics. The shrinkage, the final porosity, the hardness, the cutting characteristics of a hard metal tool, and the carbon loss during preheating are all functions of the milling conditions used, and the milling time.⁽¹⁵⁾ As was shown in Figure 5.1, the mechanical properties of hard metal alloys depend significantly on the carbon content; however, the mechanical properties also depend strongly on the milling conditions used, but considerable disagreement exists regarding the exact effects of milling conditions on mechanical properties.^{(17), (18)} Thus the processing conditions used have important influences on sintered properties, and interaction effects between the various processing variables can also occur.⁽⁶⁵⁾

Milling of the hard metal powder constituents under a protective fluid is necessary for several reasons, among which are the prevention of excessive oxidation, and to ensure sufficient homogeneity of the milled powder product.⁽¹⁶⁾ Care is necessary in the choice of the milling fluid; chlorinated organic solvents should be avoided, and the use of water results in excessive decarburisation.⁽²⁾ Direct loss of carbon can be avoided by the use of acetone

as milling fluid⁽²⁾ and gaseous pressure build up in the mills is avoided using this solvent.⁽²⁾

The ideal conditions necessary for efficient comminution of hard metal powder during milling have been considered by many investigators, taking into account such factors as the ratio of balls to powder, and the percentage of the critical speed necessary for efficient rotary milling.⁽¹⁶⁾

It was originally postulated that during milling, the carbide grains became "coated" with cobalt.⁽²⁾ This hypothesis was based on the ideas of Hoyt,⁽¹⁹⁾ that a milled hard metal powder could be attracted with a magnet, and no segregation occurred. The viewpoint now is that during milling, an initial beating of the tungsten carbide into the cobalt particles occurs. Electron photomicrographs of hard metal powders prepared in the work support this view; some electron photomicrographs of milled hard metal powders are shown in Figure 5.2.

These replicas of hard metal powders were prepared using the solid Cellofas replica techniques of Eckert,⁽²⁰⁾ based on the procedures suggested by Hinnuber, Rudiger and Kinna.⁽²¹⁾ The replicas were examined on a Philips EM 200 Electron microscope. These latter authors used 0.5% Mitowal in chloroform as lacquer, but the use of a solid replica was found greatly to facilitate specimen preparation. An acid treatment of the carbon replica is necessary to remove the cobalt; otherwise both phases would appear opaque

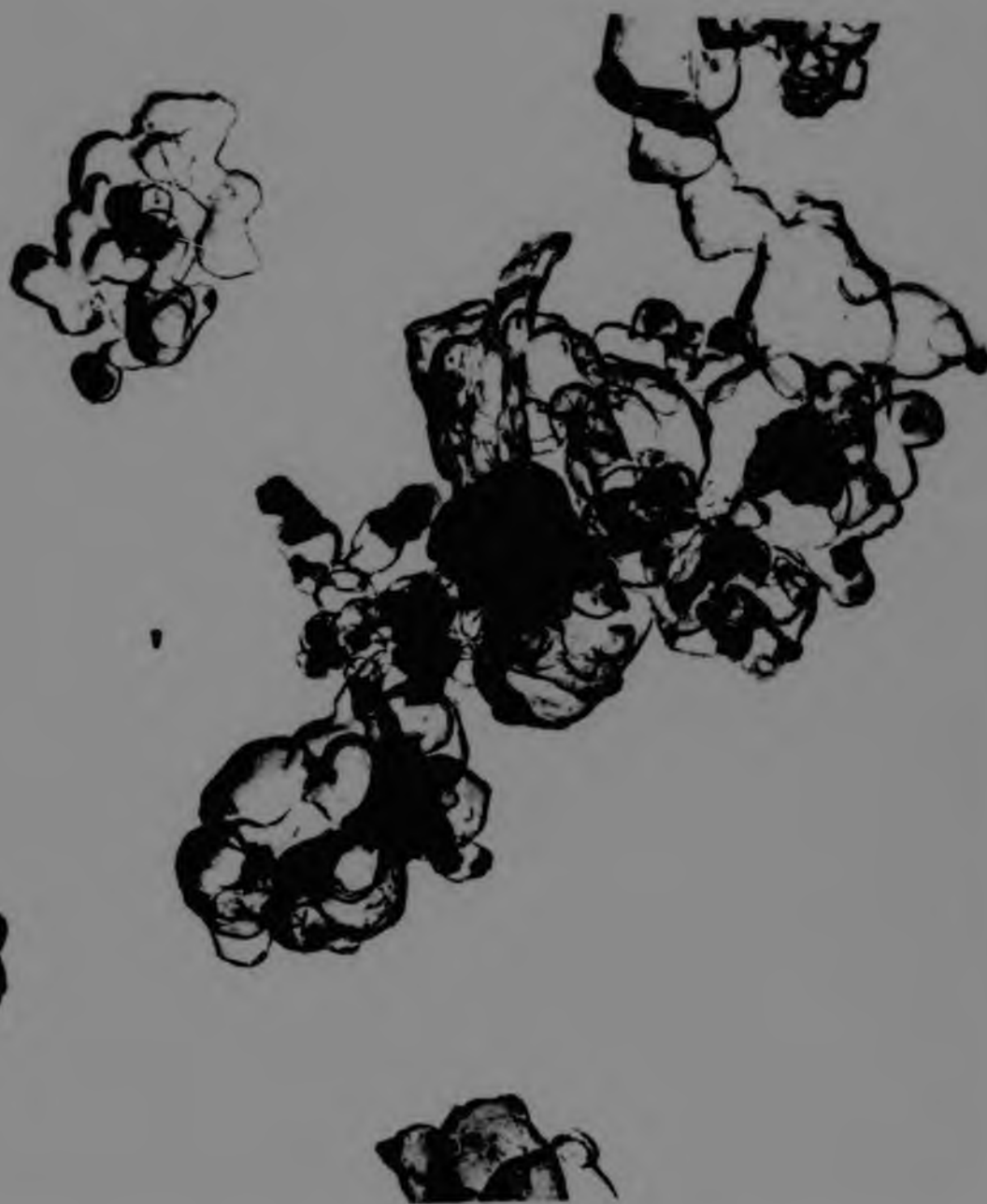


Figure 5.2.1: Showing Cobalt Agglomeration -
20% Cobalt Alloy 2 hours milling x 17,480.



Figure 5.2.2: Agglomerate of Cobalt in a 10% Cobalt Alloy milled for 2 hours x 17,250.



Figure 5.2.3: 20% Cobalt Alloy - 8 hours
milling x 17,480.



Figure 5.2.4: 10* Cobalt Alloy - 8 hours milling
x 17,250.



Figure 5.2.5: 10% Cobalt Alloy - 12 hours
milling x 17,250.

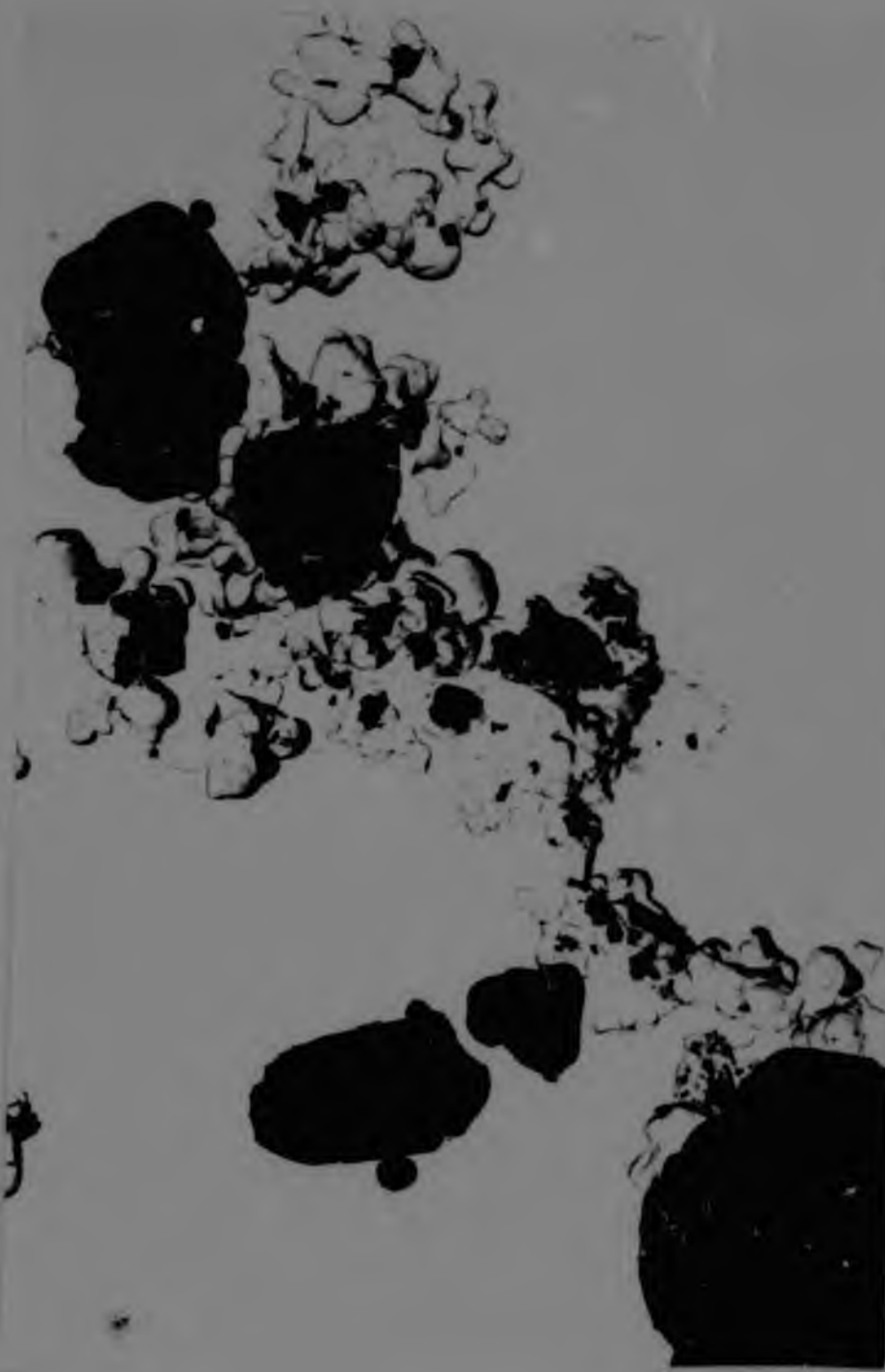


Figure 5.2.6: 20% Cobalt Alloy - 8 hours
milling x 17,250.



Figure 5.2.7: 20% Cobalt Alloy - 16 hours
milling x 17,480.

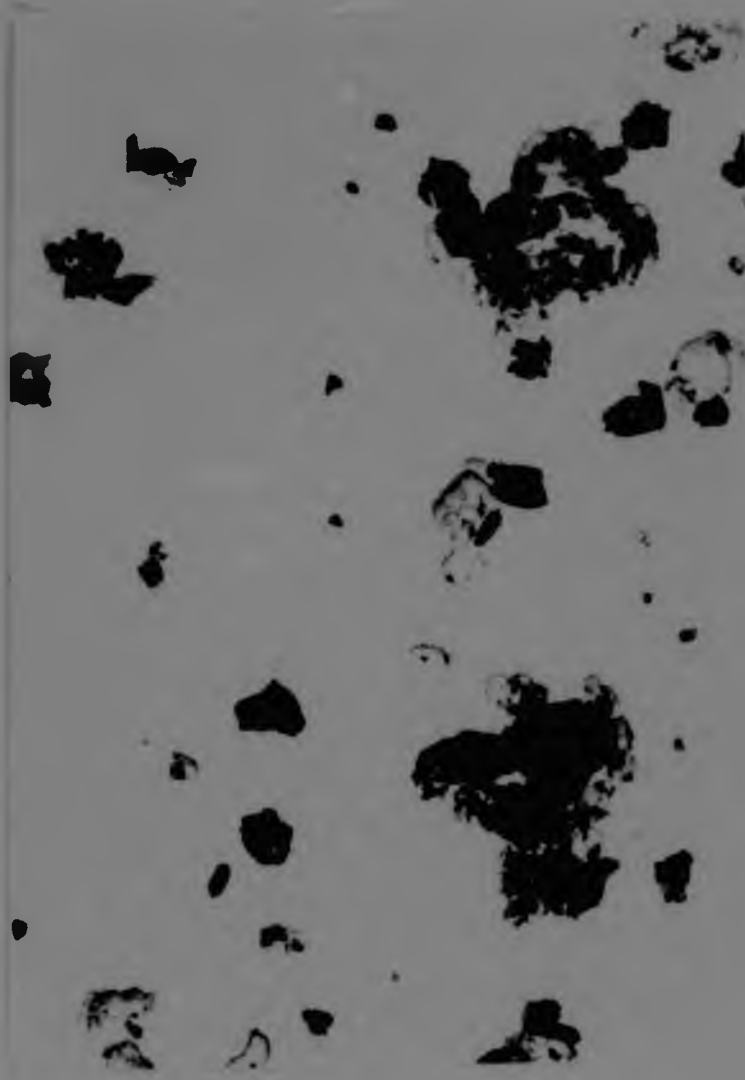


Figure 5.2.8: 20% Cobalt Alloy - 66 hours
milling x 17,480.

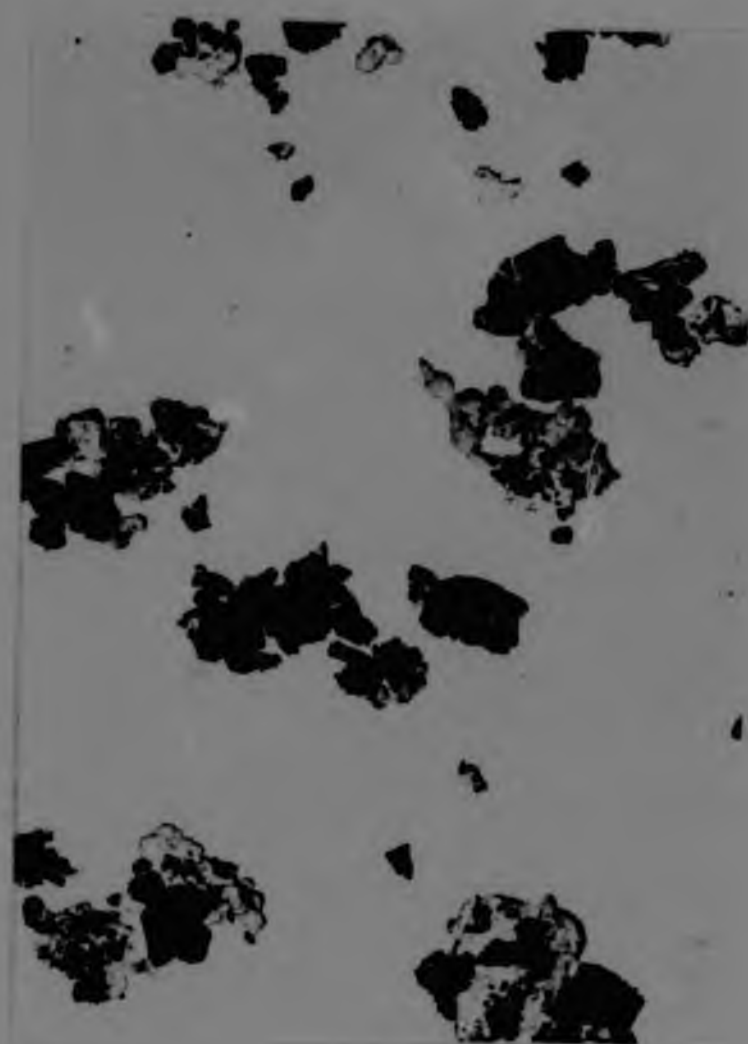


Figure 5.2.9: 20% Cobalt Alloy - 66 hours
milling x 17,480.

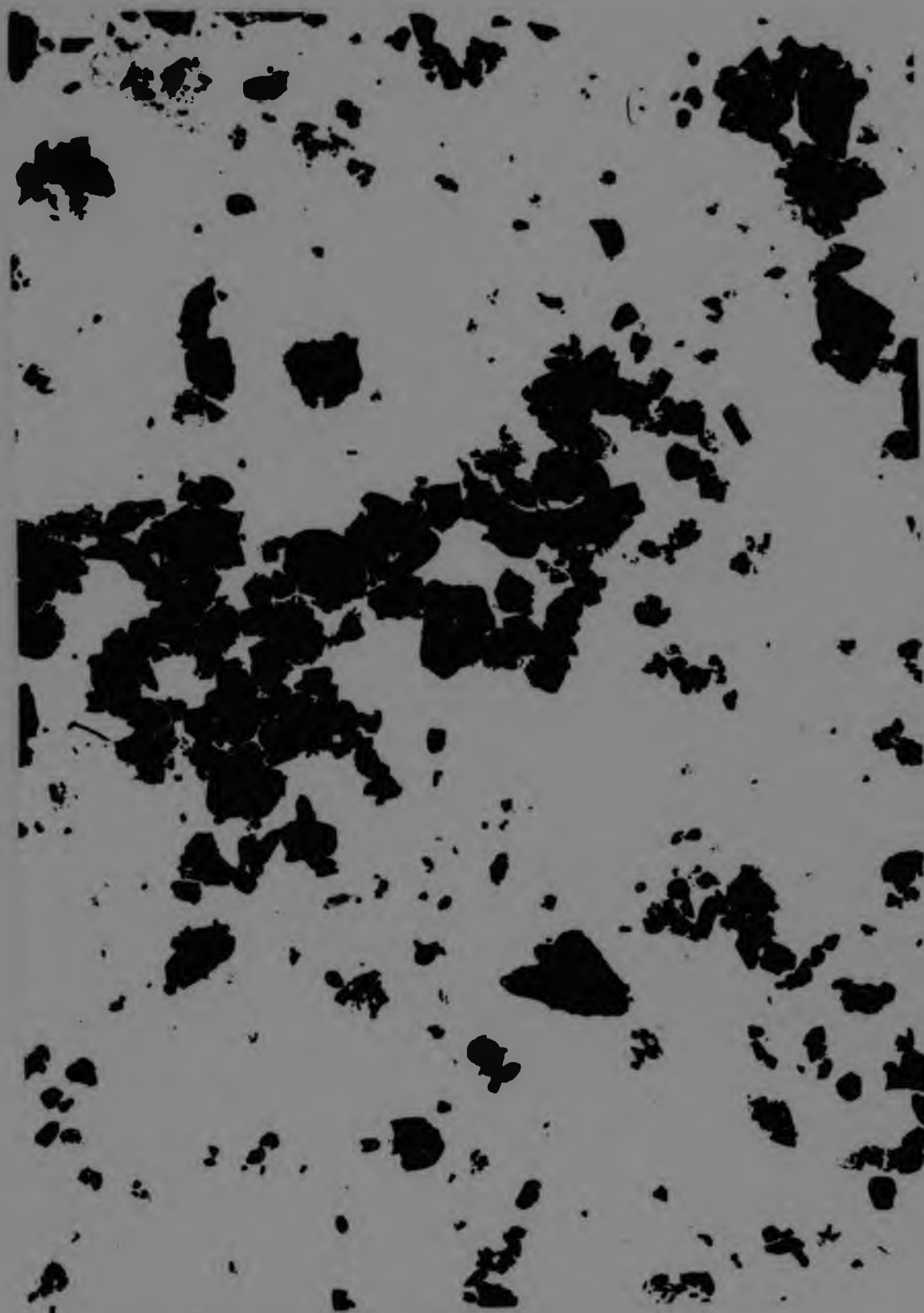


Figure 5.2.10: 10% Cobalt Alloy - 26 hours
milling x 17,480.

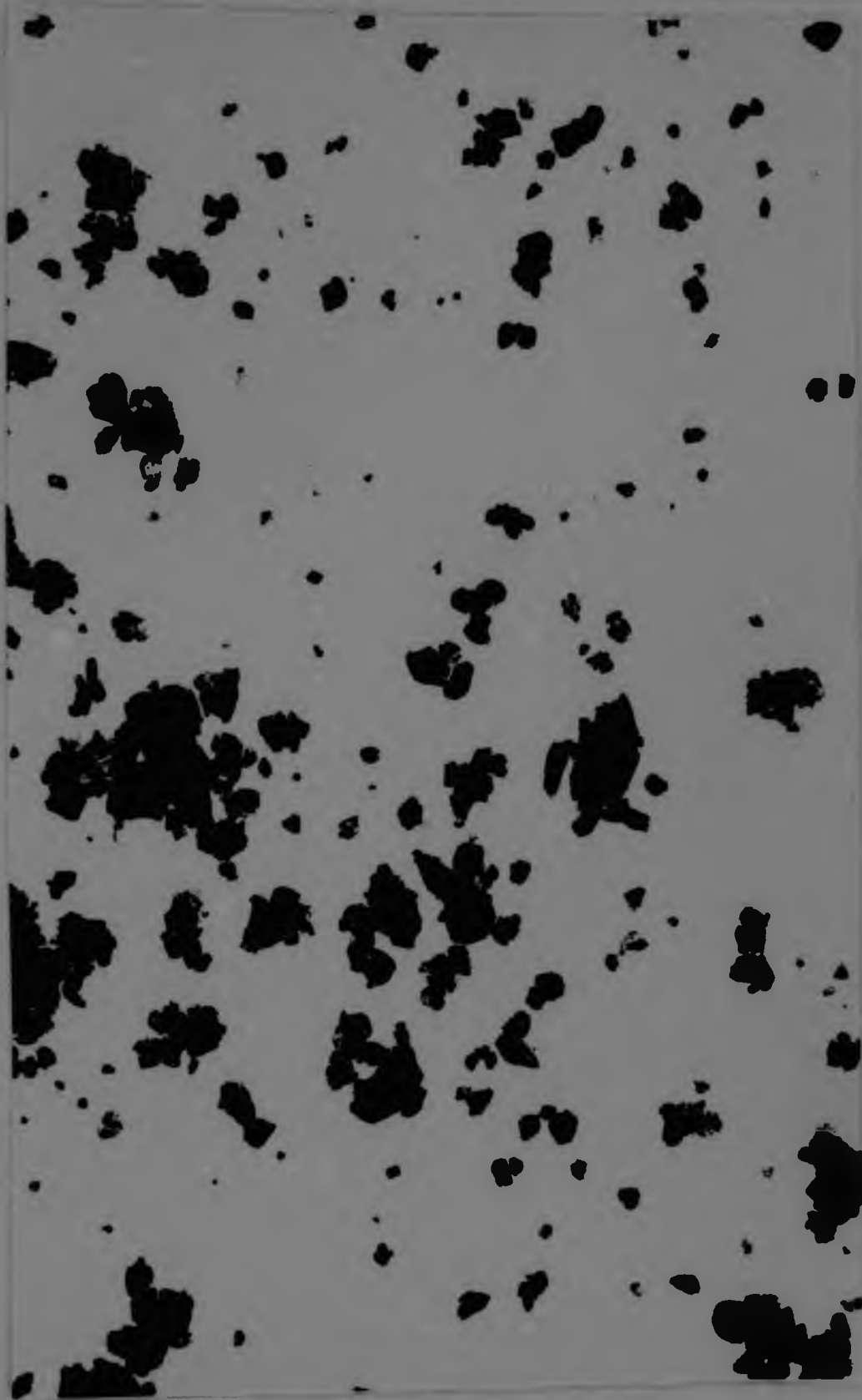


Figure 5.2.11: 10% Cobalt Alloy - 66 hours
milling x 17,480.

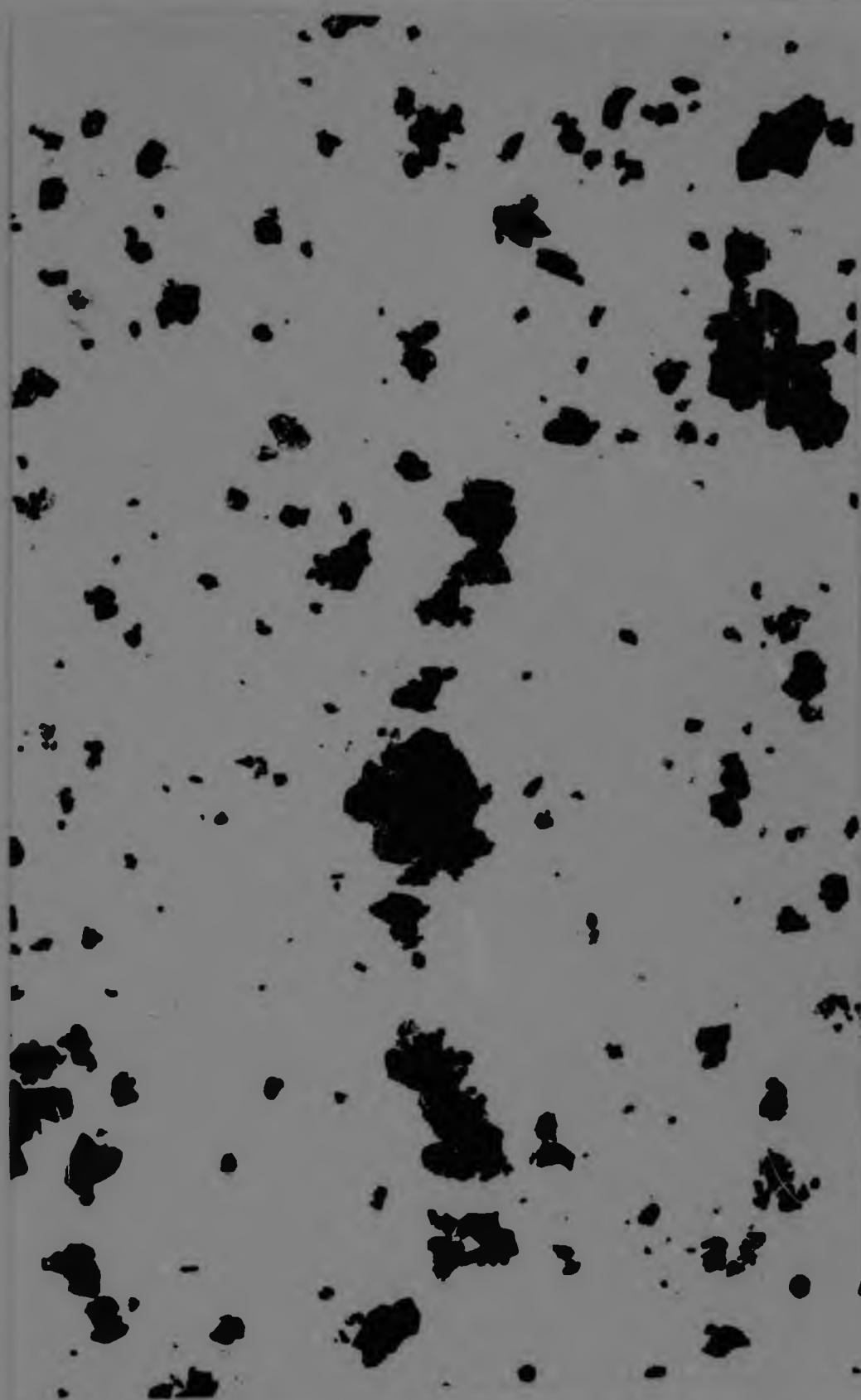


Figure 5.2.12: 10% Cobalt Alloy - 126 hours
milling x 17,480.



Figure 5.2.13: 6% Cobalt Alloy - 26 hours
milling x 29,000.

if they were examined by the usual techniques.⁽²¹⁾

The electron micrographs shown in Figure 5.2 indicates that during the initial stages of milling the cobalt powder agglomerates,--cobalt units in some cases larger than the carbide grains being present after two hours of vibratory milling. These cobalt "shells" (they are in fact only the patterns of the cobalt particles on the carbon replica, since the actual cobalt particles have been removed by treatment of the replica in acid) show that agglomeration has occurred, as they consist of aggregates of smaller discrete units. Even after a short vibratory milling period, it can be seen that some of the finer carbide particles have been beaten into the aggregates. As milling proceeds further it appears that these large aggregates of cobalt are broken down, for there is no evidence of their continued existence after extended milling periods. For example, in Figures 5.2.1 and 5.2.2 aggregates of cobalt are visible after short milling periods. In Figures 5.2.3 and 5.2.4 some of the fine carbide particles can be seen to be embedded in the cobalt aggregates. In Figures 5.2.5 and 5.2.6, a "flattening out" of the cobalt has occurred. After extended milling periods (e.g. Figure 5.2.11) the cobalt appears to be round the edges of the carbide grains. The beginning of this can be seen in Figure 5.2.13.

Particles of cobalt of the dimensions observed around the carbide particles were not present in the initial cobalt powder, and this suggests that besides the aggregates being broken down in size, a rolling into thin foil like particles also occurs during the hard metal milling. However, this change in shape does not take place in all the aggregates simultaneously, and is progressive as milling proceeds. These cobalt foils or envelopes obviously facilitate the sintering of a hard metal powder compact.

It is not possible to determine experimentally the mechanism for the change from aggregated particles of cobalt to much thinner foil like particles, but it may in fact be that the aggregates of ductile cobalt are cut by the carbide grains in the presence of the grinding balls.

It is very well known that fine grinding is one method of producing active surfaces on solids prior to sintering; ⁽²²⁾ this activity is considered to consist of two types:

- (a) activity due to increase in surface area.
- (b) activity due to a distortion of the crystal lattices. It has been found ⁽³¹⁾ that microstrains promote the sintering of materials at lower temperatures than in strain free materials. ^{(30), (31)} Greater diffusion may be possible with strained hard metal powders. Recrystallisation of the binder phase will also aid sintering.

The driving force for sintering is usually assumed to be the excess free surface energy of the

active state compared with that of the normal thermodynamic state. However, although for certain metal powder systems a close relation has been observed⁽²³⁾ between powder surface area and densification, lattice strain may contribute appreciably to the total free energy of a powder system, and should be considered in the complete characterisation of a powder prior to sintering. In other words, the sintering reactivity depends on the number and type of defects present as well as on the surface area. However, the surface free energy may be anisotropic, and is so in tungsten carbide powder.⁽²⁴⁾

At least three processes are known to occur during the sintering of cobalt - tungsten carbide alloys; these are believed to be:⁽²⁵⁾

- (1) The sintering together of the cobalt particles.

This usually starts at about 600 - 800°C depending on the composition of the alloy. All workers in this field are in agreement that this is the first process involved in hard metal sintering.

- (2) The diffusion range where carbon and tungsten atoms from the finest tungsten carbide particles go into interstitial solid solution in the cobalt phase. This solution process in the solid state has been found to promote shrinkage; for example, where a 6% Co - WC and a 9% Cu - WC alloy systems have been

compared.⁽²⁹⁾ WC has a negligible solubility in copper, and this system shows less solid state shrinkage than the Co-WC system.

Considerable temperature range overlap is believed to occur with the two processes (1 and 2) noted above.

- (3) The liquid phase sintering process itself, which has been considered by several authors, and is generally recognised to consist⁽²⁶⁾ of three sub-processes, namely re-arrangement, solution-reprecipitation and coalescence. Various models of these processes have been put forward. The models consider that rearrangement is a viscous flow process, but at least for the tungsten carbide cobalt system, the binder phase does not have to be liquid.⁽²⁹⁾ The rearrangement process for the tungsten carbide cobalt system has been described by Milner and Snowball,⁽²⁹⁾ who have criticised two important aspects of the Kingery⁽²⁶⁾ theory of solution-reprecipitation for WC - Co.

Exner and Fischmeister⁽²⁷⁾ have concluded that the shrinkage determining processes are independent of the melting point of the Co - W - C eutectic, and the same kinetics prevail for shrinkage in the diffusion and liquid phase range; i.e. isothermal shrinkage at 1,190°C, 1,280°C and 1,420°C, could be described by the equation:

$$(\Delta L/L_0) = k \left(\exp. \frac{-59,000}{RT} \right)^{-m} d^n \cdot t.$$

where m is an exponent less than unity, and is approximately $2/3$ between $1,190^{\circ}$ and $1,280^{\circ}\text{C}$.

t is the sintering time in minutes.

d is the average carbide grain size.

$(\Delta L/L_0)$ is the decrease in length divided by the length at the commencement of shrinkage at the temperature studied, and R and T have their usual meaning. Thus it would appear to be possible to achieve similar densities by sintering hard metal compacts for long periods at temperatures below that required for the formation of the liquid phase.

The lattice strain introduced during the milling of pure tungsten carbide powder has been considered by Gillies, Lewis and Porter,⁽³⁰⁾⁽⁸⁹⁾ and Hendus, Dawihl and Bartsch.⁽²⁸⁾ The former authors have also reported on a carbide - 10% cobalt milled powder mixture, and it was found that the amount of microstrain induced, was of the same order as in pure tungsten carbide powder. In the past, line broadening in the tungsten carbide X-ray spectrum had been attributed to cobalt penetrating the surface layers of the carbide. The work of Gillies and Lewis⁽³⁰⁾ demonstrated that the presence of cobalt was not necessary to induce lattice strain in the carbide.

These latter workers obtained larger induced strains than those reported by Hendus, Dawihl and Bartsch,⁽²⁸⁾ (0.0046 after 4 hours milling using the Wagner method for interpreting

the X-ray data, compared with 0.0047 after 400 hours milling where the data were interpreted by the Hall method).

In the present work a value of 0.0011 was obtained for the strain in the tungsten carbide when ball milling a 10% cobalt - coarse carbide alloy for two hours, and 0.0053 on a sample which had been vibratory ball milled for 86 hours. The line breadth method of analysis was used, and a sample of new coarse grained (5.57 μ) tungsten carbide was used as reference. This sample was annealed at 1,500°C in hydrogen prior to analysis. The relationship given by Gillies and Lewis,⁽³⁰⁾ which assumes a Cauchy strain distribution, was used:

$$(\beta^*)^2 = (1/D)^2 + 16 \epsilon \sin^2 \theta / \lambda^2$$

where D is the crystal size

ϵ is a measure of the strain

$(\beta^*)^2 = (\frac{\beta \cos \theta}{\lambda})^2$ where β is the integral line breadth obtained by dividing the area of the WC peaks by their height. Thus $(\beta^*)^2$ is plotted against $(d^*)^2$ and thus the strain and particle size effects can be obtained from the intercept and the slope.

The shrinkage of some compacts prepared from hard metal powder milled for various times was studied in a high temperature Adamel dilatometer using an atmosphere of hydrogen. The powder samples removed from the mills after various milling times were compacted at a pressure of 10 tons/in.² in a 0.475"

diameter die. These compacts were preheated at 800° in hydrogen. The cylinders were cut with a diamond impregnated slitting wheel into rectangular compacts 6 x 6 x 15 mm, suitable for the Adamel instrument. An alumina rod, separated from the specimens by a graphite end-cap, pressed gently against the presintered hard metal specimen, which was supported on a flat layer of graphite. The alumina rod followed the course of shrinkage and this was amplified by means of a tripod and pulley amplification system, linked to a pen recorder device. The same heating rate was used for all the specimens, namely $3\frac{1}{2}$ hours to the soak temperature; the heating rate was controlled by a spring loaded arm following a set pattern on a revolving drum. The temperature of the specimen, which was also directly recorded, was measured by means of a tungsten - tungsten 26% rhenium thermocouple directly below the graphite layer, on which the specimen was mounted.

The shrinkage-temperature curves for two 20% cobalt alloys are shown in Figures 5.3 and 5.4. All these alloy mixtures were prepared by vibratory milling as discussed below.

The results show clearly that prolonged milling leads to increased shrinkage, at a lower temperature for tungsten carbide cobalt compacts, and to greater final shrinkage. Furthermore, different shrinkage characteristics for different batches are evident.

FIGURE 5.3 SHRINKAGE CHARACTERISTICS AGAINST TEMPERATURE FOR A SERIES OF 20% COBALT
HARD METAL COMPACTS MILLED FOR DIFFERENT TIMES (ALL POWDERS FROM THE SAME BATCH)

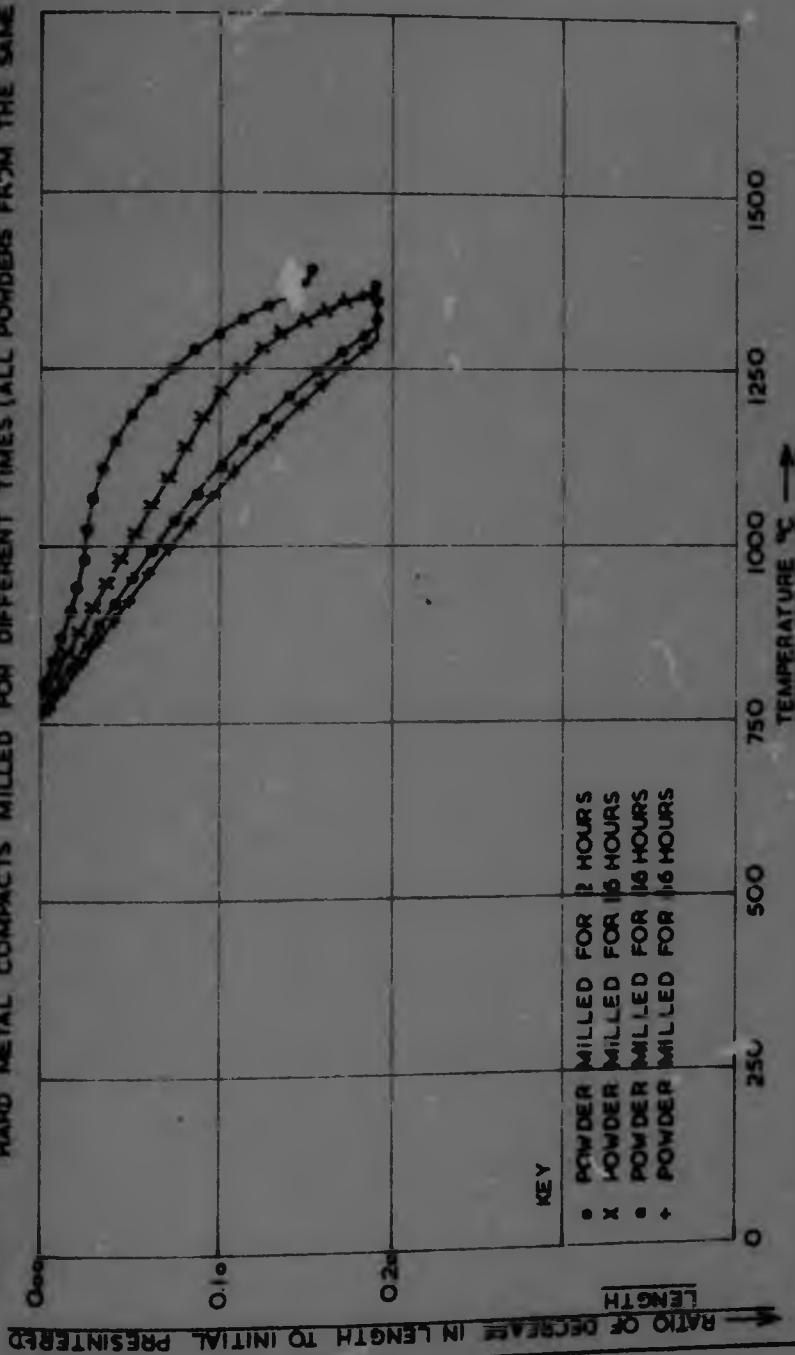
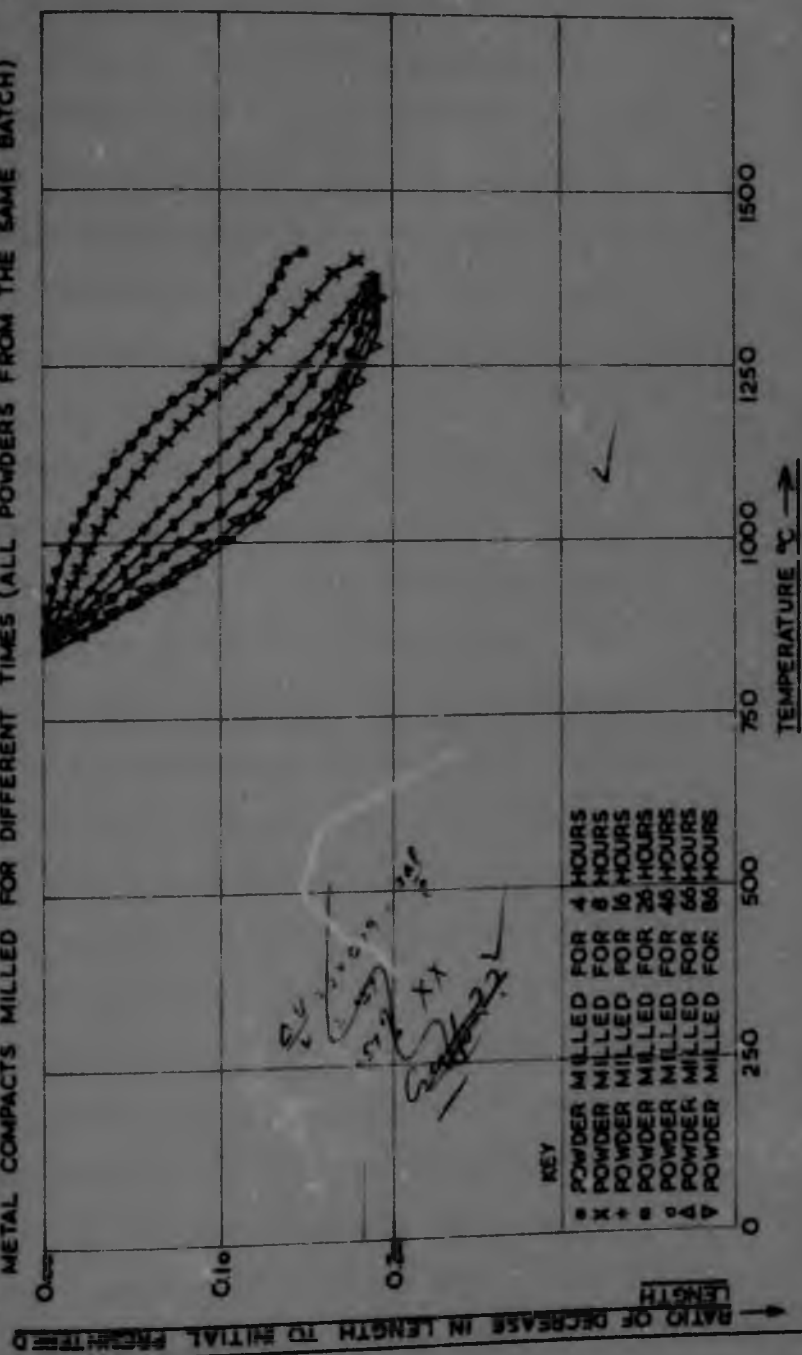


FIGURE 5.4: SHRINKAGE CHARACTERISTICS AGAINST TEMPERATURE FOR A SERIES OF 20% COBALT HARD METAL COMPACTS MILLED FOR DIFFERENT TIMES (ALL POWDERS FROM THE SAME BATCH)



This is a conclusion reached by many previous investigators in this field; the profound influence of milling time on the sintered density for a fine grained low cobalt composition has also been shown.⁽⁵⁾

As with all powder metallurgical products, sintered density of cemented carbides is an important factor in determining their industrial performance. Previous investigators^{(33), (34)} have shown that improved transverse rupture strength is obtained by the elimination of porosity. For optimum service conditions during use it is recognised that the sintered density should be between 98.8 and 99.8% of the theoretical value. In practice the actual densities obtained are always less than the theoretical, partly as a result of porosity but partly also as a result of impurities.⁽³⁴⁾

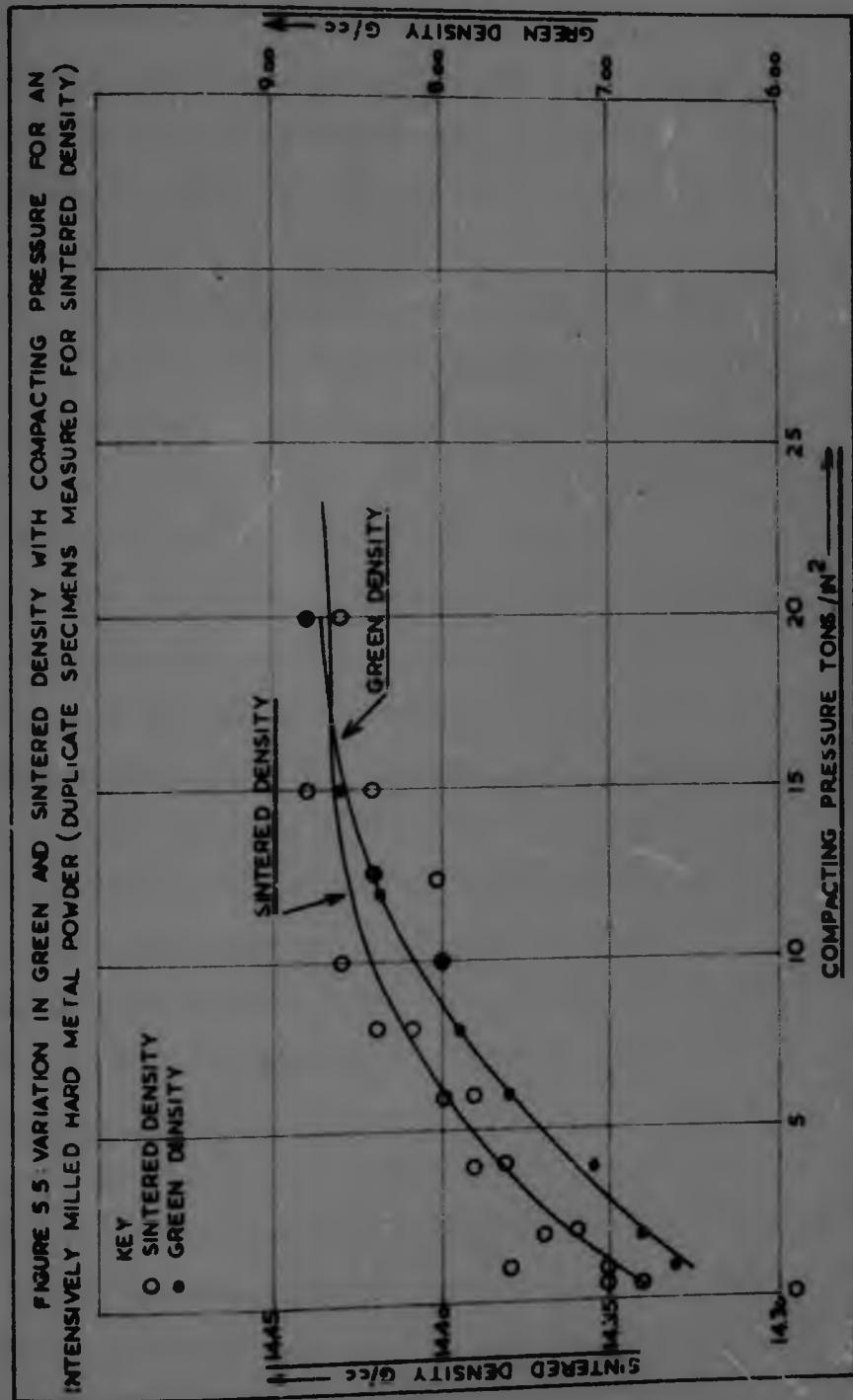
Prolonged milling only improves the densification characteristics up to a certain point. If very long milling times are used and the powder has a high surface area, it has been found that such a powder cannot be pressed to the same green density; although in liquid phase sintering systems, it has been generally assumed that the green density has no influence on the sintered density.⁽³⁵⁾ In contrast with the behaviour of other solid state metal and ceramic sintering systems,^{(36), (37)} Gurland⁽³⁸⁾ has shown that a minimum pressing pressure to cause cohesion,

is necessary for achieving a satisfactory sintered density of hard metal compacts.

As a first approximation, therefore, the number of contacts per particle can be considered as the determining factor during the initial stages of sintering. The green density obtained after pressing, depends, as is well known, on the particle size and size distribution of the powder. The repeatability of pressed density measurements is discussed in the next chapter.

The overmilling effect is of extreme importance where volume filling of dies is used in the mass production of small components. In many cases granulation of powders prior to pressing is used. This was not done in the work reported on here as it would introduce another variable, since the hard metal powder granules would have to have the same hardness and tap density.

The importance of compacting pressure is shown in Figure 5.5, where a hard metal powder was compacted at different pressures, thus varying the green density. 10 g. powder was used for each compact which was pressed in a 0.475" diameter die, a Heise gauge being attached to the press system to measure the load. As shown in Figure 5.5 the green density does influence the sintered density using pressures up to about 6 t.s.i. The compacts used in this experiment were of a 10% cobalt alloy, attrition milled for 16 hours. All the compacts of this series



were sintered together in a continuously fed D-shaped alumina tube furnace with a hydrogen atmosphere, using a sintering temperature of $1,410^{\circ}\text{C}$.

Using very high pressing pressures a decrease in transverse rupture strength has been observed;⁽³⁸⁾ this has been attributed to non uniform die yielding and pressure release, causing small cracks in the compact.

As discussed earlier, although defects and lattice strain contribute appreciably to the total driving force, it was initially decided to use the B.E.T. specific surface area as a parameter for relating the milled hard metal powder with its subsequent sintering characteristics as determined by the sintered density. Other workers have recognised the use of specific powder surface area as a control parameter for hard metal powder alloys.⁽³⁹⁾ Even simplified techniques such as the use of dye adsorption by a powder from methanol solution have been used and reported to be satisfactory,⁽³⁹⁾ although this method cannot be claimed to be precise due to the large size of the dye molecules.⁽⁴⁰⁾

5.3 Experimental.

Initially, the specific surface area - sintered density relations were studied on 5% cobalt-fine-grained alloy compositions (1 - 2 μ initial carbide particle size).⁽⁵⁾ Subsequent work was carried out on 20%, 10% and 6% cobalt-coarse-grained

(5 - 7 μ initial carbide particle size) hard metal alloys, using a series of cobalt powders from different sources, and modifying some of them by pre-annealing. All of these hard metal batches exhibited a certain minimum specific surface area, such that on sintering a satisfactory compact density was achieved. It was found possible to alter this minimum specific surface area, by changing the source of the cobalt powder, but continuing to use the same carbide powder. The properties of the carbide powder used for making the 20%, 10% and 6% cobalt alloy batches are summarised in Table I, and a photomicrograph of the powder is shown in Figure 5.6.

The hard metal powders produced in these studies were examined by X-ray diffraction (using a Philips PW 1060 unit) and electron microscopy (using the techniques described previously)⁽²¹⁾ on the Philips EM 200 Electron microscope; the specific surface areas of the powders were determined on the Perkin Elmer 212D Scryptometer.

The components of this instrument⁽⁴¹⁾ for determining the specific surface area of powders consist of a gas flow regulator, thermostat and a thermal conductivity detector, and correspond with those in a gas chromatograph. However, the readings obtained are not true gas chromatographic measurements, but rather a specialised variation of the B.E.T. method. The basic principle is that a

TABLE I.

Summarised Properties of Tungsten Carbide powder
used for making the 6%, 10% and 20% cobalt hard
metal alloys

Fisher Grain Size	5.57 μ
Specific Surface Area	0.10 m ² /g.
Total carbon	6.18%
Free carbon	0.08%
Oxygen	0.03%



Figure 5.6: Tungsten Carbide Powder examined
on Cambridge Stereoscan Microscope x 10,000.

stream of gas is passed over a cooled powder sample in a glass tube. The gas mixture consists of a known proportion of adsorbate (nitrogen) and carrier gas (helium). The effluent is monitored by the thermal conductivity detector. While the gas mixture is flowing the sample tube is cooled by immersing it in a flask of liquid nitrogen. The cooling sample adsorbs a certain amount of nitrogen from the gas mixture, and the resulting dilution is recorded on the thermal conductivity detector. The liquid nitrogen flask around the sample is then removed, and as the previously cooled sample warms up to room temperature, the adsorbed gas is released thus enriching the effluent, which is again recorded by the thermal conductivity detector. Calibration is effected by adding a known volume of nitrogen to the system. The thermal conductivity detector is connected to a pen recorder.

The density-milling time relations were studied by making up 6 kilo charges of hard metal powders and vibratory milling them under 3 litres acetone using 20 kg. $\frac{1}{2}$ " hard metal balls (of 10% cobalt composition) in eight litre stainless steel mills. Samples were removed after 2, 4, 8, 12, 16, 26, 46, 66, 86, 106 and 126 hours of vibratory milling. All undersize grinding material and broken balls were removed by hand before the addition of each powder charge. The use of smaller balls is known to result in an increased crushing rate for the

powder. (42)

After the milling periods mentioned above, scoop samples of 50 g. were taken from the slurry, after discharge into a circular stainless steel container. The powders were dried under vacuum on a water bath (for three hours) to remove the acetone. The containers were allowed to cool before opening, and the powders were screened on a 200 mesh screen to break up any agglomerates formed during drying. The specific surface areas of the hard metal powders were measured, and the powders assayed for total carbon and oxygen. Small hard metal compacts were pressed at 10 ton/in.² using 12 g. powder in a 0.475" diameter hardened steel die. No lubricant was mixed with the powder prior to pressing. To prevent excessive oxidation and decarburisation, the compacts were stored under vacuum in a desiccator, until sintering was carried out.

The sintering temperatures used were 1,350°C for the 20% cobalt alloys, 1,410°C for the 10% cobalt alloys and 1,460°C for the 6% alloys. Sintering was carried out in a hydrogen atmosphere D - shaped alumina tube furnace with a molybdenum winding. Temperature measurements were made with an optical pyrometer which had been previously calibrated against a Cambridge tungsten filament lamp. Carbon boats with well fitting lids, were used with a 0.5% carbon-alumina mixture as packing material. Carbon has to be added to the alumina packing mixture as

hydrogen, at the sintering temperatures employed is decarburising. ⁽⁴⁴⁾ All material of the same compositions was sintered in the same train of carbon boats in a single day's run.

It is well known that the sintered properties of hard metal alloys are markedly dependent on the furnace atmosphere and packing material employed during sintering. ⁽⁴⁵⁾ During sintering, hard metal compacts are particularly sensitive to moisture either in the incoming furnace gas or in the furnace environs.

Thus it is usual to measure the dew point of the exit gases from the furnace. This was done for the three runs involved and the readings were - 21° for the 20% alloys, - 16°C for the 10% alloys and - 18° for the 6% alloys.

Furthermore, the pressed components have to be carefully packed in the boats prior to sintering, to ensure that direct contact with decarburising hydrogen is avoided. All these precautions were observed in this work.

There is also an inherent variability in the properties of material from the same batch, when it is sintered in the same boat. Some examples of these variations will suffice to show this effect.

For an experiment similar to that for which the results are shown in Figure 5.7, the variations in properties shown in Table II, were obtained on batches of 20 specimens sintered in the same boat.

TABLE II.
Variations in Sintered Properties with Sintering
Temperature.

Sintering Temp. °C	Density g./cc.	Standard Deviation g./cc.	Magnetic Saturation Units % G.	Standard Deviation Units	Coercivity Oersted	Standard Deviation Oersted
1,330	14.75	0.035	70.5	2.50	218.7	6.00
1,360	15.08	0.033	69.8	2.90	234.2	9.67
1,390	15.12	0.026	68.7	2.55	234.4	8.00
1,420	15.14	0.010	69.3	3.10	235.1	3.66
1,450	15.06	0.026	76.0	3.30	227.5	6.68
1,480	15.03	0.023	72.4	3.60	214.3	5.50
1,510	15.02	0.030	70.6	2.50	205.1	7.50
1,525	14.99	0.020	62.3	2.60	191.4	16.30
1,560	14.92	0.053	55.3	4.00	167.1	13.80

These specimens contained 4½% cobalt.

The above data give an indication of the variability in sintered properties obtainable on any one batch of material. The significance of the properties measured is discussed in connection with the data described in Figure 5.7.

Nevertheless, when vacuum sintering and hydrogen sintering are compared, using sets of compacts milled for the same time and removed from the same powder batch, although density values may differ slightly, the influence of milling time is again discernible. The data in Table III show this.

The gas-vacuum cycle was chosen to give magnetic saturation values comparable with those obtained in hydrogen sintering. Further experimentation has shown that the variation in properties of the same composition, but sintered in different boats during the same run is statistically negligible. ⁽⁴⁶⁾

Using the 6 Kg. mass it would have been inadvisable to remove larger quantities of material so that several specimens, pressed from powder milled for the same time, could be sintered together, and an average density value thus calculated.

Evidence for the importance of the packing medium surrounding the components during sintering is provided by the data shown in Table IV, relating to ten pieces containing 4½% cobalt sintered in hydrogen at 1,480°C under the conditions specified.

TABLE III.
Comparisons of Sintered Properties using Vacuum and
Hydrogen Sintering.

Milling Time (Hours)	Hydrogen Sintered Specimens			Vacuum Sintered Specimens		
	Density g./cc.	Magnetic Saturation Units	Coercivity Oersted	Density g./cc.	Magnetic Saturation Units	Coercivity Oersted
2	14.36	184.4	66.3	14.40	183.3	69.0
4	14.42	183.5	69.5	14.44	186.6	70.0
8	14.44	187.0	72.2	14.45	188.3	72.6
12	14.48	188.0	78.3	14.49	190.9	76.0
16	14.50	189.6	82.4	14.52	183.5	83.0
26	14.52	187.3	87.0	14.52	185.9	87.6

TABLE IV.

Effects of Packing Media on Sintered Properties

Packing	Average Properties of the Sintered Compacts		
	Density g./cc.	Magnetic Saturation Units	Coercivity Oersted
Pure Alumina	15.11	60.0	243.0
Al ₂ O ₃ + 0.1% C	15.04	73.5	213.8
" 0.3% C	15.03	77.9	205.0
" Carbon Grit Mixture	15.00	80.5	204.0
" 0.5% C	15.02	81.8	200.0
" 2.0% C	15.00	85.9	195.0
Carbon Black	15.00	92.9	184.0
Carbon Grit	14.99	94.0	170.0

The effect of different sintering temperatures (in the range 1,330 - 1,540°C) on the three sintered compact properties namely, coercivity, magnetic saturation, and density is shown in Figure 5.7 for a series of 4½ percent cobalt fine grained alloy specimens. Twenty individual specimens were sintered at each temperature and the mean properties calculated. The obvious feature of this data is that the maxima for the various different properties do not occur at the same sintering temperature. The following observations may be offered with respect to the variations in these properties with sintering temperature:

- (1) Coercivity: The significance of this property has been discussed by Krainer,⁽⁴⁸⁾ who gives the following formula for the coercivity of a sintered hard metal compact:

$$H_c = \left\{ \frac{3/2 \lambda_s \sigma_i + bK}{J_s} \right\} \cdot \left\{ \frac{\alpha^{2/3} \cdot 2\delta/d}{1 + 2(\delta/d)^2} \right\}$$

where λ_s is the saturation magnetostriction

σ_i is the inner tension ?

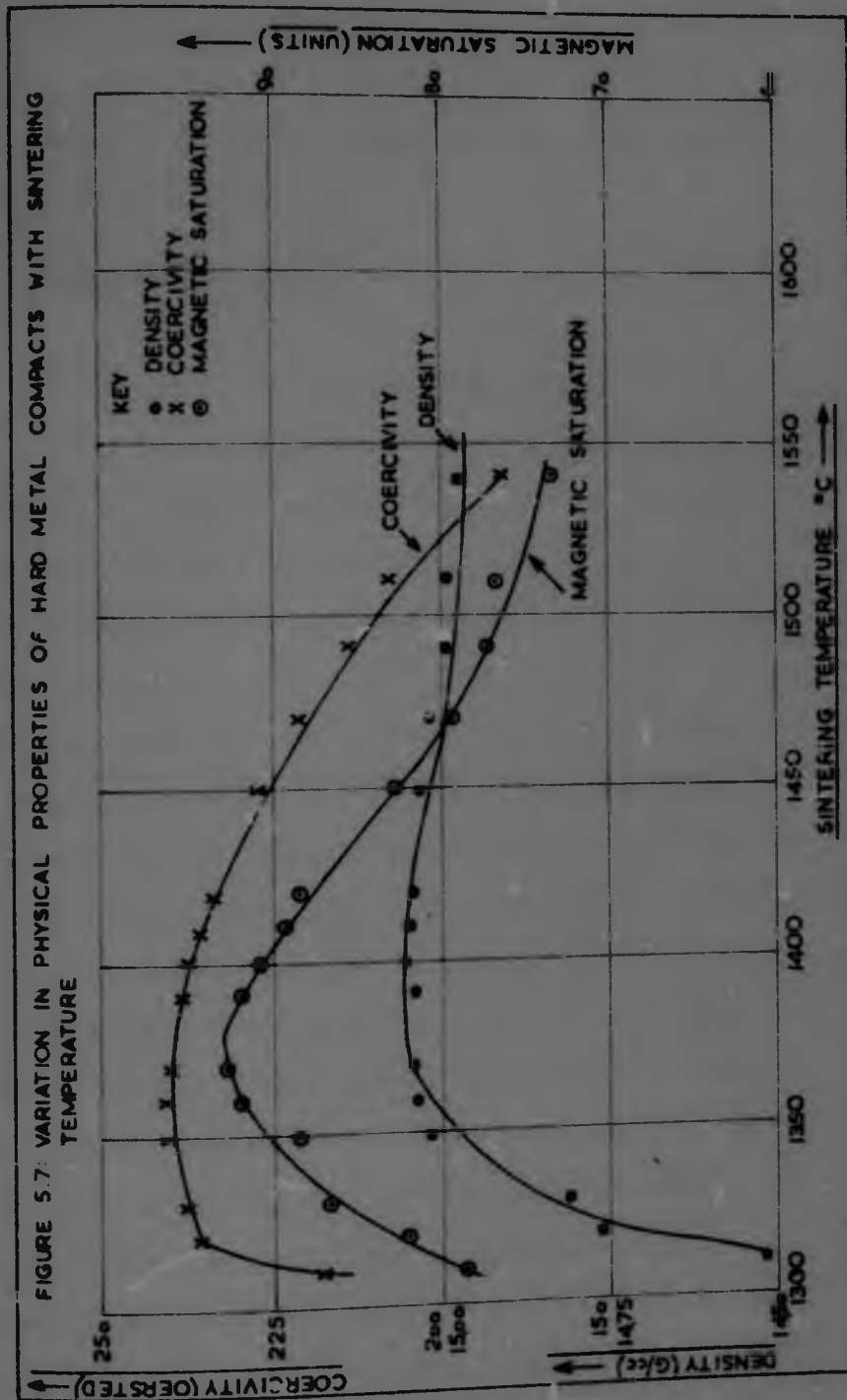
b is a constant factor with a value of approximately unity.

K is the crystal energy

α is the volume fraction of non magnetic phase

d is the average diameter of the non magnetic inclusions

FIGURE 5.7: VARIATION IN PHYSICAL PROPERTIES OF HARD METAL COMPACTS WITH SINTERING TEMPERATURE



J_s is the saturation magnetisation

δ is the so called "partition thickness"

which is $\ll$ than the carbide grain size

and is given by:

$$\delta = \sqrt{\frac{A}{3/2 \lambda_s \sigma_t + 3K}}$$

where A is the exchange energy, which is given

$$\text{by } A = \frac{k T_c}{a}$$

where a is the ferromagnetic lattice parameter

k is the Boltzmann constant

T_c is the Curie temperature

Although coercivity has long been used for the industrial control of hard metal structures, and Krainer's formula incorporates such variables as carbide grain size, the residual stress, and binder phase layer thickness, more recent work^{(49), (50)} appears to throw some doubt on the exact importance of these quantities in relation to coercivity.

Summarising the results of this later work, it may be stated that the coercivity depends on the magnetic anisotropy of ferromagnetic materials, which in turn (for hard metal specimens) depends on the amount of carbide in the binder phase, the residual stress in the binder, the presence of stacking faults, and for very thin specimens the actual specimen shape. It is difficult at this stage to offer a complete interpretation of the significance of the variation in coercivity, with sintering temperature. Krainer attributed the rise in coercivity with increasing

sintering temperature to a reduction in the level of porosity, and the decrease (after the maximum coercivity had been reached) to grain growth of the carbide phase. Bearing in mind that porosity and grain size influence such factors as the stress and binder phase layer thickness, this may at least be a partial explanation.

- (2) Density: Each point in the figure represents the mean value of the density determinations on the twenty specimens using the water displacement method, which has a precision of ± 0.01 g/cc.⁽³⁷⁾ Density increases as the sintering temperature is raised, due to the increased driving force for sintering provided by the higher temperatures. The decrease in density after the maximum has been reached has never been properly explained, although it is well known in cemented carbide technology.⁽²⁵⁾ Blistering and segregation are known to occur at high sintering temperatures, especially with larger cobalt contents.⁽⁵³⁾ Apart from the milling time used, sintering time and temperature have been considered to be of major significance in determining the density of a hard metal component.⁽²⁵⁾ In fact, an interaction exists between the time and temperature of sintering.⁽⁵⁴⁾ (These variables

together also play a major part in determining the contiguity of the carbide phase in a sintered hard metal structure).⁽⁵⁵⁾

- (3) Magnetic Saturation: This is a non-destructive test performed with a magnetic balance for estimating the amount of free ferromagnetic phase present in a material; for example, cobalt and carbon deficient tungsten carbide could combine during the sintering process to form eta phase, which is non magnetic.⁽⁵⁰⁾ This would be reflected by a decrease in the magnetic saturation of the material. The magnetic saturation is derived from the magnetic moment per unit volume or per unit weight. The numerical value is 20.2 units per one percent of free cobalt present; iron and nickel binders would, because their magnetic moments are different, yield different magnetic saturation values; a specimen of pure cobalt would have a magnetic saturation of 2020 units.⁽⁵¹⁾ The magnetic saturation is independent of the grain size of the tungsten carbide in the specimen, and depends only on the binder composition.⁽⁵⁰⁾ The carbide phase is non magnetic.⁽⁵²⁾ It has been found that the magnetic saturation depends on the specimen shape when very small specimens are measured.

In view of the above complex factors, the

rise and fall in magnetic saturation, as shown in Figure 5.7 cannot be properly explained.

Krainer⁽⁴⁸⁾ introduced the concept of an "optimum sintering temperature", being that temperature at which the coercivity reached its maximum value. However, this sintering temperature does not necessarily correspond to optimum performance during the industrial use of hard metal components. The sintering temperatures used here for the 20%, 10% and 6% cobalt compositions were thus what is generally considered to be satisfactory, for alloys of these compositions, and correspond with those used in normal industrial practice. As mentioned previously, the volume percentage of binder in liquid phase sintering decreases at a fixed temperature with decreasing cobalt content in the compacts;⁽¹³⁾ thus it was necessary to raise the sintering temperature from 1,350°C to 1,410°C to 1,460°C as the cobalt content was reduced from 20% to 10% to 6%. Gurland⁽⁴⁷⁾ has reported that the so called "optimum sintering temperature" is increased with decreasing cobalt content. It would have been impossible to determine and to vary the optimum sintering temperature with these small powder quantities obtained from the slurries removed from the vibratory mills after various milling times.

The properties of the initial cobalt powders used are summarised in Table V, where the pre-annealing conditions employed for the powders (where this was carried out) are also given. The X-ray diffraction patterns were run as described in Chapter 4.

TABLE V.

Summary of Minimum Specific Surface Areas required for achieving satisfactory density for the 20% 10% and 6% cobalt Hard Metal Alloys, and Summary of the initial cobalt powder properties.

Cobalt Powder Batch	(1) m ² /g.	(2) Allotropic Ratio	(3) Oxygen Content %	(4) f _s min. for H.M. composition m ² /g.	(5) Sintered Densities			(7)
					(6) g./cc.			
					g./cc.	g./cc.		
20% cobalt alloys								
Hoboken Annealed.	1.53	0.70	1.16	0.31	13.52	13.55	13.57	
Hoboken HML - 172.	1.07	0.77	0.62	0.30	13.52	13.55	13.57	
Annealed.	0.72	0.43	0.52	0.33	13.47	13.50	13.56	
HML - 199.	1.30	0.33	0.85	0.41* + 0.44	13.45	13.48	13.55	
HML - 201.	1.48	0.23	1.07	0.60	13.39	13.44	13.54	
HML - 172	0.91	0.27	0.93	0.52	13.42	13.46	13.54	
10% cobalt alloys								
Hoboken Annealed.	1.53	0.70	1.16	0.38	14.36	14.43	14.52	
Hoboken CF-6	1.07	0.77	0.62	0.32	14.39	14.45	14.53	
Annealed.*	0.96	0.45	0.41	0.48	14.32	14.42	14.51	
CF-6.	1.25	0.38	0.74	0.55* + 0.59	14.25	14.36	14.50	
CF-10	1.32	0.22	0.53	0.97	14.17	14.31	14.47	

TABLE V. (Cont.)

Cobalt Powder Batch	(1) $m^2/g.$	(2) Allotropic Ratio	(3) ⁺ Oxygen Content %	(4) S_s min. for H.M. comp-position $m^2/g.$	Sintered Densities		
					(5)	(6)	(7)
					g./cc.	g./cc.	g./cc.
6% cobalt alloys							
Hoboken	1.53	0.70	1.16	0.49	14.78	14.89	14.90
Annealed*							
Hoboken.	1.07	0.77	0.62	0.41	14.84	14.91	14.92
CF-6							
Annealed.*	0.96	0.45	0.41	Q.57	14.72	14.87	14.89
CF-6.	1.25	0.38	0.74	0.69 [†] + 0.70	14.66	14.87	14.91
CF-10.	1.32	0.22	0.53	1.09	14.62	14.84	14.90

Notes:

- 1) Initial Specific Surface Area of the cobalt powder ($m^2/g.$)
- 2) Intensity ratios of the (101) hexagonal to (200) cubic profiles.
- 3) Oxygen content of the cobalt powder before milling (%).
- 4) S_s Specific Surface Area of the hard metal powder required for achieving the set minimum density values.
 - * The powders were pre-annealed in hydrogen by heating at 200°/hr. to 600°C with four hours at 600°C; a 10°/hr. cooling rate was used.
 - † Repeat test mills were carried out.
- 5) Density of the sintered specimen (in $g./cc.$) after 4 hours milling.
- 6) " " " " " " " " " " " "
- 7) " " " " " " " " " " " "

The variations in density with milling time for the 20% and 6% cobalt alloys are shown in Figures 5.8 and 5.9 respectively. The effect of over milling resulting in a reduced density is clearly evident for the 20% cobalt batches. Individual plots of sintered density against specific surface area of the hard metal powders were constructed for each batch, and the values required to achieve a minimum density were determined - (these values are referred to as S_g min. in column 4 of Table V). The minimum density values were selected quite arbitrarily, and corresponded with the minimum industrial rejection limits for hard metal alloys, viz. 13.50 g/cc for a 20% cobalt alloy, 14.45 g/cc for a 10% cobalt alloy, and 14.85 g/cc for a 6% cobalt alloy.

The data in Figures 5.8 and 5.9 are replotted in Figures 5.10 and 5.11 respectively, using an extended scale for the vibratory milling time; in these figures the allotropic ratios and specific surface areas of the initial cobalt powders are also included. It is evident that for any milling time up to twelve hours, the densities of the sintered specimens increase in an order which corresponds with an increasing ratio of hexagonal to cubic allotropes in the initial cobalt powders; e.g. for the 6% cobalt alloys and a milling time of four hours, the annealed Hoboken cobalt mixture had a sintered density of 14.84 g/cc, whereas the specimen prepared with CF-10 powder had a density

FIGURE 5.8 SUMMARY OF SINTERED DENSITY AGAINST MILLING TIME FOR 20% Co COMPACTS

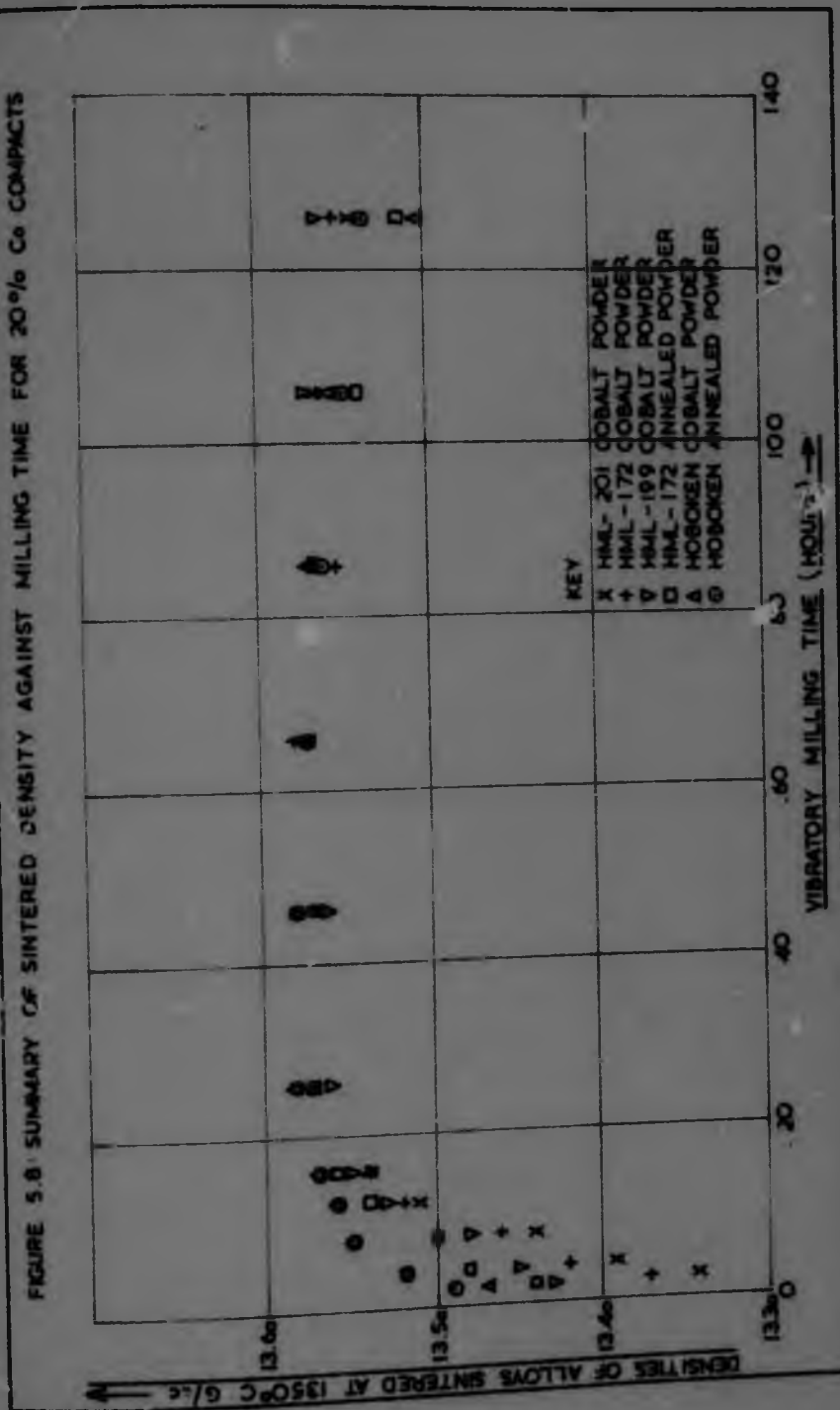


FIGURE 5.9: SUMMARY OF SINTERED DENSITIES AGAINST MILLING TIME FOR 8% COBALT ALLOYS

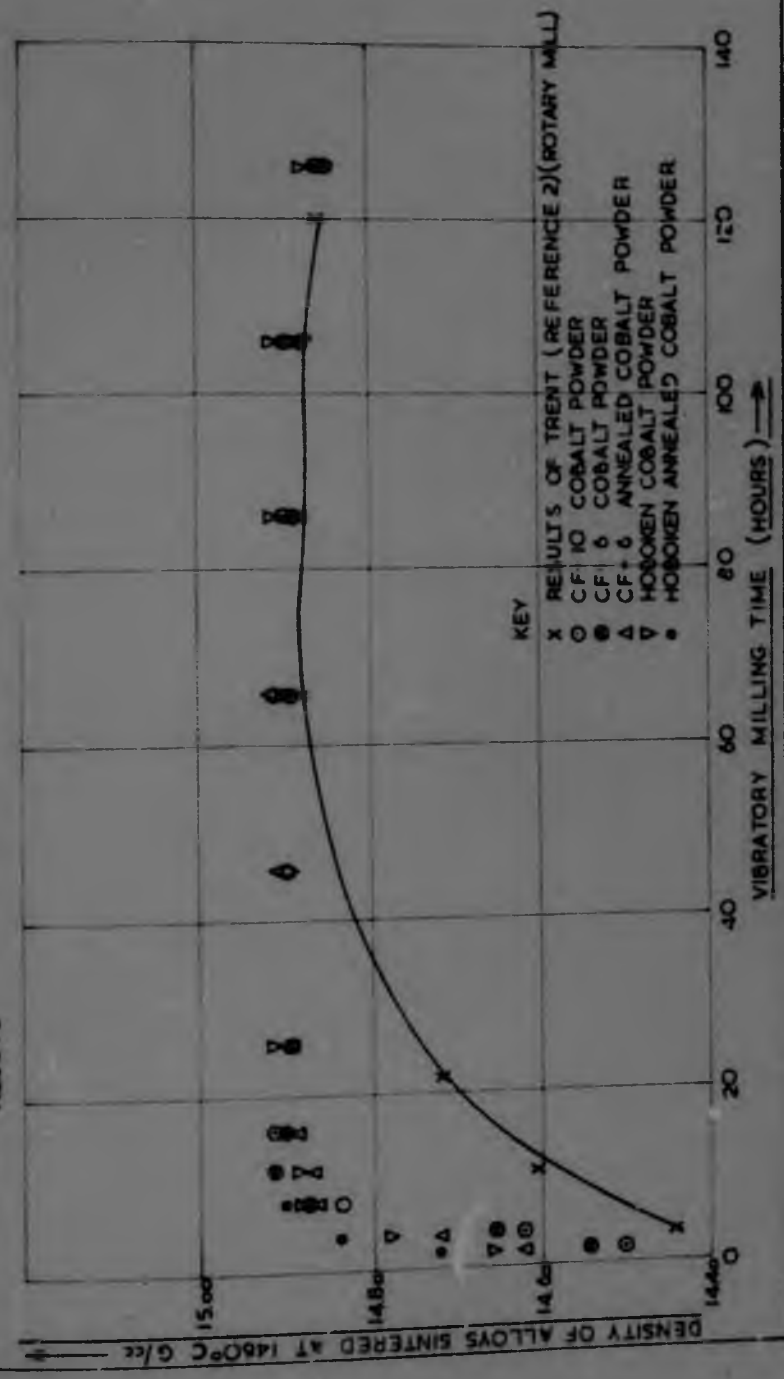


FIGURE 5.10 SUMMARY OF SINTERED DENSITIES AGAINST MILLING TIME FOR 20% COBALT COMPACTS (INITIAL PERIOD)

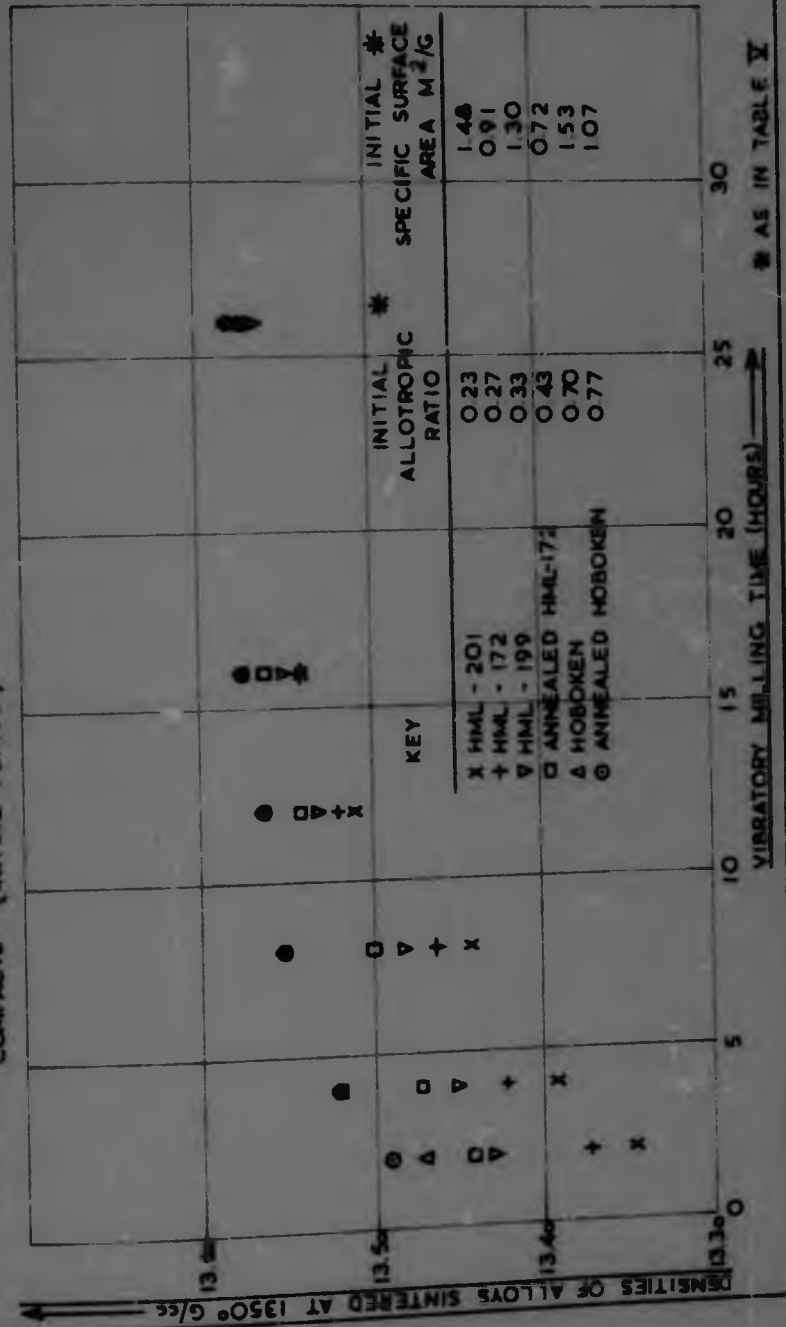
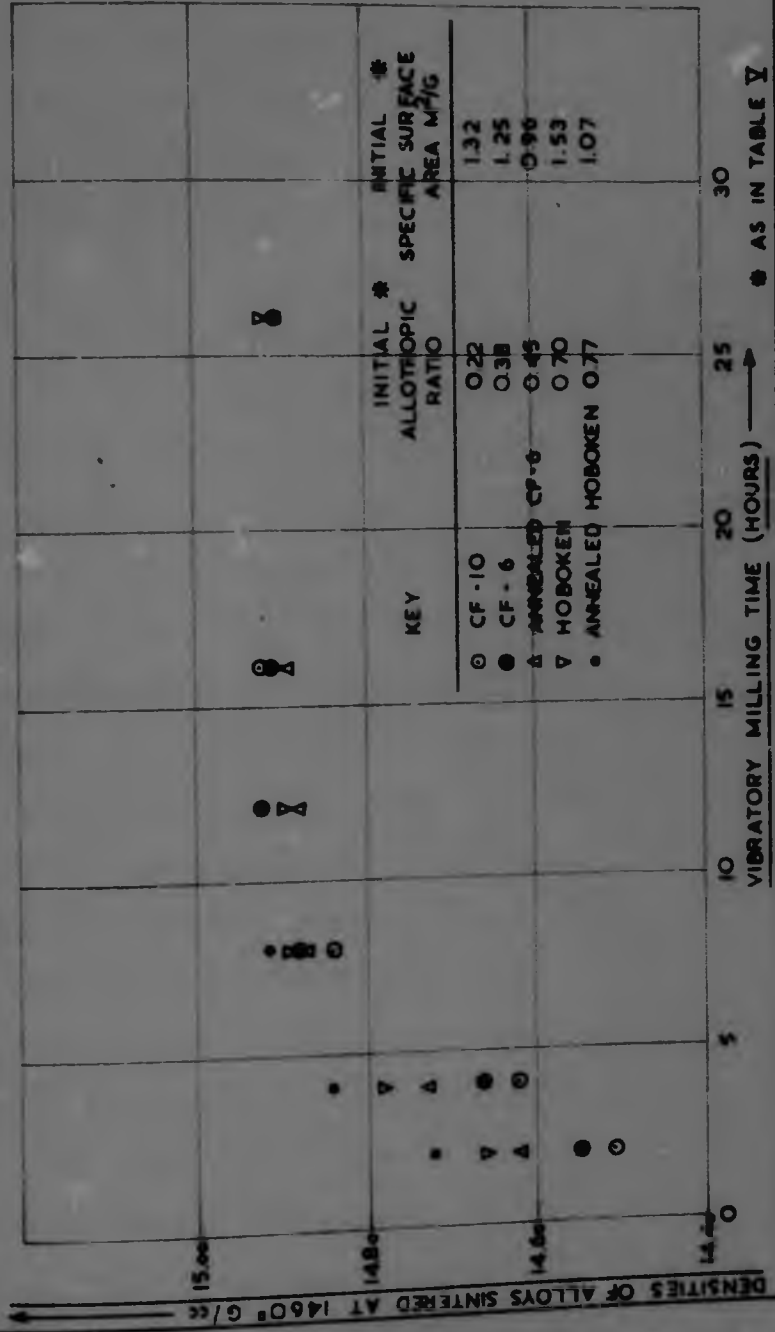
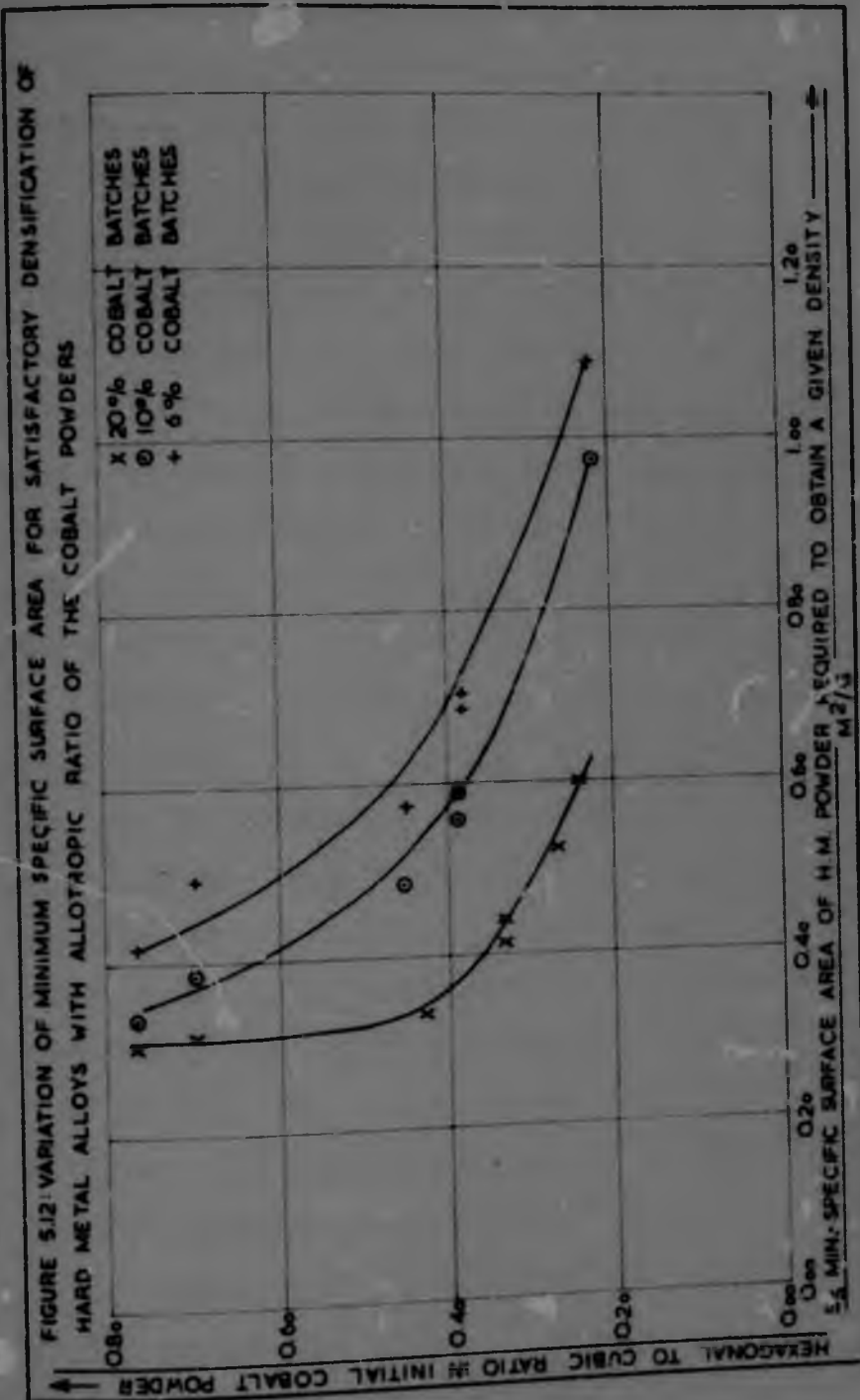


FIGURE 5.11: SUMMARY OF SINTERED DENSITY AGAINST MILLING TIME FOR 6% COBALT ALLOYS
(INITIAL STAGES OF MILLING)



of 14.62 g/cc. The ratios of hexagonal to cubic phase in the initial cobalt powders for the annealed Hoboken and CF-10 were 0.77 and 0.22 respectively. A similar comparison for the 20% cobalt alloys, after four hours of vibratory milling, showed a density of 13.52 g/cc for the specimen prepared from the annealed Hoboken cobalt powder mixture, and a density of 13.39 g/cc for the specimen prepared from the HML - 201 cobalt powder, which had an initial hexagonal to cubic phase ratio of 0.23. Examination of the data in Figures 5.10 and 5.11 shows that the differences in shapes of the sintered density - milling time curves, for the batches made with different cobalt powders, do not show any relationship to the specific surface areas of the initial cobalt powders, whereas for a fixed milling time (less than 12 hours) the densities increase with increasing ratios of hexagonal to cubic allotropes present in the initial cobalt powders. Columns 5, 6, and 7 of Table V show the sintered densities of the pressed mixtures prepared with different cobalt powders after 4, 8 and 16 hours of vibratory milling for the 20%, 10% and 6% cobalt alloys. The value of S_g .min. (column 4 of Table V) is plotted against initial allotropic ratio of the cobalt powders in Figure 5.12. This figure shows clearly that as the hexagonal to cubic allotropic ratio is decreased, the minimum specific surface area of the hard metal powder required for achieving a minimum density is increased. The effect



becomes more evident for cobalt powders with an allotropic ratio of less than 0.50; for 10% cobalt alloys reducing the allotropic ratio from 0.70 to 0.45 increases the minimum specific surface area from 0.38 to 0.48 m²/g., whereas reducing the allotropic ratio from 0.45 to 0.22 increases the minimum specific surface area from 0.48 to 0.97 m²/g.

The data in Table II indicated that the standard deviations on a set of density values for a series of 4½ per cent cobalt specimens sintered at 1,450°C - 1,500°C (which is the normal range for this composition) were in the range 0.023 to 0.030 g/cc. In view of these figures, the differences in densities for the 6% cobalt alloys made with different cobalt powders, and milled for periods up to 12 hours suggest that the density values were significantly different from one another, and were not within the spread of values normally obtained on a set of specimens of the same composition sintered together. Thus the influence on sintered density, of the cobalt powders from different sources, is clearly evident in the results for the short vibratory milling periods; after 12 hours of milling, the densities were relatively insensitive to further vibratory milling, except for the overmilling effect referred to previously.

Comparison of the specific surface area values for the carbide powder (0.10 m²/g.) and the cobalt powders used (0.72 - 1.53 m²/g.) and examination of the hard metal powder replicas (shown

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Comparison of the specific surface area values for the carbide powder (0.10 m²/g.) and the cobalt powders used (0.72 - 1.53 m²/g.) and examination of the hard metal powder replicas (shown

in Figure 5.2) indicate that cobalt agglomeration must have occurred during the initial stages of vibratory milling; the replica photomicrographs showed that the carbide grains are beaten into the cobalt aggregates during the initial stages of milling.

An attempt was made to ascertain whether electron microscopy could be used to differentiate between the hard metal powders, made with different cobalt powders. However, it was felt that this technique was not suitable for determining these effects because of the wide variations in particle sizes and phase distributions observed in different parts of the same replica.

In Chapter 4, it was shown that the annealed Hoboken cobalt powder was considerably agglomerated in its initial condition, and that on milling Hoboken cobalt powder this required less milling before a state of maximum agglomeration (i.e. minimum specific surface area) was reached than either the CF-10 or CF-6 cobalt powders. It is suggested, therefore, that these differences in agglomeration tendencies of the initial cobalt powders influence the amount of vibratory milling, that must be carried out to obtain satisfactory densification on sintering the cobalt - carbide alloy powders. After more extensive milling periods, the cobalt powders with smaller initial tendencies for agglomeration on grinding, have agglomerated sufficiently to allow the carbide particles to be beaten into the cobalt aggregates.

Table V showed the minimum specific surface areas of the hard metal powder mixtures required to achieve the minimum density value for each batch; repeat milling tests indicated only slight variations in these values, for batches of the same constituents; namely 0.41 and 0.44 m²/g. for a 20% cobalt composition; 0.55 and 0.59 m²/g. for a 10% cobalt composition, and 0.69 and 0.70 m²/g. for a 6% cobalt composition.

These values indicate that no spurious effects were operative, and the minimum specific surface area values, using cobalt from a given source, did not overlap with the values obtained for the other batches using other cobalt powders.

The sintered 20%, 10% and 6% cobalt specimens were polished for the examination of microstructure. No free graphite (which lowers the density)⁽⁶⁸⁾ or eta phase (which raises the density provided the liquid phase sintering process has not been interfered with) were evident. Thus the density differences found for the milling periods up to twelve hours could not be ascribed to the presence of any additional phases.

Therefore, it is immediately apparent, from this investigation, that the hard metal powder batches made up with cobalt powders with an initially higher proportion of the hexagonal allotrope had to be milled for shorter periods (and the powder mixtures had lower specific surface areas) to yield satisfactory

densities on sintering.

Nothing is known about the effects on the mechanical properties, of sintered hard metal alloys, of cobalt powders from different sources. It has been reported⁽⁴³⁾ that the Vickers hardness of sintered compacts made from intensively ground powders is unaffected by the use of cobalt powders from different sources. Low hardness and low density after short milling times for cobalt - carbide alloys are due to porosity and local segregation of cobalt.⁽²⁾

Certain advantages have been reported⁽⁴³⁾ in the literature following the employment of very coarse cobalt metal powders (e.g. 100 - 200 μ) for making up hard metal mixtures. Electron microscope replica studies by these authors,⁽⁴³⁾ on intensively milled hard metal mixtures have shown that the differences between a hard metal powder made from a 100 μ cobalt powder and from a 15 μ powder are such that the powders are indistinguishable from one another. The main advantage noted⁽⁴³⁾ for the use of a coarse cobalt powder is that the oxygen content is lower; oxygen is said to have an adverse effect on the sintering of hard metal mixtures.⁽⁴³⁾ In this connection, therefore, it is of interest to note that irrespective of the amount of cobalt added, the Hoboken cobalt, which of all the cobalt powders used had the highest oxygen content, gave the second lowest minimum value of specific surface area for

the hard metal powders. This is evident in column 4 of Table V.

A decrease in the amount of the cubic phase of cobalt with increasing milling of tungsten carbide - cobalt hard metal mixtures has been previously reported,⁽⁴³⁾ the martensitic type of phase change in the cobalt occurring as a result of cold working. In industrial practice, it has been reported⁽⁴³⁾ that only hexagonal cobalt is found in vibratory milled powder mixtures, milled for very long periods. This could not be confirmed in this investigation, even using vibratory milling periods of up to 126 hours.

X-ray diffraction patterns similar to those of the cobalt powders (described in Chapter 4) were taken for the 20% and 10% hard metal powder mixtures, that had been milled for different times. The intensities of the (200) cubic and (10 $\bar{1}$ 1) hexagonal profiles were measured; this has been shown to be an absolute method for determining the proportion of the two cobalt phases present, as was discussed in Chapter 2. The change in the ratio of cubic to hexagonal phase with milling time is shown for the 20% and 10% cobalt batches in Figures 5.13 and 5.14 respectively. In some cases, particularly with powders vibratory milled for long periods, it was a little difficult to isolate the (10 $\bar{1}$ 1) hexagonal peak from the adjacent WC peak.

The precision of the diffractometer values of the ratio of cubic to hexagonal phases was checked on a

FIGURE 5.13: SUMMARISED QUANTITATIVE X RAY DATA FOR 20% COBALT POWDERS SHOWING THE DECREASE IN CUBIC TO HEXAGONAL ALLOTROPIC RATIO WITH MILLING TIME

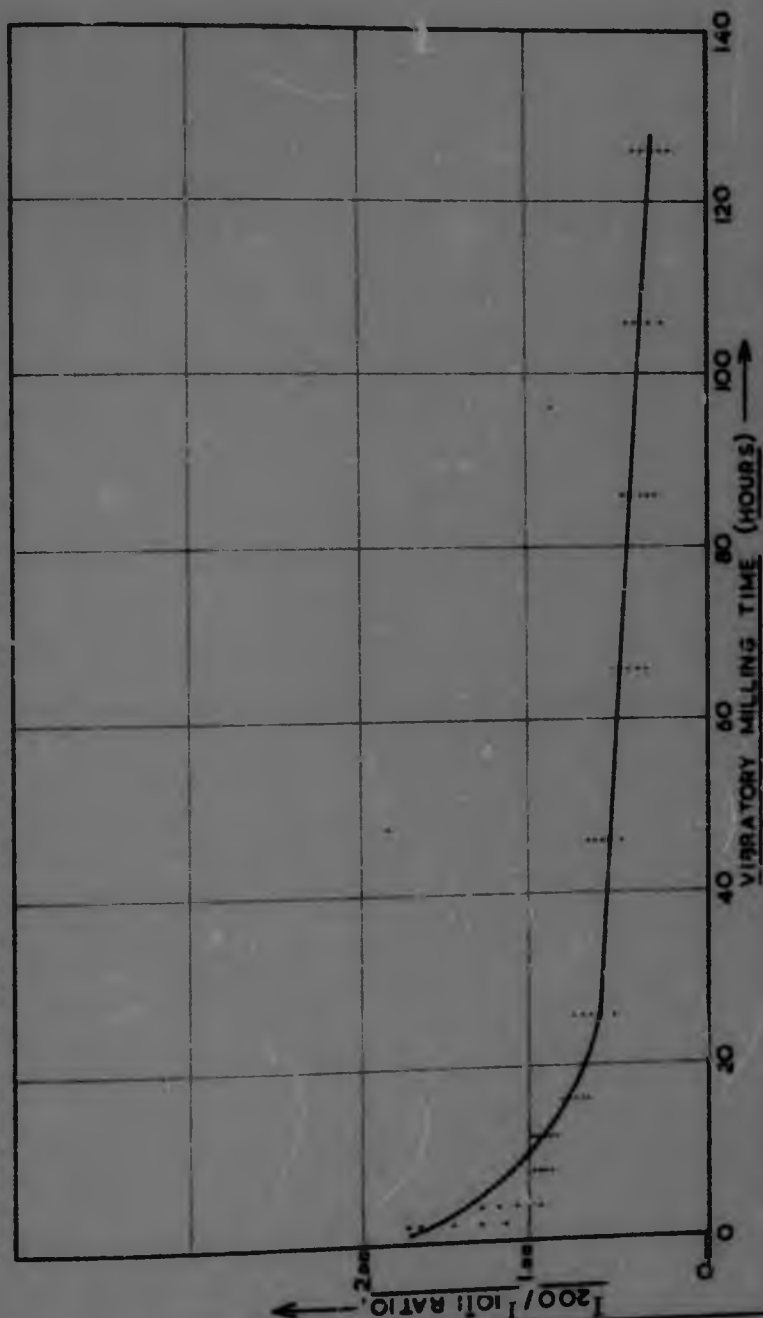
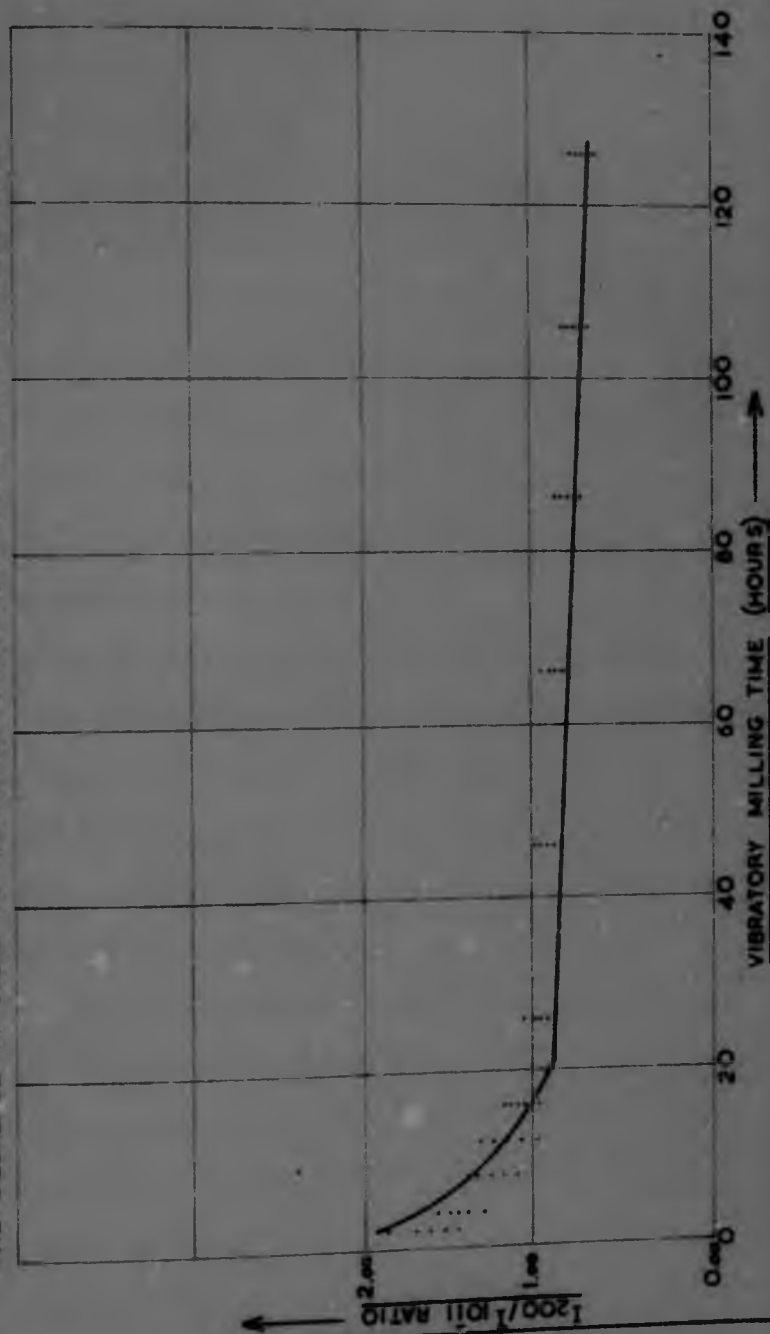


FIGURE 5.14: SUMMARISED QUANTITATIVE X RAY DATA FOR 10% COBALT POWDERS SHOWING THE DECREASE IN CUBIC TO HEXAGONAL ALLOTROPIC RATIO WITH MILLING TIME



hard metal powder which contained 20% cobalt, and which had been milled for four hours. On three repeat runs, the cubic to hexagonal phase ratio was found to be 0.96, 0.96 and 0.97. This powder was re-examined after a further 6 months had elapsed and the ratio was found to be 0.94.

No X-ray analyses were carried out on the 6% cobalt hard metal alloys; one diffraction pattern of this material showed that the cobalt peaks were so small compared with the WC peaks that they precluded the possibility of obtaining any meaningful results on the variation in allotropic ratio with milling time. However, the coercivity data showed substantially the same variations with milling time, as the 10% and 20% cobalt alloys.

5.3 Coercivity and Specific Surface Area Measurements.

In addition, the coercivities of hard metal powder pellets, pressed from powders milled for various times were measured on an Institut Forster Instrument. A strong dependence of coercivity on the compacting pressure was evident, as is shown in Table VI. The effect of compacting pressure on the coercivity of a hard metal powder compact must be due to the change from the cubic to the hexagonal phase of cobalt caused by the application of pressure. This was discussed in Chapter 4.

Various methods for preparing hard metal powders for coercivity measurement were studied to determine which yielded the most satisfactory results:

TABLE VI.

The variation in powder coercivity with
compacting pressure for a 10% cobalt fine
grained alloy

Compacting Pressure	Coercivity in Oe.
$\frac{1}{2}$ t.s.i.	196.4
$\frac{1}{2}$ t.s.i.	196.0
$\frac{1}{2}$ "	191.0
1 "	203.5
2 "	204.0
4 "	205.0
6 "	207.5
8 "	209.0
10 "	211.0
12 "	212.0
15 "	214.0
20 "	220.0

Note: The exact pressures could not be accurately controlled in the region up to 1 ton/in.².

- (1) Measurement of the coercivity of hard metal compacts pressed at 10 tons/in.².
- (2) Measurement of the coercivity of hard metal - Bakelite powder compacts prepared by intimate mixing of 5 g. hard metal powder with 5 g. Bakelite powder, followed by pressing the mixture into compacts at 10 tons/in.². This is similar to the technique used by Exner and Fischmeister.⁽⁵⁾
- (3) Measurement of the coercivity of hard metal powder - wax compacts made by adding the hard metal powder to molten paraffin wax, followed by cooling.

The relevant results are summarised in Table VII, where the coefficient of variation for the three methods is also shown. Method 1 is obviously the most satisfactory; the reasons for the large variation in coercivity of the powder-wax compositions may be due to oxidation, but oxidation has been found to have little effect on the coercivity of porous partially sintered hard metal compacts.⁽⁵⁷⁾

The precision of the specific surface area measurements, as determined on the Perkin Elmer Instrument was also checked by measuring the specific surface area of ten samples (obtained by coning and quartering) of the same hard metal powder. The results are given in Table VIII.

Two examples of the increase in coercivity and specific surface area with milling time are shown in

TABLE VII.

The dependence of powder coercivity on the
method of measurement.

Sample	Method of Mounting	Av. Coercivity for 10 pieces oersted	Coefficient of Variation (%)
A 6% cobalt alloy milled for 16 hours.	Bakelite	192.3	1.86
	Wax	183.0	4.50
	Pressed Powder	198.1	0.63
A 20% cobalt alloy milled for 66 hours.	Bakelite	220.4	2.19
	Wax	212.5	3.36
	Pressed Powder	224.3	0.76

TABLE VIII.

The Variation in Specific Surface Area on
10 samples of the same material.

This test was carried out on 10 samples of a 6% cobalt - carbide powder milled for four hours.

Sample Number	Specific Surface Area ($\text{m}^2/\text{g.}$)
1	0.49380
2	0.48766
3	0.48195
4	0.50829
5	0.48524
6	0.48473
7	0.49977
8	0.49783
9	0.48708
10	0.48983
Average	0.491648
Therefore, calculating the square of the differences from the mean, and evaluating the standard deviation yielded a value of 1.19% for the coefficient of variation.	

Figures 5.15 and 5.16 for a 20% and 10% cobalt alloy respectively. The increase in coercivity is due to reduced particle size of the cobalt, the introduction of stacking faults into the cobalt, and an increased proportion of the hexagonal phase (which has a higher crystalline magnetic anisotropy constant).

The coercivities of milled hard metal powder compacts are higher than those of milled cobalt powders; this has been ascribed by Exner and Fischmeister⁽²⁾ to be due to the inability of the cobalt surfaces to cold weld to each other in a hard metal powder mixture, whereas they can in a pure cobalt powder.

The close relation between the coercivity of the pressed powder pellets and the surface area of the hard metal powders is noteworthy. In a large attrition milling experiment carried out, involving approximately 100 samples of the same composition of hard metal, the coefficient of linear correlation between these two parameters was found to be 0.82.⁽⁵⁸⁾

5.4 Crushing Behaviour of Cobalt-tungsten carbide powder mixtures.

Various laws, or perhaps more correctly hypotheses, have been advanced to interpret the crushing and grinding of brittle materials. These have included:

- (a) Kick's Rule.
- (b) Rittinger's Rule.

FIGURE 5.15 VARIATION IN SPECIFIC SURFACE AREA AND COERCIVITY OF A 20% COBALT POWDER WITH MILLING TIME

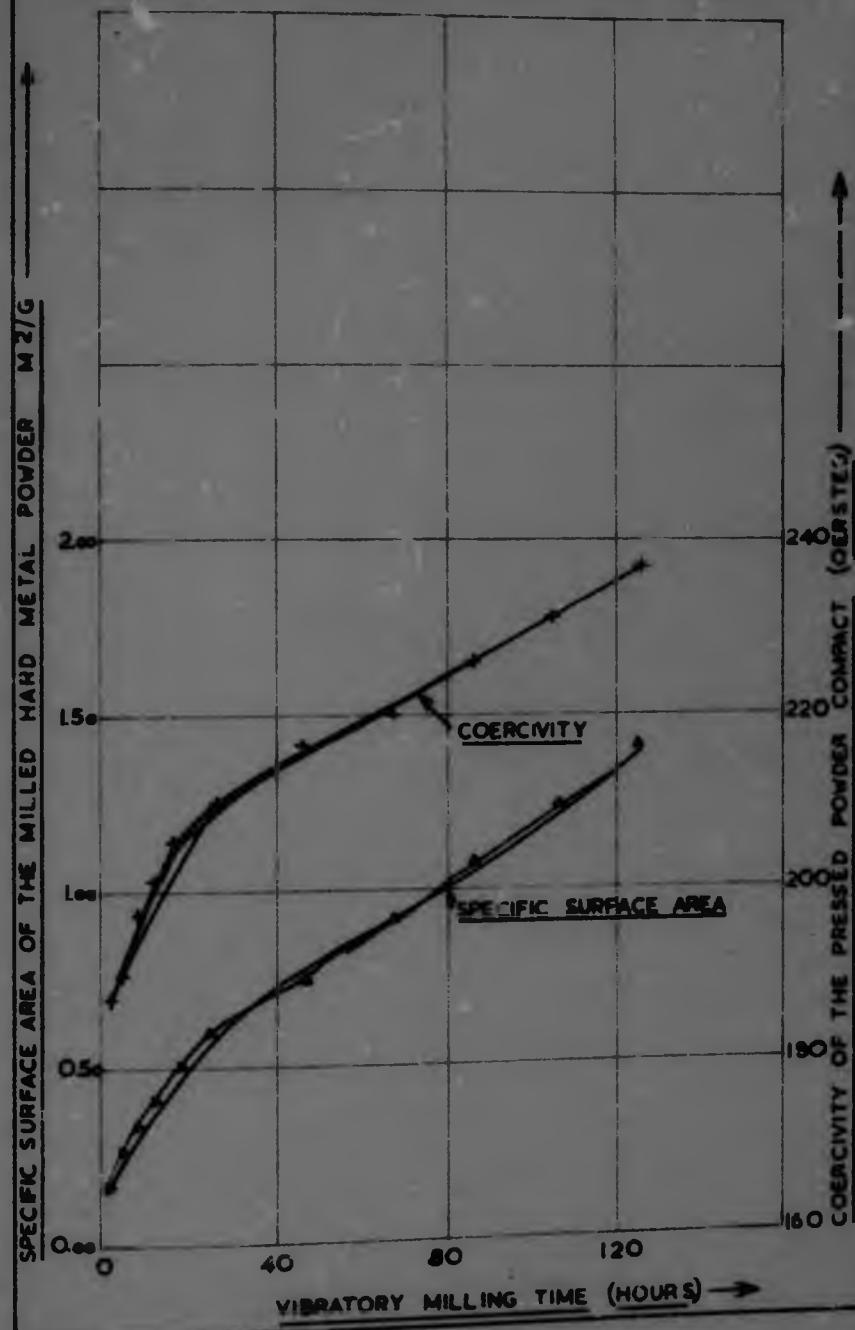
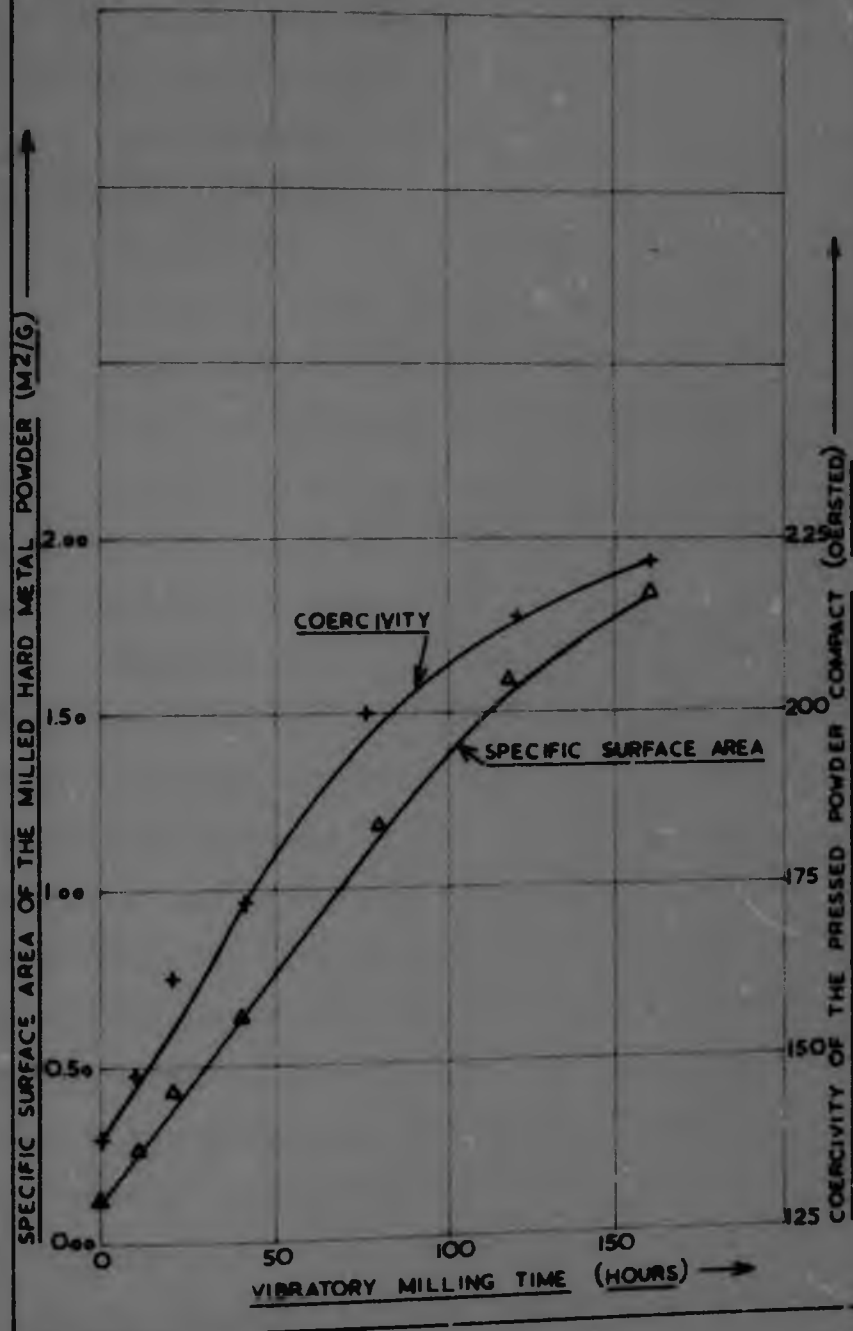


FIGURE 5.16: VARIATION IN SPECIFIC SURFACE AREA AND COERCIVITY OF A 10% COBALT POWDER WITH MILLING TIME



(c) Bond's Rule.

(d) Exner and Fischmeister's Rule. (59)

In their original form none of these rules contained a factor relating to the time of grinding, but attempts have been made to interpret time of grinding in the expressions of each of these formulae.

The expressions of the various hypotheses then have the following forms:

(a) Kick's Rule : $\log S - \log S_0 \sim t$

(b) Rittinger's Rule : $S - S_0 \sim t$

(c) Bond's Rule : $\sqrt{S} - \sqrt{S_0} \sim t$

(d) Exner and Fischmeister's Formula : $S^2 - S_0^2 \sim t$

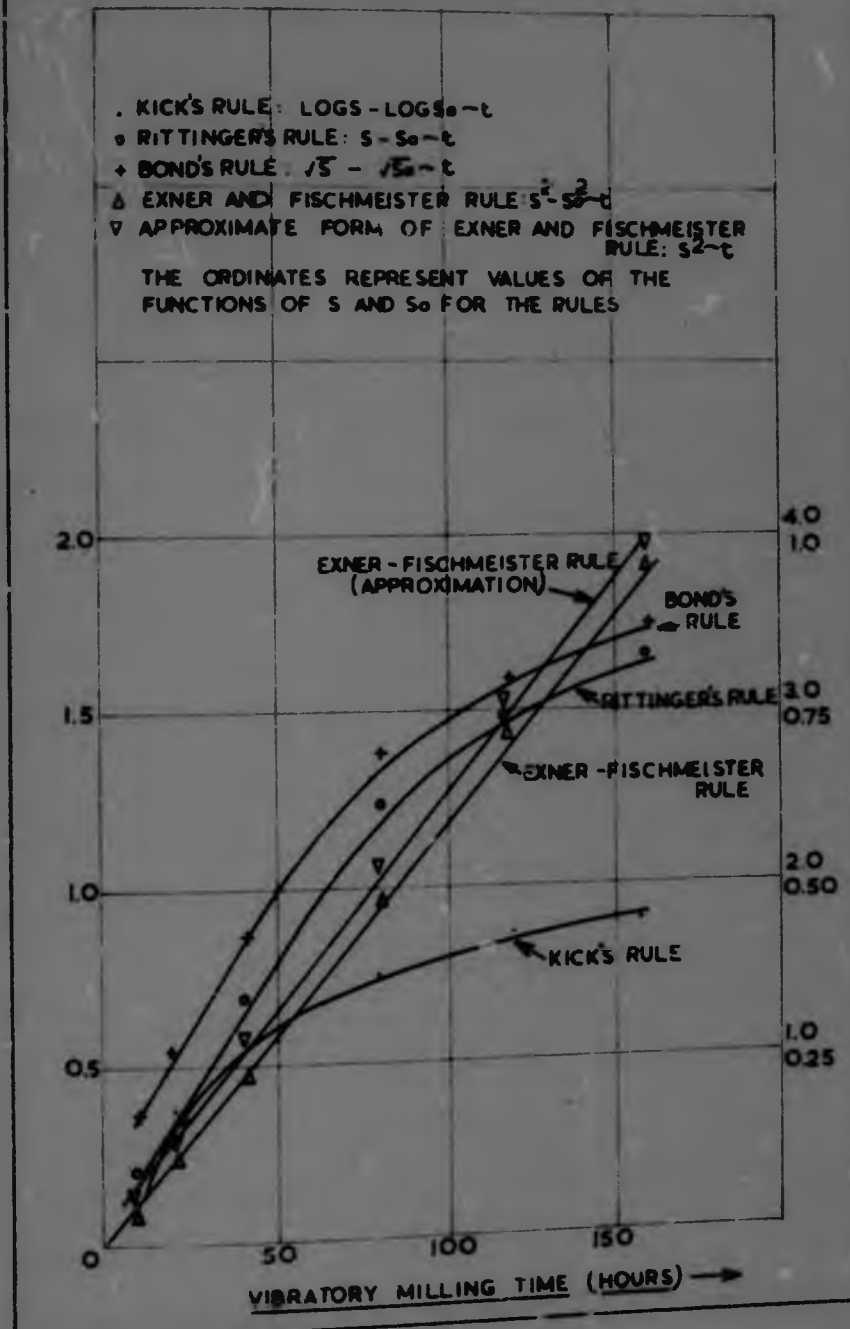
(In the above expressions S is the specific surface area of the powder after time t , and S_0 is the initial specific surface area).

Applying these hypotheses in the above forms to the surface area-milling time data for a 10% coarse grained alloy (carbide grain size $5 - 7 \mu$) gives the relationships shown in Figure 5.17. The linear correlation coefficient for the equation $S^2 - S_0^2 = kt$ was 0.97. The same hypothesis was applied to a 10% cobalt alloy containing fine ($2 - 3 \mu$) carbide; here the correlation coefficient was 0.96. The following values of the correlation coefficient (r) were obtained on 10% cobalt alloys containing mixed carbide powders.

(a) 10% cobalt + 1/3 by wt. of fine carbide + 2/3
by wt. of coarse carbide $r = 0.97$

(b) 10% cobalt + 1/3 by wt. of coarse carbide + 2/3
by wt. of fine carbide $r = 0.98$

FIGURE 5.7: FITTING OF SPECIFIC SURFACE AREA OF 10% COBALT POWDER TO VARIOUS CRUSHING RULES



The formula was applied to another batch of 4 mills using a cobalt powder from a different source, but with the same carbide mixtures as the above. The coefficients of linear correlation were 0.99, 0.96, 0.99 and 0.96 respectively. Apart from the crushing formula of Exner and Fischmeister, the other rules do not appear to have any applicability to the crushing of tungsten carbide-cobalt powders.

5.5 The significance of hexagonal cobalt in hard metal powders.

In 1952 Dawihl⁽⁶⁰⁾ suggested that it was possible that during milling of hard metal powders a diffusion of the hexagonal tungsten carbide into hexagonal cobalt might occur. In a subsequent paper⁽⁶¹⁾ he showed that the appearance of tungstic oxide on leaching a sintered hard metal compact in hydrochloric acid was due to the carbide present in solid solution in the cobalt phase. However, he recognised that some of this could be due to entrained oxygen associated with the milling process.

It is known that the oxygen associated with hard metal powder is not only present as physically adsorbed oxygen, but chemisorbed oxygen is also present in the powder. Scriggs⁽⁶²⁾ has shown that it is possible to isolate tungstic oxide from a hard metal powder by shaking the powder with ammonium hydroxide solution, followed by precipitation of the tungstic oxide. A similar result was obtained in this work,

as shown in Table IX, when using caustic soda for removing the WO_3 . This evidence shows conclusively that some of the oxygen is in chemisorbed form on the tungsten carbide grains; oxygen chemisorbed on tungsten powders at a low temperature is a well known phenomenon.

However, the leaching of hard metal powder slurries (removed directly from the mills and not exposed to air) with hydrochloric acid also results in the formation of tungstic oxide; special precautions were observed when carrying this out, to ensure that the powder was always covered with liquid and no oxidation occurred by direct heating. This results in the formation of a larger amount of WO_3 compared with that obtained on shaking with caustic soda. Although the amount of WO_3 isolated with hydrochloric acid increased with increasing milling time, the duplicate results of the technique used were not good, and there was no evidence to show that an increased amount of WO_3 resulted when using cobalt powders of higher hexagonal to cubic ratio.

The concepts of Dawihl on the preferential diffusion of the hexagonal tungsten carbide into the cobalt of similar lattice structure during sintering must be treated with some reserve in view of the findings of Giamei et al.⁽⁶³⁾ These authors have studied the equilibrium diagram of the cobalt rich end of the Co - WC system; their results are shown in Figure 5.18, and indicate that above $950^{\circ}C$

TABLE IX.

Isolation of WO_3 from Hard Metal Powders with
Caustic Soda.

Sample	Description of Sample	WO_3 (mg. per 10 g. sample) isolated with NaOH	Actual O_2 content %	Mg. WO_3 per 10 g. that could be produced assuming all the O_2 was present as WO_3
Tungsten Carbide *	Fine grained material 2-3 μ unmilled	43	0.09	48
Hard Metal Powder	Milled for 1 hour in attrition mill	32	0.20	106
"	Milled for 4 hours	35	0.27	142
"	Milled for 12 hours	67	0.40	211
"	Milled for 16 hours	89	0.53	280
"	Milled for 8 hours	73	0.33	174
"	Milled for 8 hours	61	0.23	121
"	Milled for 4 hours	57	0.23	121
"	Milled for 4 hours	36	0.24	132
"	Milled for 2 hours	50	0.29	153

* The hard metal powder samples were prepared by attrition milling of hard metal powder batches of 10% cobalt - composition for the times stated.

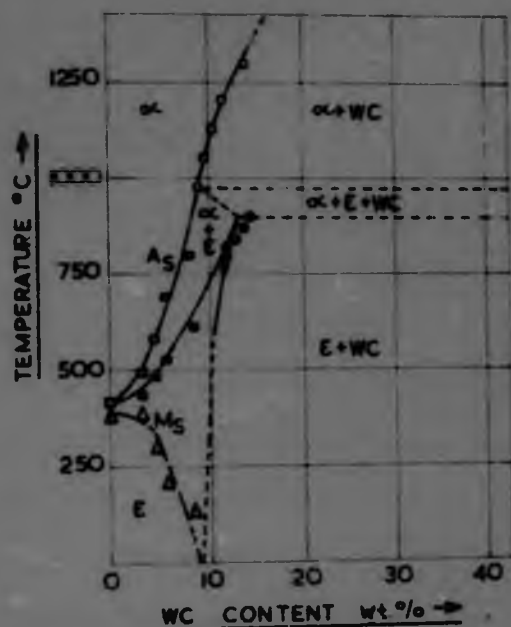


FIGURE 5.18:

COBALT RICH END OF
Co-W-C ISOPLETH SECTION FROM
Co-W-C TERNARY SYSTEM ILLUSTRATING
THE SOLID-STATE EQUILIBRIUM IN THE
Co-W-C SYSTEM.

□ $E' \rightarrow \alpha$ DILATOMETER ○ α SOLVUS X-RAY
■ $E \rightarrow \alpha$ DILATOMETER ○ E SOLVUS X-RAY
△ $\alpha \rightarrow E'$ DILATOMETER

cubic cobalt and WC are the stable phases.

5.6 Evidence for the importance of cobalt agglomeration.

Evidence that some agglomeration of the cobalt is beneficial for achieving satisfactory densification of hard metal alloys is provided by the following tests on hand mixed hard metal powders prepared in a mortar with a pestle, using cobalt powders which had been milled for different times.

The cobalt powder used had been milled in exactly the same way as that for which the results were given in 4.4 (Figure 4.4.) The alloy mixtures were made with the same 5 - 7 μ carbide powder. 10 g. compacts containing 10% cobalt were mixed by mortar and pestle for 30 minutes, followed by pressing into compacts at 10 tons/in.², and sintering in the same boat in hydrogen at 1,410°C. The physical properties of the sintered pieces are shown in Table X.

Maximum density with these hand mixed powders was achieved with the most agglomerated powder i.e. the one milled for 20 hours. It has been reported⁽¹⁶⁾ in the literature that the premilling of the cobalt offers no advantages to the sintering characteristics of hard metal alloys. However, the state of the cobalt after the premilling was not discussed.

5.7 Further evidence for the importance of hexagonal cobalt on the minimum specific surface area of cobalt - carbide powder mixtures and the use of cobalt powders from different sources.

In Section 4.4, various results on the crushing

TABLE X.

Summarised densities and magnetic properties for hand mixed 10% cobalt hard metal powders, pressed and sintered, prepared from the same carbide powder and cobalt milled for different times.

Milling Time for the Cobalt (hours)	Density g./cc.	Magnetic Saturation Units	Coercivity Oersted
0	13.62	178.5	66.8
5	13.78	181.5	72.0
10	14.20	184.3	76.6
20	14.43	185.9	80.0
30	14.38	177.4	88.0
50	14.34	182.3	84.0
70	14.28	178.2	87.0
90	14.25	181.9	79.2
110	14.16	176.5	84.5
130	14.05	174.2	92.4

of different batches of cobalt were presented, and it was shown that at some stage of the milling process, agglomeration occurred. Considerable agglomeration was already evident in the annealed materials.

The logical deduction from the previous work was that on mixing and milling cobalt and tungsten carbide powders, satisfactory densification of the sintered hard metal compacts is achieved after a shorter milling time when the cobalt is present predominantly in the hexagonal form. To confirm the superiority of hexagonal cobalt as compared with cubic cobalt, three batches (each containing 10% by weight of cobalt) were made up with the same tungsten carbide powder in 800 ml. stainless steel mills under 300 ml. acetone with 2 Kg. $\frac{1}{4}$ " hard metal balls as the grinding medium.

In each case vibratory milling was carried out for a total of 46 hours, samples being removed after 2, 4, 8, 12, 16, 26 and 46 hours. Specific surface area determinations and analyses were carried out on a small amount of the powder, and 8 g. compacts were pressed at 10 tons/in.² in a 0.475" diameter single acting die. These compacts were sintered, in the same boat, using a packing mixture of alumina and 0.5% carbon at 1,410°C.

The cobalt powders used were:

- (a) A fine pure hexagonal cobalt powder similar to that described in Chapter 4 with an initial specific surface area of 2.89 m²/g. This powder

showed no traces of the (200) cubic cobalt diffraction profile.

- (b) The CF-6 powder (with a hexagonal to cubic phase ratio of 0.38), the milling of which was described in Chapter 4.
- (c) A very coarse sintered cobalt powder consisting of hard aggregates prepared by the hydrogen reduction of black cobalt oxide at 800°C for four hours. This powder was completely cubic in structure, and had a specific surface area of $0.40 \text{ m}^2/\text{g}$.

The carbon and oxygen contents of the hard metal powders after various milling times are shown in Table XI, as also are the sintered compact properties. The increase in density with milling time, for these three batches, is shown in Figure 5.19.

It was shown in 4.4 that powder (a) on milling on its own, had a strong tendency to agglomerate, and exhibited a continuous decrease in specific surface area with milling time up to 90 hours. Powder (c) (similar to that described in Chapter 2.3.1 Figure 2.5) had an already sintered appearance, and consisted after reduction of hard lumps.

The magnetic saturation results for the sintered pellets (Table XI) show that the density results cannot be ascribed to gross variations in composition of the sintered carbide.

Distinct differences were evident in the photomicrographs of the CF-6 and the CF-6 annealed

FIGURE 5.19: INCREASE IN DENSITY OF SINTERED COMPACTS WITH MILLING TIME FOR BATCHES MADE WITH THE SAME CARBIDE POWDER AND COBALT POWDER FROM DIFFERENT SOURCES

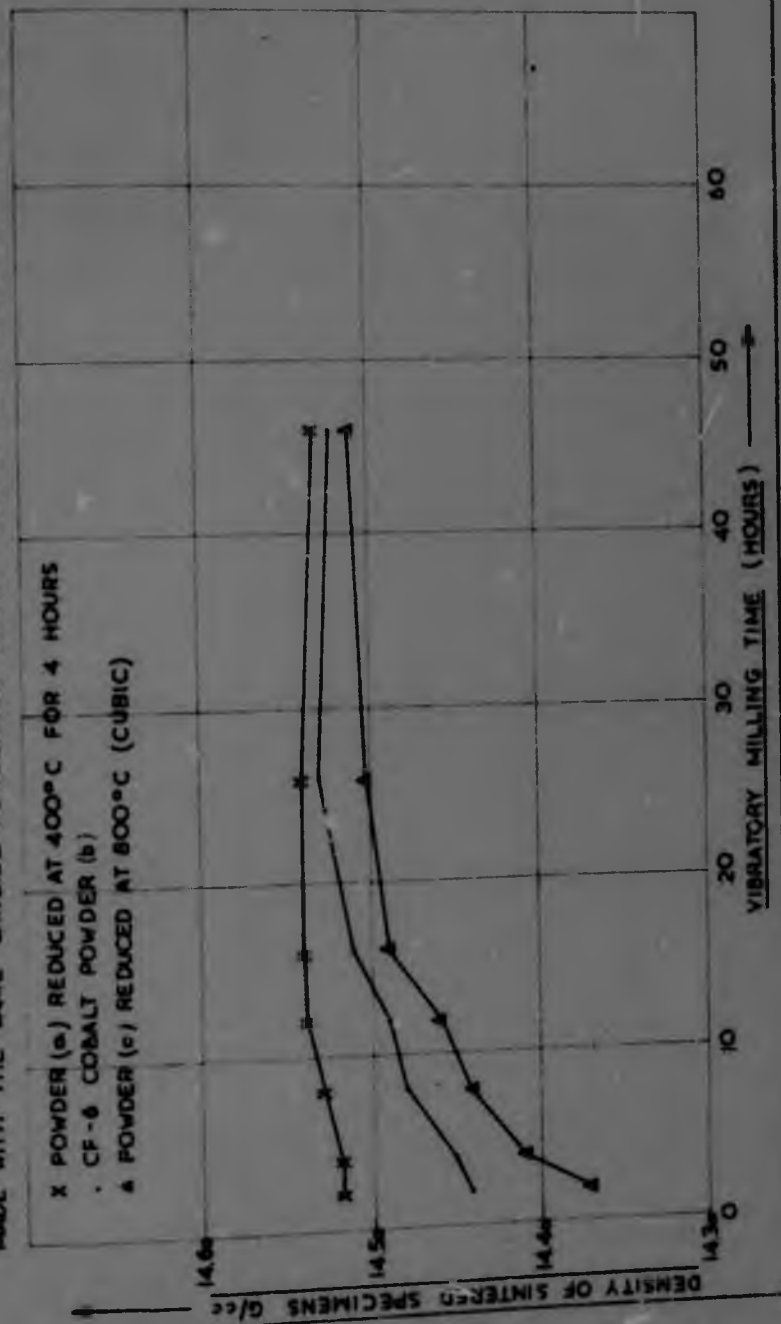


TABLE XI.

Summarised Properties of 10% Cobalt Hard Metal Batches
made using the same carbide powder, but using cobalt
powders from different sources.

Cobalt Powder Batch (See Text)	Milling Time (Hours)	Assay Total Carbon %	Assay Oxygen %	Properties of Sintered Specimens		
				Density g./cc.	Magnetic Saturation Units	Coercivity Oersted
Powder reduced at 400°C	2	5.56	0.10	14.52	180.8	70.0
	4	5.54	0.11	14.52	187.0	70.6
	8	5.57	0.13	14.53	179.0	78.3
	12	5.59	0.15	14.54	183.8	84.4
	16	5.58	0.19	14.54	183.9	86.2
	26	5.59	0.20	14.54	185.3	88.6
	46	5.60	0.30	14.53	189.1	103.5
CP-6 Cobalt Powder	2	5.58	0.09	14.44	182.8	64.4
	4	5.57	0.09	14.45	187.7	82.6
	8	5.59	0.11	14.48	188.0	85.0
	12	5.62	0.14	14.49	181.0	89.4
	16	5.56	0.16	14.51	181.3	90.6
	26	5.57	0.18	14.53	191.0	94.8
	46	5.60	0.20	14.52	189.8	100.0

TABLE XI. (Cont.)

Cobalt Powder Batch (See Text)	Milling Time (Hours)	Assay Total Carbon %	Assay Oxygen %	Properties of Sintered Specimens		
				Density g./cc.	Magnetic Saturation Units	Coercivity Oersted
Powder reduced at 800°C	2	5.58	0.04	14.37	179.1	65.4
	4	5.56	0.08	14.41	191.0	66.0
	8	5.60	0.09	14.44	183.1	71.5
	12	5.54	0.11	14.46	183.9	78.0
	16	5.58	0.11	14.49	187.2	84.5
	26	5.55	0.19	14.50	186.6	93.5
	46	5.60	0.18	14.51	185.3	98.0

powders shown in Chapter 4 (Figures 4.7 and 4.16 respectively) regarding their initial degree of agglomeration; likewise between the CF-6 and Hoboken cobalt powders. In each case, the more agglomerated cobalt powder in its initial condition required less milling when carbide was present to achieve a satisfactory density of the sintered cobalt - carbide compact.

It is clear that predominantly hexagonal cobalt powders are either considerably agglomerated in their initial condition, or have a strong tendency to agglomerate as milling proceeds.

The sintering of cobalt metal powder compacts has been previously studied,⁽⁶⁸⁾ but the initial phases present in the powder have not been considered, and from a study of the temperature shrinkage relations, the kinetics and activation energies have been evaluated.

5.8 Conclusions:

- (1) It has been shown that hard metal powder mixtures prepared from cobalt powders containing an initially higher proportion of the hexagonal phase have to be milled for less time to achieve satisfactory sintered densities than do hard metal mixtures prepared from a predominantly cubic cobalt powder.
- (2) It was found that electron microscopy was not a satisfactory technique for explaining differences in sintering reactivity of different hard metal powders after closely spaced milling intervals.
- (3) The importance of cobalt agglomeration on the sintered density of hard metal alloys has been shown.

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CHAPTER 6.

The Relations between hard metal powder properties and sintered compact properties

6.1 Introduction

In the previous chapter, it was shown that the use of cobalt powders from different sources exerted an influence on sintered alloy densities, obtained after various milling intervals. Several other factors which influence the sintered properties were briefly mentioned, namely, the carbon content of the powder, the oxygen content of the powder and the grainsize of the carbide particles. Certain of these powder characteristics are influenced by the milling time, e.g. oxygen content and grainsize. In addition, it has recently been found⁽¹⁾ that certain added chemical impurities can influence the physiomechanical properties of sintered hard metal alloys.

The aim of the work described in this Chapter was to attempt to relate all the known chemical and physical properties of hard metal powders to the physical properties of the sintered compacts, prepared from the various powders. Simple linear correlation analysis has been used for relating the powder properties to the sintered compact properties.

6.2 Influences of powder properties on sintered compact properties previously reported.

A number of qualitative and quantitative influences of various powder properties on the properties

of the sintered compacts have been previously reported in the literature. The following summarises the important findings:

6.2.1 Oxygen Content of the Powder.

The cobalt and carbide constituents used in making up hard metal compacts all contain oxygen; the amount, in general, depending on the grainsize and previous storage conditions used for the powder.

Excessive oxygen in the powder or presintered compact may result in a "zoned" sintered product.⁽²⁾ Lower sintering reactivity has also been ascribed to excessive oxygen in the powder.⁽¹²⁾ However, the exact effects of oxygen on the properties of sintered alloys have never been quantitatively explained.

As noted in Chapter 5, some of the oxygen associated with the carbide may be in a chemisorbed form on the particle surfaces. Oxygen content of the powders naturally increases with the milling time but this varies considerably.

The adverse influence of oxygen in the compacts is very noticeable when no reducing gas is used during sintering,⁽³⁾ (i.e. in vacuum sintering) for the oxygen in the compact reacts with the carbide thus reducing the overall carbon level.

6.2.2 Carbon Content.

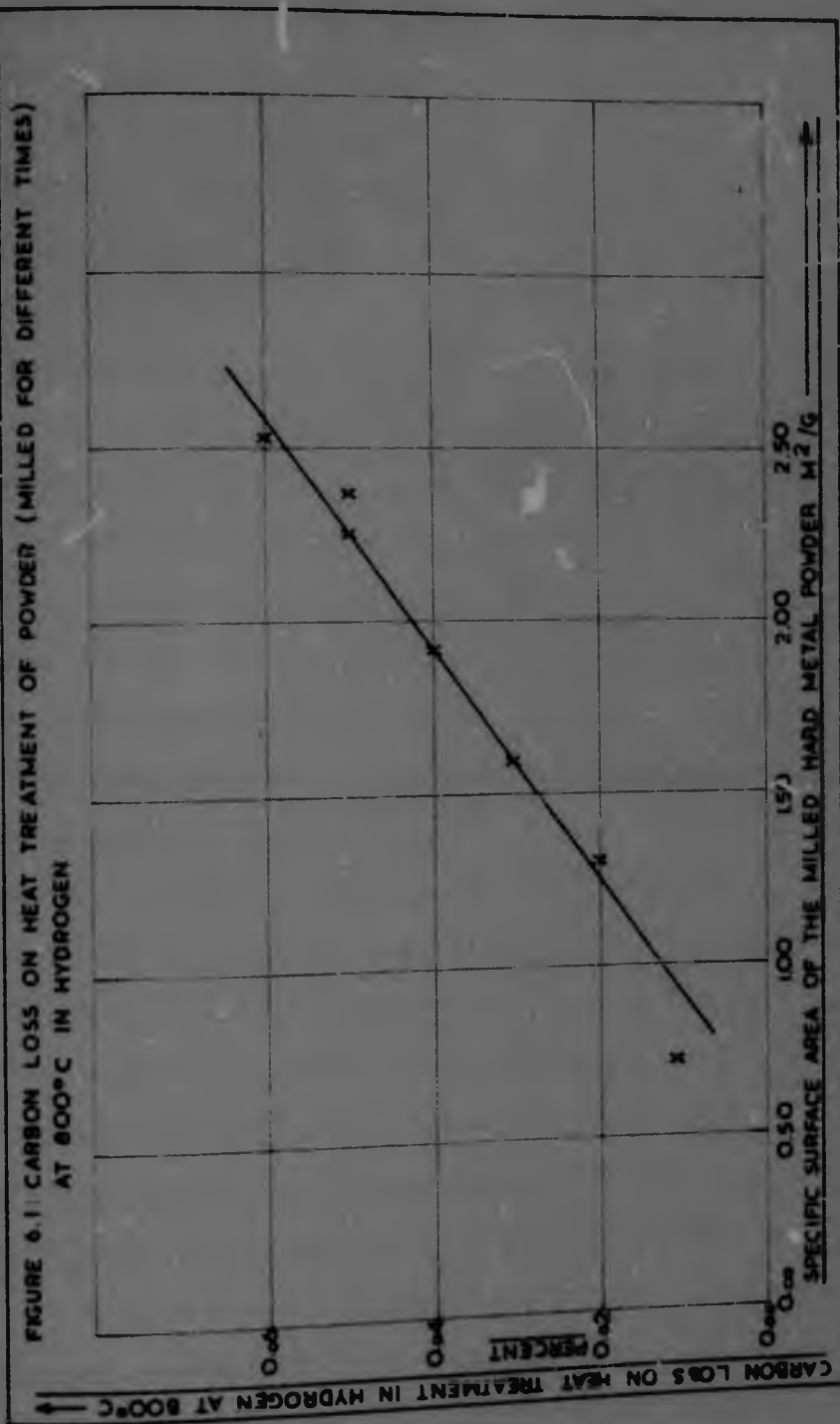
Reference was made in Chapter 5 to the narrow two phase WC + Co region in the W - C - Co diagram. The equivalent total carbon range for a two phase hard

metal structure has been shown⁽⁴⁾ to lie between 6.04% and 6.22% for a given cobalt content. However, alteration in carbon content may occur in the processing steps prior to sintering, and during the actual sintering process itself, whether this is carried out in hydrogen or vacuum. The degree of milling may also affect the carbon loss on subsequent heat treatment as shown in Figure 6.1. In this case a series of 5% cobalt-fine-grained alloy samples were removed from a mill after various milling times up to a total of 100 hours, and were dried under vacuum; 10 g. samples were pressed at 10 tons/in.² in a 0.475" diameter die, the pressed pellets being then heated in hydrogen at 800°C. Heating and cooling rates of 200°/hour were used with one hour on temperature at 800°C. The preheated compacts were crushed and assayed. Figure 6.1 shows that a good correlation between carbon loss and specific surface area of the powder was obtained. The decarburising influence of hydrogen on heating hard metal powders is well known, more especially if there is any water vapour in the hydrogen.⁽⁵⁾

6.2.3 Carbide Particle Size Distribution.

Exner and Fischmeister⁽⁶⁾ have shown that the specific surface area of the carbide particles rather than the size distribution determines the shrinkage speed during sintering of a cobalt - carbide compact. The specific surface area of the

FIGURE 6.1 CARBON LOSS ON HEAT TREATMENT OF POWDER (MILLED FOR DIFFERENT TIMES)
AT 800°C IN HYDROGEN



carbide particles is obtained after dissolution of the cobalt in the hard metal powder in hydrochloric acid. Polarographic techniques have been used by Kubota et al.⁽⁷⁾ to show that tungsten carbide powder is hardly attacked by 9 N HCl.

Of all the methods of characterising particle sizes, measurement of specific surface area has been considered⁽⁸⁾ most satisfactory for sintering studies.

6.2.4 Properties of the Tungsten Carbide Powders.

In general tungsten carbide powders may be characterised by grain size, grain size distribution, shape, purity and stoichiometric composition. However, these properties are not altogether satisfactory, and are insufficient completely to describe the sintering reactivity.⁽⁹⁾ The composition of the individual grains is also of importance, and in tungsten carbide grains larger than 4 μ , sometimes a centre or core of W_2C is present. This phenomenon has been found in powders from many different sources. A method has been evolved whereby these differences may be studied.⁽⁹⁾ As discussed in Chapter 5, stress in the powder particles should also be considered.

6.3 Correlations of hard metal powder compact properties and those of the sintered compacts.

It is a general characteristic of powder metallurgical processes, that the properties of the powdered raw materials are not all changed during the sintering process to the same extent as happens in a

conventional fusion process. However, it has been generally accepted⁽¹⁰⁾ that no physical model can explain the sintering behaviour of hard metal alloys, and explain differences in sintering behaviour between different batches. This situation exists because of the large number of variables involved in their preparation; one important aspect of variability, - the use of cobalt powders from different sources having been discussed in the previous chapter.

Several workers have searched for some correlation between properties of the milled powders and those of the sintered alloys. These correlations have been re-investigated here, and an attempt has been made to relate the known properties of hard metal powders to those of the sintered alloys.

6.3.1 Correlations previously reported.

Exner, Fischmeister and Lindelof⁽¹⁰⁾ tested four carbide samples differing in powder specific surface area, but of the same chemical composition, pressed and sintered under the same standard conditions. The sintered coercivities of the compacts were measured, and good correlation was obtained between the specific surface area of the powder (measured with a variety of techniques), and the sintered coercivity. However, this test was concerned with only one variable of the powder, ignoring the others, which may be influenced considerably by the processing conditions.

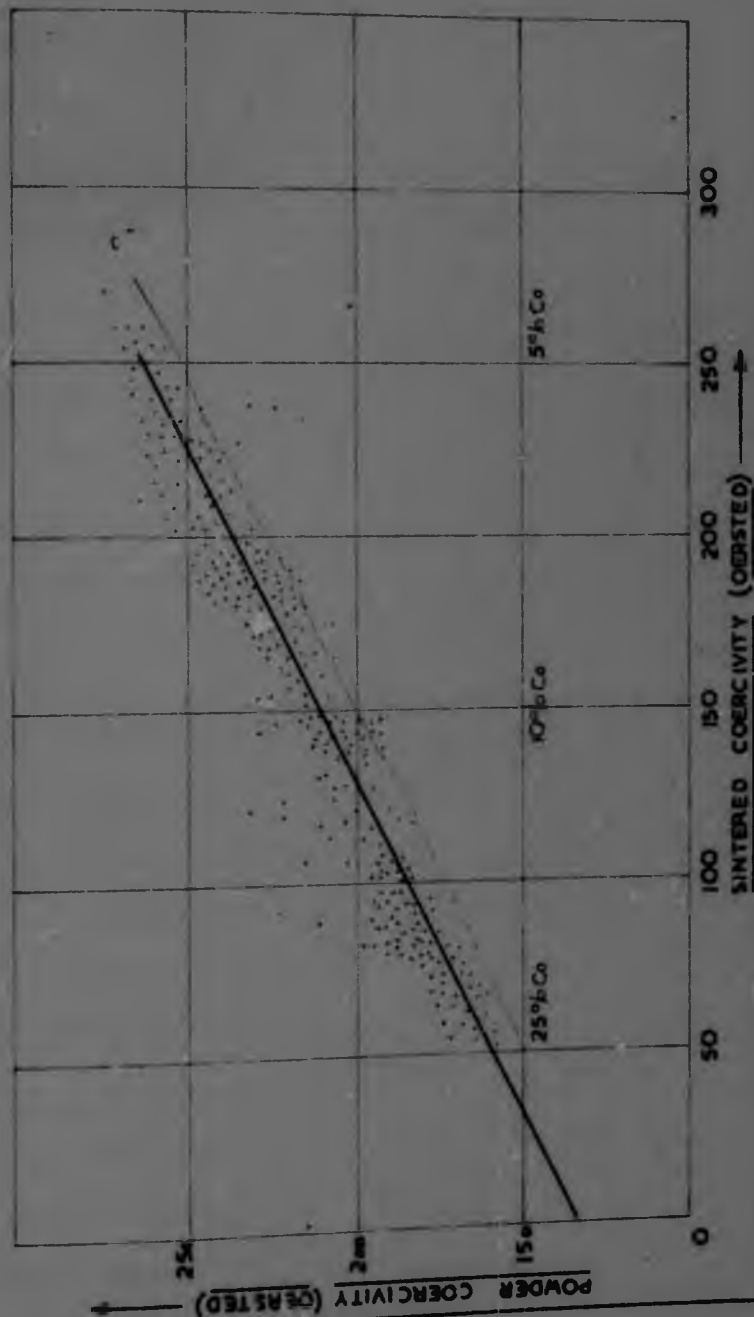
An attempt at correlation between coercivity of the powder (which was shown⁽¹¹⁾ to be correlated

with the specific surface area of the powder) and the coercivity of the sintered compacts has been made in this investigation for various commercial hard metal alloys. These ranged from 25% cobalt coarse grained compacts to 5% cobalt fine-grained compacts, containing eta phase. The results are shown in Figure 6.2. Although the overall correlation coefficient was computed to be 0.93, considerable scatter within groups of material is evident. This is probably because a large number of processing variables have been ignored, and also different sintering treatments have been used. However, besides being the only method available for the development of a model for hard metal compacts, it is of vital importance to know more about the relations between powder and sintered properties, so that alloys may possibly be tailored to specific applications.

Correlations between specific surface area of the leached carbide, and the specific surface of the carbide phase in the sintered structure have also been considered by Exner and Fischmeister.⁽¹²⁾ In this case good correlation was obtained between these factors.

These authors have also derived⁽¹³⁾ mathematical relationships between the grain size of the carbide particles, and the carbide grain size of the sintered product, assuming that the carbide grain sizes in all hard metal alloys follow a log normal distribution. Substantial deviations from log normal distributions have, however, been reported by other workers,⁽¹⁴⁾ subsequent

FIGURE 6.2. RELATION OF POWDER COERCIVITY TO SINTERED COERCIVITY FOR COMMERCIAL HARD METAL ALLOYS CONTAINING 5 AND 25% COBALT



to the work of Exner and Fischmeister.

6.4 Experimental work considering correlations between powder properties and sintered material properties.

In view of the large number of properties involved, it was decided to consider the interrelations between all the powder properties and those of the sintered products, viz.,

<u>Powders and Green Compacts.</u>	<u>Sintered Compacts</u>
Specific surface area	Density
Coercivity	Magnetic Saturation
Total Carbon	Coercivity
Free Carbon	Hardness
Oxygen	Crack Length
Pressed Density	Carbide Specific Surface
Magn Cobalt Content	Carbide grain size
Leached Carbide Surface Area	

For 6 Kg. charges of material were made up of
Leached Carbide Surface Area

For 6 Kg. charges of material were made up of
the following compositions and ground in vibratory mills:

- (i) A coarse grained carbide powder (5 - 7 μ):
Total Carbon 6.15%, Oxygen 0.03%
Specific Surface Area 0.11 m²/g.
- (ii) A fine grained carbide powder (2 - 3 μ):
Total Carbon 6.11%, Oxygen 0.11%
Specific Surface Area 0.42 m²/g.
- (iii) 1/3 by weight of the coarse carbide and 2/3
by weight of the fine carbide.

(iv) $1/3$ by weight of the fine carbide and $2/3$ by weight of the coarse carbide.

(v - (viii) were of the same composition as (i) - (iv).

Hoboken cobalt powder was used for batches (i) - (iv) and CF-6 powder in batches (v) - (viii). The properties of these powders are given in Table V of Chapter 5.

All eight batches contained 10% by weight of cobalt.

The batches were vibratory milled under 3 litres of acetone for 10, 20, 40, 80, 120 and 160 hours, exactly as described in Chapter 5. Four 20 g. scoop samples were removed from each mill after each of the stated milling times, and from each of these samples a pellet of 12 g. was pressed at 10 tons/in.² in a 0.475" diameter die. 2 g. of each sample was reserved for leaching with hydrochloric acid to remove the cobalt, so that particle size measurements could be carried out on the carbide particles. 6 g. of the samples were used for specific surface area measurements and for assay.

Hand mixed compositions were also prepared by mixing 100 g. quantities of compositions (i) - (viii) in a mortar with a pestle for 30 minutes.

One compact from each set of samples was sintered at 1,370°C in an alumina - (0.5%) - carbon mixture in a hydrogen atmosphere furnace with a 30 minute feed rate.

Sintering was carried out in a train of three boats on the same day. The dewpoint from the exit gases from the furnace was measured at half hourly intervals during the run, and varied between -17°C and -21°C .

Two similar runs were carried out on the remaining compacts, with the furnace set at $1,480^{\circ}\text{C}$; on one of these runs the dew point varied between -2° and -6°C . The series at $1,480^{\circ}$ was therefore repeated, when the dew point varied between -16° and -19°C .

The importance of dew point of the exit gases has been discussed in several investigations;⁽¹⁹⁾ the importance of dry gases has been emphasised and is known qualitatively, but the quantitative significance of moisture in sintering gases has never been properly explained.

The sintered specimens, after their properties had been measured, were mounted with Araldite on a steel plate for rough grinding, which was carried out with a silicon carbide wheel on a Jones and Shipman machine, removing $0.25\text{C}''$, from the ends of each of the specimens. The specimens were then ground for 30 minutes with a resin bonded 400 mesh diamond wheel; followed by 5 minutes polishing with $8 - 15 \mu$ diamond powder, and five minutes with $0 - 2 \mu$ powder.

Specimen preparation is of extreme importance for reproducible measurements of crack length (around Vickers diamond pyramid indentations), which are said to be a measure of the toughness of the alloy. Palmqvist⁽¹⁵⁾

and others^{(16), (17)} have discussed the theory of these measurements. Over a wide range of cobalt contents, it has been found⁽¹⁸⁾ that crack length can be correlated with magnetic properties but within the same composition much scatter is evident. Also there is some doubt as to whether crack length is related to toughness (measured by transverse rupture strength) of the alloys.⁽¹⁸⁾ This characteristic feature of sintered compacts has recently received considerable attention, but its full significance has not been properly assessed; the measurement of crack length around Vickers hardness indentations was only measured here as a matter of interest, to see how it correlated with the other physical properties.

Five indentations were made on each specimen using a 30 Fg. load with a Vickers diamond pyramid indenter with a 136° angle. The cracks emanating from these indentations were measured on an optical microscope at 500 X magnification, using the graticule to estimate the length of the cracks. The average crack length per indentation was calculated for each specimen.

Quantitative metallography was carried out on each specimen, using the techniques proposed by Exner and Fischmeister.⁽²³⁾

All the results are presented in tabular form in Tables I - VIII for the individual hard metal batches. (An explanation of the method of presentation of the data is also given).

TABLE I - VIII EXPLANATION OF CODED DATA

COLUMN NUMBER	DATA RECORDED	UNITS	POSITION OF DECIMAL POINT	EXAMPLE	NOTES								
1	SINTERING CODE	—	—	<table><tr><td>1</td><td>0</td></tr></table>	1	0	0 = SPECIMEN SINTERED AT 1370°C 1 = SPECIMEN SINTERED AT 1480°C (HIGH DEW POINT OF EXIT GASES) 2 = SPECIMEN SINTERED AT 1480°C (LOW DEW POINT OF EXIT GASES) SYMBOL = C						
1	0												
2-4	MILLING TIME	HOURS	NONE	<table><tr><td>2</td><td>3</td><td>4</td></tr><tr><td>1</td><td>2</td><td>0</td></tr></table>	2	3	4	1	2	0	= 120 HOURS OF MILLING SYMBOL = MT.		
2	3	4											
1	2	0											
5-7	SPECIFIC SURFACE AREA OF MILLED H.M. POWDER	M ² /G	BETWEEN COLUMNS 5 AND 6	<table><tr><td>5</td><td>6</td><td>7</td></tr><tr><td>0</td><td>4</td><td>1</td></tr></table>	5	6	7	0	4	1	= 0.41 M ² /G SYMBOL = S _S		
5	6	7											
0	4	1											
8-11	POWDER COERCIVITY	OERSTED	BETWEEN COLUMNS 10 AND 11	<table><tr><td>8</td><td>9</td><td>10</td><td>11</td></tr><tr><td>1</td><td>3</td><td>0</td><td>0</td></tr></table>	8	9	10	11	1	3	0	0	= 130.0 OERSTED SYMBOL = (H _c) _i
8	9	10	11										
1	3	0	0										
12-14	TOTAL CARBON CONTENT OF MILLED H.M. POWDER	PERCENT	BETWEEN COLUMNS 12 AND 13	<table><tr><td>12</td><td>13</td><td>14</td></tr><tr><td>5</td><td>5</td><td>0</td></tr></table>	12	13	14	5	5	0	= 5.50% CARBON SYMBOL = TC		
12	13	14											
5	5	0											
15, 16	OXYGEN CONTENT OF MILLED H.M. POWDER	PERCENT	BEFORE COLUMN 15	<table><tr><td>15</td><td>16</td></tr><tr><td>0</td><td>4</td></tr></table>	15	16	0	4	= 0.04% OXYGEN SYMBOL = O ₂				
15	16												
0	4												
17, 18	FREE CARBON CONTENT OF MILLED H.M. POWDER	PERCENT	BEFORE COLUMN 17	<table><tr><td>17</td><td>18</td></tr><tr><td>0</td><td>9</td></tr></table>	17	18	0	9	= 0.09% FREE CARBON SYMBOL = FC				
17	18												
0	9												
19-22	COBALT CONTENT OF MILLED POWDER	PERCENT	BETWEEN COLUMNS 20 AND 21	<table><tr><td>19</td><td>20</td><td>21</td><td>22</td></tr><tr><td>0</td><td>9</td><td>9</td><td>7</td></tr></table>	19	20	21	22	0	9	9	7	= 9.97% COBALT SYMBOL = Co
19	20	21	22										
0	9	9	7										

TABLE I - VIII EXPLANATION OF CODED DATA (CONTINUED)

COLUMN NUMBER	DATA RECORDED	UNITS	POSITION OF DECIMAL POINT	EXAMPLE	NOTES								
23-25	SPECIFIC SURFACE AREA OF LEACHED CARBIDE	M ² /G	BETWEEN COLUMNS 23 AND 24	<table><tr><td>23</td><td>24</td><td>25</td></tr><tr><td>1</td><td>0</td><td>2</td></tr></table>	23	24	25	1	0	2	= 102 M ² /G SYMBOL = S ₅ LG.		
23	24	25											
1	0	2											
26-28	DENSITY OF PRESSED COMPACT	G/cc	BETWEEN COLUMNS 26 AND 27	<table><tr><td>26</td><td>27</td><td>28</td></tr><tr><td>8</td><td>1</td><td>2</td></tr></table>	26	27	28	8	1	2	= 812 G/cc. SYMBOL = (P)		
26	27	28											
8	1	2											
29-32	MAGNETIC SATURATION OF PRESSED COMPACT	UNITS	BETWEEN COLUMNS 31 AND 32	<table><tr><td>29</td><td>30</td><td>31</td><td>32</td></tr><tr><td>1</td><td>9</td><td>4</td><td>0</td></tr></table>	29	30	31	32	1	9	4	0	= 194.0 UNITS SYMBOL = (4 π σ)
29	30	31	32										
1	9	4	0										
33-36	DENSITY OF SINTERED COMPACT	G/cc	BETWEEN COLUMNS 34 AND 35	<table><tr><td>33</td><td>34</td><td>35</td><td>36</td></tr><tr><td>1</td><td>4</td><td>4</td><td>8</td></tr></table>	33	34	35	36	1	4	4	8	= 14.48 G/cc. SYMBOL = ρ
33	34	35	36										
1	4	4	8										
37-40	MAGNETIC SATURATION OF SINTERED COMPACT	UNITS	BETWEEN COLUMNS 39 AND 40	<table><tr><td>37</td><td>38</td><td>39</td><td>40</td></tr><tr><td>1</td><td>7</td><td>9</td><td>3</td></tr></table>	37	38	39	40	1	7	9	3	= 178.3 UNITS SYMBOL = 4 π σ
37	38	39	40										
1	7	9	3										
41-44	COERCIVITY OF SINTERED COMPACT	OERSTED	BETWEEN COLUMNS 43 AND 44	<table><tr><td>41</td><td>42</td><td>43</td><td>44</td></tr><tr><td>0</td><td>7</td><td>7</td><td>8</td></tr></table>	41	42	43	44	0	7	7	8	= 778 OERSTED SYMBOL = H _c /2
41	42	43	44										
0	7	7	8										
45-48	VICKERS HARDNESS OF SINTERED COMPACT	KG/MM ²	NOTE	<table><tr><td>45</td><td>46</td><td>47</td><td>48</td></tr><tr><td>1</td><td>2</td><td>5</td><td>0</td></tr></table>	45	46	47	48	1	2	5	0	= 1250 KG/MM ² SYMBOL = VPN
45	46	47	48										
1	2	5	0										
49-51	AVERAGE CRACK LENGTH AROUND A VICKERS HARDNESS INDENTATION	GRATICULE UNITS AT 500X ON AN OPTICAL MICROSCOPE	BETWEEN COLUMNS 50 AND 51	<table><tr><td>49</td><td>50</td><td>51</td></tr><tr><td>1</td><td>2</td><td>7</td></tr></table>	49	50	51	1	2	7	127 GRATICULE UNITS SYMBOL = c		
49	50	51											
1	2	7											

TABLE I - VIII EXPLANATION OF CODED DATA (CONTINUED)

COLUMN NUMBER	DATA RECORDED	UNITS	POSITION OF DECIMAL POINT	EXAMPLE	NOTES						
52-54	SPECIFIC SURFACE OF CARBIDE IN SINTERED STRUCTURE	M ² /G	BEFORE COLUMN 52	<table><tr><td>53</td><td>54</td></tr><tr><td>0</td><td>6</td></tr><tr><td>6</td><td>6</td></tr></table>	53	54	0	6	6	6	$\approx 0.066 \text{ M}^2/\text{G}$ SYMBOL $\approx S_{5WC}$
53	54										
0	6										
6	6										
55-57	AVERAGE WC PHASE GRAIN SIZE IN SINTERED STRUCTURE	MICRONS	BETWEEN COLUMNS 55 AND 56	<table><tr><td>55</td><td>56</td><td>57</td></tr><tr><td>4</td><td>2</td><td>7</td></tr></table>	55	56	57	4	2	7	$\approx 4.27 \mu$ SYMBOL $\approx d_{WC \mu}$
55	56	57									
4	2	7									
58-59	STANDARD DEVIATION ON d_{WC}	MICRONS	BEFORE COLUMN 58	<table><tr><td>58</td><td>59</td></tr><tr><td>5</td><td>9</td></tr></table>	58	59	5	9	$\approx 0.59 \mu$ SYMBOL $\approx \sigma_{dWC \mu}$		
58	59										
5	9										
60-62	SPECIFIC SURFACE OF COBALT PHASE IN SINTERED STRUCTURE	M ² /G	BEFORE COLUMN 60	<table><tr><td>60</td><td>61</td><td>62</td></tr><tr><td>3</td><td>7</td><td>2</td></tr></table>	60	61	62	3	7	2	$\approx 0.372 \text{ M}^2/\text{G}$ SYMBOL $\approx S_{5Co}$
60	61	62									
3	7	2									

X = DATA NOT MEASURED

X = DATA NOT MEASURED

TABLE 1 : SUMMARISED DATA FOR BATCH (1)

HARC METAL POWDER PROPERTIES										PROPERTIES OF THE SINTERED COMPACTS									
LEACHED CARBIDE										PRESSED COMPACT									
C	MT	SS	(Hc) ₁	TC	O ₂	FC	Co	S ₅ LC	(ρ)	(4T _σ)	ρ	4T _σ	(Hc) ₂	VPN	ΣL	S _{5mc}	dwca	ρ _{max}	S _{5Ca}
1	234	567	891011	121314	15161718	19202122	232425	262728	29303132	3334353637	383940	41424344	45464748	495051	525354	5556575859606162			
0	000	018	1300	5600	0400	1000	5000	0300	8002	1886	1445	1827	0701	1203	1270	0634	1991	2111	
1	000	018	1321	5600	0300	1000	5000	0368	0500	1886	1429	1522	0748	1099	1400	0654	0286	3021	
2	000	017	1298	5600	0300	1000	5000	0300	0300	1886	1437	1760	0723	1129	1350	0664	0107	5309	
3	000	017	1302	5600	0300	1000	5000	0300	0300	1886	1447	1884	0666	1149	2040	0793	2829	2525	
0	010	003	1761	5630	0400	0905	0905	0488	1200	1922	1447	1884	0666	1149	2040	0793	2829	2525	
1	010	003	1710	5600	0400	0905	0905	0478	1500	1942	1436	1509	0698	1149	1950	0673	7222	0294	
2	010	003	1740	5600	0300	0905	0905	0300	0900	1942	1439	1818	0572	1191	1650	0623	8124	0208	
3	010	003	1746	5600	0300	0905	0905	0300	0900	1942	1439	1818	0572	1191	1650	0623	8124	0208	
0	020	004	1830	5600	0300	1038	1038	0600	0842	1884	1453	1731	0818	1226	2240	0852	9923	3311	
1	020	004	1860	5600	0400	0905	0905	0558	0700	1884	1439	1566	1316	1149	2000	0763	3531	3422	
2	020	004	1855	5600	0300	0905	0905	0300	0841	1865	1448	1770	0641	1160	1820	0683	4134	2166	
3	020	003	1821	5600	0300	0905	0905	0300	0846	1884	1448	1770	0641	1160	1820	0683	4134	2166	
0	040	007	1920	5540	0710	0907	0907	0700	0855	1866	1448	1924	0884	1226	2420	0862	8329	2297	
1	040	007	1974	5600	0500	0905	0905	0740	0688	1884	1453	1534	0724	1129	2060	0763	3835	3223	
2	040	007	1990	5600	0300	0905	0905	0300	0876	1941	1446	1895	0769	1129	2060	0763	3531	3286	
3	040	003	1984	5600	0300	0905	0905	0300	0873	1884	1452	1904	0870	1126	2721	0125	4163	4242	
0	080	113	2055	5530	0610	0983	0983	1328	0571	1804	1452	1904	0870	1126	2721	0125	4163	4242	
1	080	107	2110	5590	0900	0905	0905	1348	0610	1884	1440	1639	0900	1171	2580	0743	5254	3655	
2	080	112	2105	5600	0300	0905	0905	0300	0851	1794	1448	1841	0813	1192	2860	0823	1430	3055	
3	080	003	2080	5600	0300	0905	0905	0300	0857	1884	1448	1841	0813	1192	2860	0823	1430	3055	
0	120	137	2125	5622	0551	0985	0985	2328	0300	1708	1448	1904	0957	1261	2951	1122	1422	3277	
1	120	143	2145	5555	0400	0985	0985	2400	0827	1884	1440	1541	0761	1139	1800	0663	8529	3033	
2	120	139	2165	5600	0300	0985	0985	0300	0829	1690	1446	1897	0817	1203	2250	0753	0432	3111	
3	120	003	2150	5600	0300	0985	0985	0300	0832	1884	1448	1897	0817	1203	2250	0753	0432	3111	
0	160	151	2250	5600	1508	1004	1004	2722	0773	1824	1448	1851	0999	1261	3081	1282	0154	1111	
1	160	147	2260	5641	1508	0985	0985	2647	0533	1884	1438	1609	0839	1192	2090	0713	3551	2877	
2	160	148	2222	5600	0300	0985	0985	0300	0769	1818	1444	1890	0815	1226	2091	0683	4629	2688	
3	160	003	2221	5600	0300	0985	0985	0300	0767	1884	1448	1890	0815	1226	2091	0683	4629	2688	

TABLE II: SUMMARISED DATA FOR BATCH (ii)

HARD METAL POWDER PROPERTIES										PROPERTIES OF THE SINTERED COMPACTS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
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C	MT	SS	(Hc) ₁	TC	O ₂	FC	Co	5SLC	(10)	(4πσ)	ρ	4πσ	(Hc) ₂	VPN	ΣE	SSWC	dwc ₁	dwc ₂	5SCo																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																
1	23	45	67	89	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000

TABLE III: SUMMARISED DATA FOR BATCH (iii)

[illegible]

TABLE IV. SUMMARISED DATA FOR BATCH (IV)

HARD METAL POWDER PROPERTIES										PROPERTIES OF THE SINTERED COMPACTS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
C	MT	SS	(Hc)	TC	O2	FC	Co	LEACHED CARBIDE		PRESSED COMPACT		PROPERTIES OF THE SINTERED COMPACTS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
								SSLC	10/	(4TTσ)	ρ	4TTσ	(Hc)2	VPN	KL	SSMC	dMCA	Fdms	SSCo																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
1	23	45	67	89	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
0	00	00	35	12	75	56	00	03	04	09	09	50	05	00	05	04	08	00	09	00	05	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09	00	05	00	09

TABLE V: SUMMARISED DATA FOR BATCH (V)

[illegible]

TABLE VI: SUMMARISED DATA FOR BATCH (VI)

HARD METAL POWDER PROPERTIES										PROPERTIES OF THE SINTERED COMPACTS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
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C	MT	Ss	(Hch)	TC	O ₂	FC	Co	SsLC	(Q)	(4πσ)	Q	4πσ	(Hc) ₂	VPN	κL	Sswc	dwa	Pdwa	SsCo																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															
1	23	45	67	89	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
0	00	00	05	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	105	110	115	120	125	130	135	140	145	150	155	160	165	170	175	180	185	190	195	200	205	210	215	220	225	230	235	240	245	250	255	260	265	270	275	280	285	290	295	300	305	310	315	320	325	330	335	340	345	350	355	360	365	370	375	380	385	390	395	400	405	410	415	420	425	430	435	440	445	450	455	460	465	470	475	480	485	490	495	500	505	510	515	520	525	530	535	540	545	550	555	560	565	570	575	580	585	590	595	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795	800	805	810	815	820	825	830	835	840	845	850	855	860	865	870	875	880	885	890	895	900	905	910	915	920	925	930	935	940	945	950	955	960	965	970	975	980	985	990	995	1000	1005	1010	1015	1020	1025	1030	1035	1040	1045	1050	1055	1060	1065	1070	1075	1080	1085	1090	1095	1100	1105	1110	1115	1120	1125	1130	1135	1140	1145	1150	1155	1160	1165	1170	1175	1180	1185	1190	1195	1200	1205	1210	1215	1220	1225	1230	1235	1240	1245	1250	1255	1260	1265	1270	1275	1280	1285	1290	1295	1300	1305	1310	1315	1320	1325	1330	1335	1340	1345	1350	1355	1360	1365	1370	1375	1380	1385	1390	1395	1400	1405	1410	1415	1420	1425	1430	1435	1440	1445	1450	1455	1460	1465	1470	1475	1480	1485	1490	1495	1500	1505	1510	1515	1520	1525	1530	1535	1540	1545	1550	1555	1560	1565	1570	1575	1580	1585	1590	1595	1600	1605	1610	1615	1620	1625	1630	1635	1640	1645	1650	1655	1660	1665	1670	1675	1680	1685	1690	1695	1700	1705	1710	1715	1720	1725	1730	1735	1740	1745	1750	1755	1760	1765	1770	1775	1780	1785	1790	1795	1800	1805	1810	1815	1820	1825	1830	1835	1840	1845	1850	1855	1860	1865	1870	1875	1880	1885	1890	1895	1900	1905	1910	1915	1920	1925	1930	1935	1940	1945	1950	1955	1960	1965	1970	1975	1980	1985	1990	1995	2000	2005	2010	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060	2065	2070	2075	2080	2085	2090	2095	2100	2105	2110	2115	2120	2125	2130	2135	2140	2145	2150	2155	2160	2165	2170	2175	2180	2185	2190	2195	2200	2205	2210	2215	2220	2225	2230	2235	2240	2245	2250	2255	2260	2265	2270	2275	2280	2285	2290	2295	2300	2305	2310	2315	2320	2325	2330	2335	2340	2345	2350	2355	2360	2365	2370	2375	2380	2385	2390	2395	2400	2405	2410	2415	2420	2425	2430	2435	2440	2445	2450	2455	2460	2465	2470	2475	2480	2485	2490	2495	2500	2505	2510	2515	2520	2525	2530	2535	2540	2545	2550	2555	2560	2565	2570	2575	2580	2585	2590	2595	2600	2605	2610	2615	2620	2625	2630	2635	2640	2645	2650	2655	2660	2665	2670	2675	2680	2685	2690	2695	2700	2705	2710	2715	2720	2725	2730	2735	2740	2745	2750	2755	2760	2765	2770	2775	2780	2785	2790	2795	2800	2805	2810	2815	2820	2825	2830	2835	2840	2845	2850	2855	2860	2865	2870	2875	2880	2885	2890	2895	2900	2905	2910	2915	2920	2925	2930	2935	2940	2945	2950	2955	2960	2965	2970	2975	2980	2985	2990	2995	3000	3005	3010	3015	3020	3025	3030	3035	3040	3045	3050	3055	3060	3065	3070	3075	3080	3085	3090	3095	3100	3105	3110	3115	3120	3125	3130	3135	3140	3145	3150	3155	3160	3165	3170	3175	3180	3185	3190	3195	3200	3205	3210	3215	3220	3225	3230	3235	3240	3245	3250	3255	3260	3265	3270	3275	3280	3285	3290	3295	3300	3305	3310	3315	3320	3325	3330	3335	3340	3345	3350	3355	3360	3365	3370	3375	3380	3385	3390	3395	3400	3405	3410	3415	3420	3425	3430	3435	3440	3445	3450	3455	3460	3465	3470	3475	3480	3485	3490	3495	3500	3505	3510	3515	3520	3525	3530	3535	3540	3545	3550	3555	3560	3565	3570	3575	3580	3585	3590	3595	3600	3605	3610	3615	3620	3625	3630	3635	3640	3645	3650	3655	3660	3665	3670	3675	3680	3685	3690	3695	3700	3705	3710	3715	3720	3725	3730	3735	3740	3745	3750	3755	3760	3765	3770	3775	3780	3785	3790	3795	3800	3805	3810	3815	3820	3825	3830	3835	3840	3845	3850	3855	3860	3865	3870	3875	3880	3885	3890	3895	3900	3905	3910	3915	3920	3925	3930	3935	3940	3945	3950	3955	3960	3965	3970	3975	3980	3985	3990	3995	4000	4005	4010	4015	4020	4025	4030	4035	4040	4045	4050	4055	4060	4065	4070	4075	4080	4085	4090	4095	4100	4105	4110	4115	4120	4125	4130	4135	4140	4145	4150	4155	4160	4165	4170	4175	4180	4185	4190	4195	4200	4205	4210	4215	4220	4225	4230	4235	4240	4245	4250	4255	4260	4265	4270	4275	4280	4285	4290	4295	4300	4305	4310	4315	4320	4325	4330	4335	4340	4345	4350	4355	4360	4365	4370	4375	4380	4385	4390	4395	4400	4405	4410	4415	4420	4425	4430	4435	4440	4445	4450	4455	4460	4465	4470	4475	4480	4485	4490	4495	4500	4505	4510	4515	4520	4525	4530	4535	4540	4545	4550	4555	4560	4565	4570	4575	4580	4585	4590	4595	4600	4605	4610	4615	4620	4625	4630	4635	4640	4645	4650	4655	4660	4665	4670	4675	4680	4685	4690	4695	4700	4705	4710	4715	4720	4725	4730	4735	4740	4745	4750	4755	4760	4765	4770	4775	4780	4785	4790	4795	4800	4805	4810	4815	4820	4825	4830	4835	4840	4845	4850	4855	4860	4865	4870	4875	4880	4885	4890	4895	4900	4905	4910	4915	4920	4925	4930	4935	4940	4945	4950	4955	4960	4965	4970	4975	4980	4985	4990	4995	5000	5005	5010	5015	5020	5025	5030	5035	5040	5045	5050	5055	5060	5065	5070	5075	5080	5085	5090	5095	5100	5105	5110	5115	5120	5125	5130	5135	5140	5145	5150	5155	5160	5165	5170	5175	5180	5185	5190	5195	5200	5205	5210	5215	5220	5225	5230	5235	5240	5245	5250	5255	5260	5265	5270	5275	5280	5285	5290	5295	5300	5305	5310	5315	5320	5325	5330	5335	5340	5345	5350	5355	5360	5365	5370	5375	5380	5385	5390	5395	5400	5405	5410	5415	5420	5425	5430	5435	5440	5445	5450	5455	5460	5465	5470	5475	5480	5485	5490	5495	5500	5505	5510	5515	5520	5525	5530	5535	5540	5545	5550	5555	5560	5565	5570	5575	5580	5585	5590	5595	5600	5605	5610	5615	5620	5625	5630	5635	5640	5645	5650	5655	5660	5665	5670	5675	5680	5685	5690	5695	5700	5705	5710	5715	5720	5725	5730	5735	5740	5745	5750	5755	5760	5765	5770	5775	5780	5785	5790	5795	5800	5805	5810	5815	5820	5825	5830	5835	5840	5845	5850	5855	5860	5865	5870	5875	5880	5885	5890	5895	5900	5905	5910	5915	5920	5925	5930	5935	5940	5945	5950	5955	5960	5965	5970	5975	5980	5985	5990	5995	6000	6005	6010	6015	6020	6025	6030	6035	6040	6045	6050	6055	6060	6065	6070	6075	6080	6085	6090	6095	6100	6105	6110	6115	6120	6125	6130	6135	6140	6145	6150	6155	6160	6165	6170	6175	6180	6185	6190	6195	6200	6205	6210	6215	6220	6225	6230	6235	6240	6245	6250	6255	6260	6265	6270	6275	6280	6285	6290	6295	6300	6305	6310	6315	6320	6325	6330	6335	6340	6345	6350	6355	6360	6365	6370	6375	6380	6385	6390	6395	6400	6405	6410	6415	6420	6425	6430	6435	6440	6445	6450	6455	6460	6465	6470	6475	6480	6485	6490	6495	6500	6505	6510	6515	6520	6525	6530	6535	6540	6545	6550	6555	6560	6565	6570	6575	6580	6585	6590	6595	6600	6605	6610	6615	6620	6625	6630	6635	6640

TABLE VII SUMMARISED DATA FOR BATCH (VII)

HARD METAL POWDER PROPERTIES										PROPERTIES OF THE SINTERED COMPACTS																									
LEACHED CARBIDE										PRESSED COMPACT																									
C	MT	SS	(Hc)	TC	O2	FC	Co	55LC	55Co	Q	486	(Hc)	VPN	IL	SSMC	dwCA	Edm	55Co																	
1	23	45	67	89	1011	1213	14	1516	1718	1920	2122	2324	2526	2728	2930	3132	3334	3536	3738	3940	4142	4344	4546	4748	4950	5152	5354	5556	5758	5960	6162				
0	00	00	03	3	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03			
1	00	00	03	2	07	22	55	3	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03	14	03		
2	00	00	03	3	07	02	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX		
3	00	00	03	3	07	04	33	07	04	33	07	04	33	07	04	33	07	04	33	07	04	33	07	04	33	07	04	33	07	04	33	07	04	33	
0	01	00	05	0	13	60	5	2	10	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
1	01	00	06	1	13	52	5	7	10	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
2	01	00	05	6	13	28	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX		
3	01	00	05	6	13	28	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX	XX		
0	02	00	08	1	14	40	5	5	10	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
1	02	00	08	5	14	65	4	6	5	5	4	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
2	02	00	08	2	14	25	4	2	5	4	3	0	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3
3	02	00	08	2	14	25	4	2	5	4	3	0	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3
0	04	00	09	9	15	50	5	5	10	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
1	04	00	09	5	15	62	5	6	2	5	4	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
2	04	00	09	5	15	62	5	6	2	5	4	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
3	04	00	09	5	15	62	5	6	2	5	4	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
0	08	01	17	1	17	10	5	7	2	6	5	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
1	08	01	17	1	17	10	5	7	2	6	5	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
2	08	01	17	1	17	10	5	7	2	6	5	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
3	08	01	17	1	17	10	5	7	2	6	5	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3	
0	12	01	54	1	18	70	5	5	5	2	2	0	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3
1	12	01	54	1	18	70	5	5	5	2	2	0	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3
2	12	01	54	1	18	70	5	5	5	2	2	0	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3
3	12	01	54	1	18	70	5	5	5	2	2	0	1	0	4	4	6	1	2	0	3	0	3	0	3	0	3	0	3	0	3	0	3	0	3
0	16	01	66	1	19	75	5	5	9	0	2	7	8	7	7	1	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5
1	16	01	66	1	19	75	5	5	9	0	2	7	8	7	7	1	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5
2	16	01	66	1	19	75	5	5	9	0	2	7	8	7	7	1	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5
3	16	01	66	1	19	75	5	5	9	0	2	7	8	7	7	1	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5	0	1	4	5

TABLE VIII: SUMMARISED DATA FOR BATCH (VIII)

(189)

Author Rees G J

Name of thesis The alpha-eta transformation in Cobalt with particular reference to the use of Cobalt in Cemented Carbides
1972

PUBLISHER:

University of the Witwatersrand, Johannesburg

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