Certain measurements were not carried out on all the powders and specimens:

(1) The specific surface areas of the hard metal powders were measured on only three of the four samples.

(2) The specific surface areas of the leached carbide samples were measured on only two samples of the four removed after each milling time.

(3) The magnetic saturation was measured on only two pressed powder samples removed after each milling time. The results cannot be regarded with accuracy because of the "softness" of the material, and the tendency for the surface of the powder to be removed during the handling operation.

(4) Assays were carried out on two of the samples of each set of four. (By measuring the properties of several powder samples, a measure of the spread in the data could be obtained.)

No lubricant was added to these powder samples prior to pressing; small quantities of milled powders would have had to be waxed manually in a beaker on an electric hotplate, and uncontrolled oxidation could have occurred. Furthermore, in such an operation the wax is not easily dispersed, and this can result in porosity and other irregularities in the sintered product. Since no lubricant was added, and no machining operations were to be carried out prior to sintering, the pellets did not have to be preheated. This offered certain advantages: (1) The coercivity of the material would not be lowered

prior to sintering. Coercivity is reduced during preheating for the reasons given in Chapter 5. Therefore relationships involving coercivity with the other parameters could perhaps be more readily found.

(2) Although the oxygen content of the powders would be reduced by reaction with the hydrogen during preheating, the influence of this variable would be more clearly seen if the oxygen content was higher, as it was with the powders.

(3) The carbon level of the material would be altered by preheating. If the powders were pressed and sintered directly, the carbon content of the material would be the same as that of the powder removed from the mills.

The main disadvantage of not preheating the compacts prior to sintering was that the pellets tended to be soft and powdery, which reduced the precision with which green density measurements could be made.

6.5 Results.

6.5.1 Qualitative Observations from the data.

(a) Immediately apparent from the data in Tables I - VIII is the effect of the initial cobalt powder on the sintered density of the hand mixed specimens. The samples sintered in hydrogen at 1,370° from charges (i) - (iv) (made with the Hoboken cobalt) had sintered densities in the rage of 14.43 - 14.50 g./cc.; whereas the samples from mills (v) - (viii) (made with the CF-6 powder) were in

the range of 13.46 to 13.63 g./cc.

Microphotographs of the two cobalt powders used in this experiment were shown in Chapter 4, and the differences in density must be ascribed to the differences in the initial states of agglomeration of the cobalt powders.

The sintered density differences between the two series (using the two cobalt powders) were not very noticeable when the powders had been milled for 10 hours. This confirms the results shown in Table V of Chapter 5, i.e. as milling proceeds the differences in sintered density, when using cobalt powders from different sources, become smaller.

(b) Using a sintering temperature of 1,480°C, and exit gases with a low dew point resulted in lower sintered densities compared with those obtained at 1,370°C. This is the well known but unexplained effect of the variation in sintered density with sintering temperature, discussed in Chapter 5.

(c) Using a sintering temperature of 1,480°C and exit gases with a high dew point resulted in a considerable decrease in sintered density and magnetic saturation, compared with the specimens sintered at 1,480°C with a low dew point of the exit gases. The water present in the sintering atmosphere must consume carbon and interfere with the liquid phase sintering process.

(d) Total carbon variations of up to 0.05% were evident in some of the series of the two sets of samples which were removed from the same mill after the same milling time. There is an uncertainty in the determination of total carbon of $\pm$ 0.02%. The maximum range in total carbon found in these samples was from 5.48 to 5.63%, which corresponds with an equivalent total carbon content for the carbide phase of 6.09% to 6.25% for a 10% cobalt alloy.

(e) All of the sintered specimens were examined for the presence of eta phase and free graphite. Neither phase was present in any of the specimens. The lowest magnetic saturation found (140 units), was in the series of specimens sintered at 1,480°C with exit gases of high dew point. Suzuki et al.[4] in their work on 10% cobalt alloys reported that eta phase started to form when the magnetic saturation was 154 units. However, special care was taken with the micro-examination of the specimens with magnetic saturations in the 140 - 150 unit range, with respect to the presence of eta phase, but none was observed.

(f) Of all the data shown in the Tables, the free carbon assays showed the largest proportional variation; in some cases this was between 0.03% and 0.13%; these variations in free carbon may possibly be ascribed to a catalytic influence of

the cobalt in the presence of the organic milling fluid, - acetone.

(g) A decrease in pressed compact magnetic saturation is evident in all cases with increasing milling time. This is due to the non-magnetic cobalt oxide present; however, the direct correlation between magnetic saturation and oxygen is poor.

(h) One parameter measurement which did not yield satisfactory duplication of the results in all cases was that of the specific surface area of the leached carbide. Agglomeration with all fine powders is a problem that has to be considered; reliable de-agglomeration prior to measurement is a necessary pre-requisite for all powders. The forces causing physical agglomeration may be listed[10] as follows:

(1) Physical adhesion.

(2) Capillary forces (in the presence of moisture or entrained milling fluid).

(3) Electrostatic forces.

(4) Magnetic forces.

(5) Cold welding.

There are various methods of de-agglomeration including dry rubbing, wet rubbing and ultrasonic dispersion. The latter is the best and the most satisfactory when particle size measurements are carried out in a liquid. It also avoids problems associated with incipient grinding.[10] Thus any particle size measurement will be a function both

of the powder under study, and the method of de-agglomeration used. For fine powders with pronounced agglomeration tendencies, complete de-agglomeration is physically impossible. Attempts must therefore be made to find a reproducible state of partial de-agglomeration. Here, where the removal of the cobalt from the carbide entailed leaching with hydrochloric acid, followed by repeated centrifuging until neutral with litmus, followed finally by drying, the powders were lightly crushed in a mortar with a pestle prior to measurement. It can be seen from the tables, that the reproducibility between the two samples studied became worse as the particle size decreased i.e. the finer powders had a greater tendency to agglomerate.

(i) Little evidence of zone-formation due to overmilling was evident in this experiment; the largest decrease in density with increasing milling was (for the specimens sintered at 1,370°C) 0.05 g./cc. As has been pointed out in Chapter 5, the influences of overmilling become less as the cobalt content is reduced; nevertheless some slight evidence for the overmilling effect was discernible in this experiment.

(j) One aspect of this experiment which could be open to criticism is the use of an optical microscope for the quantitative metallography;

however, it has been shown that reproducible results can be obtained by different operators on the same fields in the same specimen, using counting techniques.[20] As has been pointed out by Exner and Fischmeister,[23] the grains in tungsten carbide samples consist of only one ditrigonal-bipyramidal crystal type with angular corners, and not the so called α_1 (non-recrystallised round grains), and the α_2 (recrystallised grains) types, as was previously supposed. All electron microscope studies of sintered cemented carbide samples indicate that all the grains have been recrystallised during the course of sintering. It has been stated[23] that all the grain shapes observed in sintered carbide micro-structures can be interpreted as sections of the grinding plane with ditrigonal-bipyramidal crystals with blunt edges.

It was found in this experiment that the grain size could be counted satisfactorily on an optical microscope with no necessity for the preparation of replicas of the carbide surfaces. The smallest average carbide grain size found in these specimens was 2.01 μ which is amenable to measurement on an optical microscope at 1500 magnification.

(k) As was noted above, the major disadvantage of not preheating these specimens prior to sintering was

that the specimens were "soft" and powdery, which rendered difficult the determination of the green density (carried out by mensuration and weighing) of the specimens; this is confirmed by the scatter in the green compact densities of up to 0.1 g./cc. on a set of four compacts removed after the same milling interval. Noteworthy is the manner in which the pressed density varies with the milling time for the various alloy mixtures made with carbide powders of different initial particle sizes; the data also show that the source of cobalt powder influences the pressed compact density - the CF-6 powder yielding slightly higher pressed compact density values than the Hoboken cobalt mixtures for the shorter milling intervals. Except for batches (i) and (v), the data show that the Hoboken powder mixture compacts reached a maximum pressed density after 80 hours of milling, whereas the compacts prepared from the CF-6 cobalt powder reached a maximum density after 40 hours milling.

In general, the data in Tables I - VIII yield a measure of the spread encountered in the property data for the cobalt - tungsten carbide hard metal system.

6.5.2 Quantitative Relations obtained from the data.

The linear correlation coefficients $\left[r = 1/N \cdot \frac{\Sigma(x-\bar{x})(y-\bar{y})}{\sigma_x \sigma_y}\right]$ (where there there are N observations and σ_x and σ_y are, respectively, the standard deviations for the x and y values), for the individual relations, between all the

parameters measured, are summarised in Table IX. It must be emphasised that the linear correlation coefficients were calculated, i.e. r values between - 1 and + 1 could be obtained, the former value indicating a perfect negative linear association, and the latter a perfect positive linear association between the variables. It is important to note this point, as, for the equation $y = x^2$, r is equal to zero, although there is a perfect functional relationship between y and x.

In order to test the significance of the correlations obtained, student's t values were calculated for each of the correlations; the t values obtained are summarised in Table X, and the significance of the relations was obtained from standard statistical tables. In Table X the following symbols have been used to indicate the levels of significance:

(a) where there was no significance ≡ N.S.

(b) between the 5% probability of significance and the 1% probability of significance ≡ P.S. i.e. possibly significant.

(c) between the 1% probability of significance and the 0.1% probability ≡ S i.e. significant.

(d) larger than the 0.1% probability level ≡ H.S. i.e. highly significant.

The following observations from the data are noteworthy:

(a) Inter-relations with correlation coefficients greater than $\pm$ 0.90.

r values of 0.90 or greater indicate a high

TABLE IX. CORRELATION MATRICES FOR POWDER - POWDER AND POWDER - SINTERED PROPERTIES

CORRELATION BETWEEN POWDER PROPERTIES

	MT	S_S	$(Hc)_1$	TC	O_2	FC	Co
MT		0.93 0.93 0.92	0.73 0.76 0.77	-0.04 0.08	0.61 0.65	0.27	0.12
S_S			0.75 0.77 0.74	-0.15 0.06	0.66 0.69	0.32	0.22
$(Hc)_1$				0.12 0.30	0.44 0.46	0.40	-0.02
TC					-0.15 -0.20	-0.03	-0.69
O_2						0.21	0.13
FC							0.07
Co							

CORRELATION BETWEEN POWDER AND SINTERED PROPERTIES

	ρ	$4\pi\sigma$	$(Hc)_2$	VPN	$\Sigma\ell$	$S_S wc$	dwc	$S_S Co$	MT	S_S	$(Hc)_1$	TC	O_2	FC	Co	C
ρ		0.01 -0.03 0.23	0.35 0.00 0.30	0.94 0.14 0.89	0.50 -0.04 0.51	0.39 -0.03 0.38	-0.56 -0.03 -0.61	-0.11 0.04 0.08	0.31 -0.12 0.35	0.36 -0.17 0.41	0.59 0.02 0.71	0.28 0.26	0.25 -0.11	-0.01	-0.11	0 1 2
$4\pi\sigma$			0.22 -0.04 0.58	0.09 0.06 0.37	0.26 0.19 0.37	0.17 0.34 0.59	-0.22 -0.40 -0.54	-0.03 0.12 0.50	0.26 0.35 0.77	0.33 0.38 0.74	0.28 0.21 0.62	-0.53 -0.09	0.16 0.31	0.16	0.75	0 1 2
$(Hc)_2$				0.55 0.23 0.54	0.78 0.31 0.70	0.78 0.09 0.77	-0.80 -0.12 -0.80	0.65 0.57 0.58	0.93 0.04 0.78	0.95 0.06 0.87	0.76 0.26 0.51	-0.07 0.18	0.67 0.05	0.29	0.11	0 1 2
VPN					0.63 0.40 0.64	0.52 0.38 0.54	-0.67 -0.44 -0.77	0.05 0.35 0.54	0.49 0.33 0.53	0.56 0.39 0.59	0.66 0.64 0.75	0.16 0.18	0.40 0.26	0.10	0.02	0 1 2
$\Sigma\ell$						0.79 0.74 0.65	-0.87 -0.80 -0.77	0.43 0.50 0.53	0.77 0.37 0.76	0.77 0.41 0.72	0.78 0.51 0.65	0.03 0.06	0.46 0.20	0.27	0.00	0 1 2
$S_S wc$							0.90 0.89 0.84	0.59 0.40 0.71	0.88 0.47 0.67	0.79 0.56 0.74	0.73 0.54 0.57	0.16 0.09	0.53 0.34	0.31	-0.02	0 1 2
dwc								-0.47 -0.45 -0.67	-0.82 -0.49 -0.76	-0.80 -0.54 -0.80	-0.82 -0.56 -0.71	-0.15 -0.03	0.52 0.37	0.33	-0.02	0 1 2
$S_S Co$									0.69 0.33 0.68	0.61 0.38 0.70	0.35 0.55 0.36	0.06 0.12	0.36 0.12	0.26	-0.02	0 1 2

SYMBOLS AND SINTERING CODE AS IN TABLES I - VIII ; MT = MILLING TIME.

THE LEVEL OF THEIR SIGNIFICANCE

	$\Sigma\ell$		S_{gwc}		dwc/s		$S_S Co$		MT		S_S		$(Hc)_1$		TC		O_2		FC		Co		C
HS	4.21	HS	3.11	S	4.95	HS	0.83	NS	2.42	PS	2.86	S	5.25	HS	2.00	NS	1.88	NS	0.00	NS	0.83	NS	0
NS	0.29	NS	0.22	NS	0.30	NS	0.29	NS	0.89	NS	1.26	NS	0.15	NS	1.98	NS	0.83	NS					1
HS	4.45	HS	3.00	S	5.70	HS	0.60	NS	2.75	S	3.30	S	7.35	HS									2
NS	2.00	NS	1.40	NS	1.60	NS	0.21	NS	2.00	NS	2.59	PS	2.14	PS	4.59	HS	1.19	NS	1.19	NS	8.40	HS	0
NS	1.68	NS	2.66	S	3.20	S	0.84	NS	2.72	S	3.00	S	1.54	NS	0.61	NS	2.42	PS					1
S	2.91	S	5.39	HS	4.90	HS	4.28	HS	8.81	HS	8.10	HS	5.75	HS									2
HS	9.20	HS	9.20	HS	9.82	HS	6.25	HS	18.50	HS	22.4	HS	8.60	HS	0.70	NS	5.85	HS	2.24	PS	0.81	NS	0
NS	2.20	PS	0.61	NS	0.89	NS	5.12	HS	0.30	NS	0.50	NS	1.99	NS	1.34	NS	0.40	NS					1
HS	7.21	HS	8.85	HS	9.80	HS	5.25	HS	9.30	HS	13.1	HS	4.36	HS									2
	5.90	HS	4.50	HS	6.64	HS	0.40	NS	4.15	HS	4.95	HS	6.40	HS	1.19	NS	3.20	S	0.90	NS	0.15	NS	0
	3.20	S	3.01	S	3.89	S	2.72	S	2.55	S	3.11	S	5.95	HS	1.59	NS	2.00	NS					1
	5.95	HS	4.70	HS	8.90	HS	4.70	HS	4.59	HS	5.40	HS	8.20	HS									2
			9.50	HS		HS	3.49	S	8.90	HS	8.70	HS	9.24	HS	0.21	NS	3.80	S	2.07	PS	0.00	NS	0
			8.10	HS	9.80	HS	4.24	HS	2.92	S	3.31	S	4.35	S	0.44	NS	1.50	NS					1
			6.25	HS	8.90	HS	4.59	HS	8.60	HS	7.68	HS	6.28	HS									2
					15.1	HS	5.45	HS	13.4	HS	9.50	HS	7.89	HS	1.19	NS	4.70	HS	2.42	PS	0.15	NS	0
					14.6	HS	3.21	S	3.88	S	4.99	HS	4.70	HS	0.66	NS	2.65	S					1
					11.4	HS	7.35	HS	6.65	HS	8.10	HS	5.11	HS									2
							3.88	S	10.40	HS	9.80	HS	10.90	HS	1.20	NS	4.49	HS	2.55	PS	0.15	NS	0
							3.69	S	4.15	HS	4.72	HS	4.45	HS	0.22	NS	2.90	S					1
							6.65	HS	8.62	HS	9.80	HS	7.35	HS									2
									7.10	HS	5.70	HS	2.74	PS	0.45	NS	2.84	PS	2.00	NS	0.15	NS	0
									2.58	PS	3.05	S	4.80	HS	0.84	NS	0.84	NS					1
									7.05	HS	7.20	HS	2.84	S									2

ARE USED AS IN TABLE IX

LEFT HAND VALUE INDICATES THE
HAND THE SIGNIFICANCE.

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probability of linear association, and the following relations in Table IX are in this category:

(i) The relation between milling time and specific surface area of the milled hard metal powder.

(ii) The relation between density of the sintered compact and its Vickers hardness for the specimens sintered at 1,370°C and 1,480°C with a low dew point of the exit gases.

(iii) The relationship between sintered coercivity and milling time and between sintered coercivity and specific surface area of the milled hard metal powder, for the specimens sintered at 1,480°C and 1,370°C with a low dew point of the exit gases.

(iv) The relationship between d_{WC} and S_gWC.

The following comments apply to these relationships:

(i) In Chapter V it was shown that the relationship between specific surface area of the hard metal powder and the milling time was $S^2 - So^2 = kt$. However, the relation between S and t is a form of Rittinger's Formula (i.e. $S - So \sim t$), which was shown in Figure 5.17. The correlation coefficient for the data shown in Figure 5.17 for Rittinger's Rule is 0.94, which is similar to the values found here.

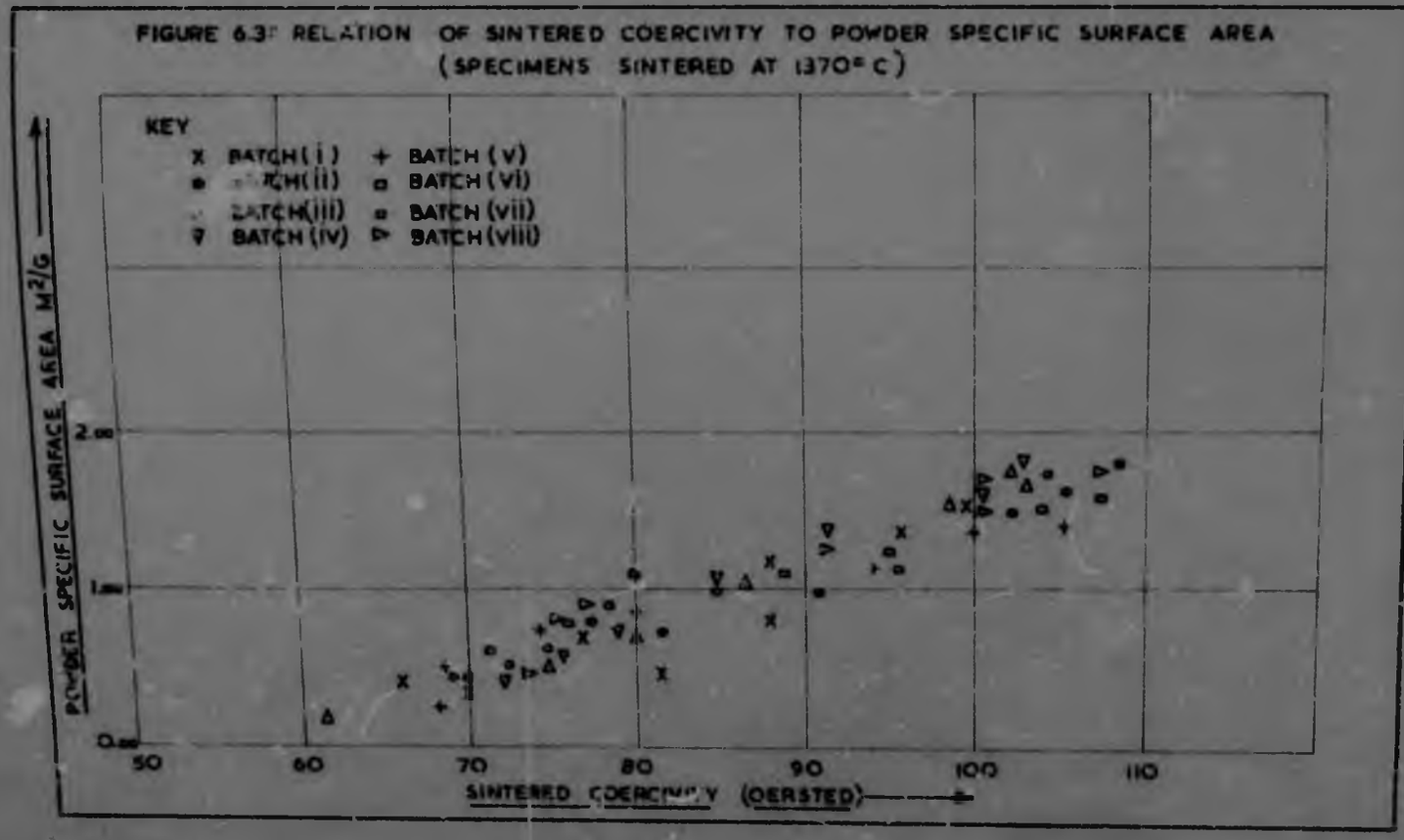
(ii) Sintered density and Vickers hardness: as porosity is eliminated and the incidence of

cobalt pooling is reduced so the hardness of a hard metal compact is increased. This was noted in Chapter V. The results obtained show that this relation is approximately linear over the range studied.

(iii) Sintered coercivity and specific surface area (and sintered coercivity and milling time): the results show that with a wide range of grain sizes and grain size distributions, an approximately linear correlation exists between sintered coercivity and specific surface area of the hard metal powder provided the samples are sintered together under ideal conditions (i.e. low dew point of the exit gases). The results for the specimens sintered at 1,370°C are shown plotted in Figure 6.3. It is important to emphasise that the samples were sintered together as in a previous set of experiments,[11] where a set of specimens, which had been prepared from powders of the same composition but milled for different times were sintered in different runs, under the same nominal conditions, the correlation was poor ($r = 0.36$). This indicates that the sintering atmosphere has very important consequences on the inter-relations between properties.

The inter-relation between sintered coercivity and milling time is so, because of the inter-relation between specific surface area and

FIGURE 6.3: RELATION OF SINTERED COERCIVITY TO POWDER SPECIFIC SURFACE AREA
(SPECIMENS SINTERED AT 1370° C)



milling time discussed in (i) above.

(iv) The relationship between d_{WC} and S_gWC: this is as expected, for as the grain size is reduced, so the specific surface of the carbide phase is increased. The deviations from perfect linearity must be ascribed to the errors involved in quantitative metallography on an optical microscope.

The significance of (i) - (iv) are confirmed by the data in Table X.

(b) Inter-relations with correlation coefficients less than $\pm$ 0.10.

In this category are relations where there is no linear correlation at all or another perfect functional relationship between the variables. The following inter-relations fall into this group:

(v) The relation between milling time and the carbon content of the powders.

(vi) The relation between specific surface area and the carbon content of the powders.

(vii) The relation between the powder coercivity and the cobalt content of the powder.

(viii) The relation between total carbon and free carbon of the powder samples.

(ix) The relation between free carbon and cobalt of the powder samples.

(x) The relation between sintered density and specific surface of the binder phase (S_gCo) in the sintered compacts.

(xi) The relation between density and free carbon and cobalt contents (r = - 0.11) of the powder samples.

(xii) The relation between magnetic saturation and hardness of the sintered compacts.

(xiii) The relation between magnetic saturation and S_gCo.

(xiv) The relation between Vickers hardness of the sintered compacts and total and free carbon and cobalt contents of the powder.

(xv) The relation between crack length ($\lambda 2$) and total carbon and cobalt contents of the powder.

(xvi) The relation between S_gWC of the sintered compacts and the total carbon and cobalt contents of the powders.

(xvii) The relation between d_{wc} and total carbon and cobalt contents of the powder samples.

(xviii) The relation between S_gCo and total carbon and cobalt contents of the powder samples.

These correlation coefficients are very low because there is no reason to expect any correlation between the parameters mentioned in (v) - (xviii). However, there are deviations at two points in the data - this is discussed below:

(v) The composition of the powders should remain constant with the milling time, and thus the carbon content should not vary with the milling time. Similarly the cobalt content remains constant with the milling time - the value of r

found was 0.12. Similar comments apply to (vi), and (vii) - where, although the powder coercivity changes due to comminution, the cobalt content should remain constant.

(viii) and (ix) - no inter-relationship would be expected in these two cases; furthermore, the free carbon variations were very scattered, as was commented on above. In the case of (x) no inter-relation would be expected.

(xi) The free carbon level was not sufficiently high to influence the sintered density. Density of fully sintered compacts naturally varies with the cobalt content over a wide range of cobalt contents, but the range of cobalt contents studied here was obviously so small that its influence on density was insignificant. Similarly (xii) - over a wide range of cobalt contents, the magnetic saturation would be related to the hardness, but here the cobalt content was constant so the magnetic saturation should have remained constant, apart from the influence of the sintering conditions, and the relation between magnetic saturation and cobalt content (noted below). No reasons can be advanced for the significant value of $t = 2.91$ ($1,480^{o}C$-low dew point of the furnace exit gases).

(xiii) No explanation can be given for the t value of 4.28 found for the $4 \pi \sigma - S_s Co$ relation (for the specimens sintered at $1,480^{o}$ with a low

dew point of the exit gases). No relation would be expected between $4\pi\sigma$ and S_gCo.

(xiv) No relation would be expected between these parameters.

(xv) No explanation can be given for the significance of the $\Sigma\ell - O_2$ and $\Sigma\ell$ - FC relations, - in one case the $\Sigma\ell - O_2$ relation was of no significance.

(xvii) - (xviii) Generally the structural parameters of the sintered compacts were not influenced by the chemical compositions of the powders.

(c) The remaining inter-relations with $0.10 < |r| < 0.90$.

The following fall into this group:

(xvix) The relation between milling time and powder coercivity.

(xx) The relations between milling time (and specific surface area) and oxygen content of the powders. The relation between powder coercivity and oxygen ($r = 0.44, 0.46$) also falls into this category.

(xxi) The relation between oxygen content of the powder and its free carbon content.

(xxii) The relations between sintered density and powder coercivity, crack length, grain size, milling time, and specific surface area.

(xxiii) All the relations between magnetic saturation and powder properties with the exception of those discussed in (b) above.

(xxiv) All the relations between $(Hc)_2$, V.P.N., $\Sigma\ell$, S_gWC, d_{WC} and S_gCo excepting those discussed in (a) and (b) above.

The following comments apply to these relations:

(xvix) As was shown in Chapter 5 (Figures 5.15 and 5.16) a curved relation between powder coercivity and milling time exists. An initially rapid rise in powder coercivity occurs as milling proceeds followed by a more gradual rise in powder coercivity with further milling. In this case, therefore, another functional relationship exists between these two parameters. It can be seen from Figure 5.16 (which was for a 10% cobalt composition) that a linear relation exists up to about 80 hours of milling.

(xx) As was noted in 6.2.1, the oxygen content of hard metal powders increases with milling time, but much scatter is evident. This scatter explains the lower correlation coefficients (r = 0.5 ~ 0.7) between the parameters, which change with the milling time, e.g. specific surface area and powder coercivity. A similar scatter between oxygen content and particle size was found by Hendus, Dawihl and Bartsch[22] on crushing pure tungsten carbide powders.

(xxi) No relation would be expected between the oxygen content of a powder and its free carbon content. No significance is attached to the correlation (r = 0.21).

(xxii) It was shown in Chapter 5 that the sintered density increases rapidly with initial milling,

followed by a levelling out, as the density tended towards its theoretical value. Thus a linear relationship is not to be expected. The correlations between density and crack length and grain size are a result of these two parameters varying with the milling time.

(xxiii) As noted in (b) above the magnetic saturation (as a measure of the cobalt content) should remain constant except for changes, as a result of sintering conditions, occurring in the binder phase composition. The high significance of the correlation noted between cobalt content and magnetic saturation was a consequence of the small changes in cobalt content in the samples removed from the charges after different milling times.

(xxiv) The correlations of $(Hc)_2$ with the other sintered properties of hardness, crack length and grain size: in general, it is known that as the sintered coercivity increases so the hardness increases and the grain size is reduced, but the scatter in the results found here shows, that these relations are not at all linear.

The relation between sintered coercivity and specific surface of the binder phase (S_sCo) deserves special comment in view of the findings of Exner and Fischmeister.[23] Over a wide range of cobalt contents, in compacts, where the coercivity ranged from 40 to 160 Oe, and S_sCo from 0.1 to 0.3 $m^2/g.$, these authors found the following relation:

$Hc = 160\ S_gCo$. However, Krainer's formula for coercivity (which was quoted in Chapter 5) implies that stress contributed to the coercivity. Stresses in sintered compacts arise from the differences in coefficients of thermal expansion of cobalt and tungsten carbide, and occur on cooling from the sintering temperature. Other evidence for the importance of stresses on the coercivity is that plastic deformation during use of components alters the coercivity but does not alter the microstructure.[24] In the experiment carried out here, the linear correlation coefficients were poor (0.65, 0.57 and 0.58 for the three sets of sintering conditions); this experiment was related only to much narrower ranges of coercivity and specific surface area of the binder phase than those considered by Exner and Fischmeister. These authors, from the good relationships they obtained between sintered coercivity and S_gCo concluded that cooling stresses exerted little influence on the sintered coercivity; furthermore, if cooling stresses were of importance they should vary with the cobalt contents of the alloys, and as their relation between sintered coercivity and S_gCo covered a range of cobalt contents, the influences of stresses were discounted. If stresses, in their work, exerted a considerable effect on the coercivity, alloys with the same cobalt layer thicknesses, but with different cobalt contents should show different coercivities. According to them, this was found not to be the case. It is unfortunate that over a narrow range of properties (as investigated here) that there is no distinct

relationship between S_sCo and $(Hc)_2$, since the average cobalt layer thickness (ℓ_{Co}) is related to such mechanical properties of hard metal as the transverse rupture strength.[13],[21] S_sCo is related to ℓ_{Co} by the equation $S_sCo = \frac{4}{\ell_{Co}\rho_{Co}}$ where ρ_{Co} is the density of pure cobalt in g./cc.[23] The statistical treatment (Table X) indicates a high level of significance for the $(Hc)_2$ - S_sCo relation, but as discussed above the relation was certainly not linear over the range studied.

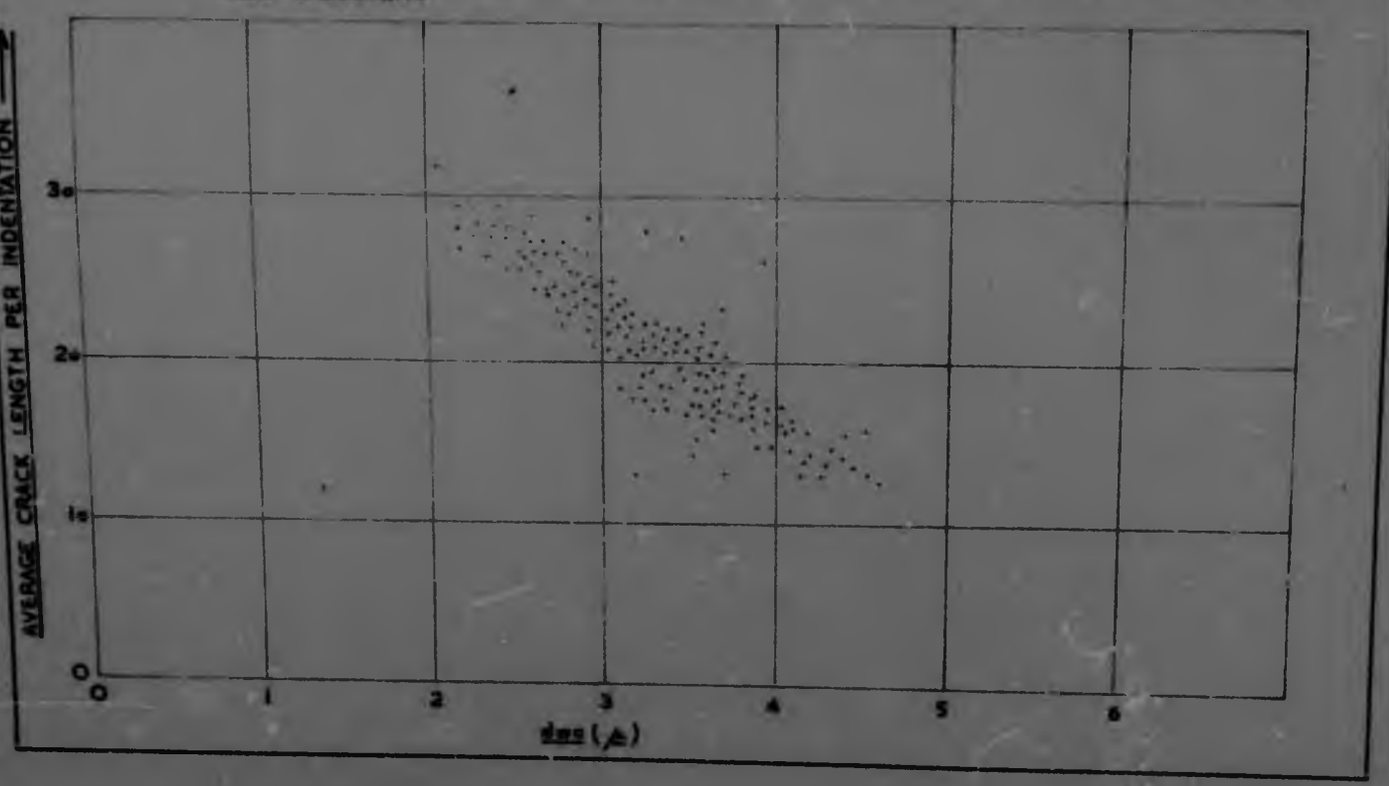
The relations between sintered grain size and crack length are shown in Figure 6.4.

(d) The general value of the experiment.

This experiment has shown that certain of the powder properties are related to certain of the sintered properties of hard metal alloys. Some of the correlations are approximately linear and for others there is a high degree of statistical significance among the relations. These could have some practical implications, although there is, in general, a very poor relationship[25] between performance during use and properties; (this probably arises because of the wide variations encountered during the use of hard metal components).

The relation between S_s and $(Hc)_2$ (using favourable sintering conditions) was the best linear relation found. Calculation of the standard error of the estimate for coercivity, i.e. $S_y = \sigma_y\sqrt{1 - r^2}$ (where S_y is the standard error of the estimate, and σ_y is the standard deviation) indicates that in about 3.90% of the cases considered, the values for coercivity will be outside of the range of

FIGURE 6.4 · RELATION OF CRACK LENGTH PER INDENTATION AGAINST AVERAGE GRAIN SIZE FOR ALL SPECIMENS



two standard deviations from the true regression line relating specific surface area of hard metal powder to coercivity of the sintered component. These two properties may be easily measured and are suitable for control purposes, provided constant sintering conditions are used.

Other important considerations arising from the data in Tables IX and X are the importance of dew point of the hydrogen and the sintering temperature. Water vapour present in the sintering atmosphere may exert an influence sufficiently powerful virtually to eliminate any relation between powder and sintered properties: for example, the correlation coefficients for the S_s - $(Hc)_2$ relations were 0.95, 0.06 and 0.87 for 1,370° (low dew point), 1,480° (high dew point) and 1,480°C (low dew point) respectively. Further, as the sintering temperature is raised - (1,480°C is excessive for a 10% cobalt composition) - all the significant correlations become poorer.

Statistical evaluation of results is often used when a large number of variables is involved, as closely controlled experimentation is more or less impossible. Only in a few cases, discussed in (a) above, were closely linear correlations obtained. However, the data in Table X show that a number of the other correlations are statistically significant to a high degree, and could provide a basis for further experimentation, which would assess the influences of different sintering treatments on the inter-relations between powder and sintered compact properties.

The major disadvantages of statistical experimentation are that a number of correlations which appear to be statistically significant may arise in cases where no relationship is expected. Some of these were discussed in (c) above.

6.6 Discussion:

The most important property of the powder which is inter-related with the sintered properties is the specific surface area of the hard metal powder. In view of the precision, noted in Chapter 5, with which this property may be measured, its control during milling is obviously of great importance. The influence of this property seems to overshadow all other properties of the powder such as total carbon, free carbon and cobalt contents (within the levels studied). Specific surface area of the hard metal powder correlates also reasonably well with such properties as sintered grain size and crack length. It is difficult to explain in detail why specific surface area should correlate well with the coercivity of a sintered hard metal compact for, as noted above, the theory of the factors influencing sintered coercivity is not well known. Specific surface area of a hard metal powder is a measure of both the grain size of the carbide particles, and the size of the cobalt grains. From previous results,[23] certain empirical correlations between coercivity, carbide grain size and thickness of binder phase layer are known but the reasons for these correlations are not explained. It is logical to assume that there would be some correlation between specific

surface area of hard metal powder and the sintered carbide grain size, but the correlation with the coercivity is not easily explained, for the coercivity is also a measure of the state of the cobalt phase both with respect to its grain size and structure (i.e. faulting or stresses). The grain size of the cobalt phase in sintered hard metal alloys is practically impossible to determine because a suitable metallographic technique for revealing Co - Co grain boundaries has not been developed,[21] but X-ray diffraction analysis has shown[21] that the cobalt grains are much larger than the carbide grains, and an estimate of 1 mm. for their size has been obtained, i.e. a very large number of carbide grains are embedded in a cobalt grain, and it is assumed that all the cobalt grains are in contact with one another. It is possible that sintering studies of hard metal powders with an electron microscope would yield information on the relation between specific surface area of the hard metal powder and the nature of the cobalt in the fully sintered state.

The uncertainty of the nature of some of the correlations found is a consequence of a lack of detailed knowledge of the mechanism of the sintering process in cobalt - carbide alloys.

6.7 Conclusions:

Linear correlation coefficients between all known hard metal powder and sintered properties have been evaluated. When sintering conditions were such that the furnace exit gases had a low dew point, the specific surface area of the milled hard metal powder was closely

related to the sintered properties: coercivity, crack length, specific surface of the carbide phase in the sintered structure, and the sintered carbide phase grain size.

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CHAPTER 7.

Discussion and Conclusions

7.1 Findings.

The following have been shown:

(1) The milling time required for the satisfactory densification of cobalt - tungsten carbide hard metal alloys during sintering has been shown to depend on the properties of the initial cobalt powder.

(2) The proportions of the two allotropes of cobalt obtained by reduction of black cobalt oxide with hydrogen depend on the reduction time and temperature used.

(3) Milling of cobalt powders has shown:

  (a) Severe agglomeration occurs on milling a pure hexagonal cobalt powder.

  (b) The ease of agglomeration appears to be associated with the initial hexagonal to cubic phase ratio present in the powder provided the material has not been annealed prior to milling.

  (c) Cobalt powders from different sources behave in a different manner on milling, especially with respect to their agglomeration characteristics.

(4) Important inter-relations between the powder properties of cobalt - tungsten carbide mixtures and the sintered hard metal compact properties have been shown.

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

The allotropic modifications of cobalt metal powder produced by the hydrogen reduction of black cobalt oxide in relation to the reduction temperature and time, are in agreement with the results presented by previous investigators;[1] i.e. the hexagonal cobalt modification is produced by reduction at low temperatures, and the hexagonal modification is the stable low temperature form; conversely the cubic modification (which is the stable high temperature form) is primarily obtained by reduction at higher temperatures (600 - 850°C). The proportion of the two allotropes obtained also depends on the reduction time.

The hexagonal cobalt produced by reduction at low temperatures was shown to be faulted, containing stacking faults.

Special precautions must be taken to prevent spontaneous oxidation of the fine grained predominantly hexagonal cobalt powders prepared at a low reduction temperature.

A new finding is that black cobalt oxide can be reduced in hydrogen at temperatures as low as 200°C provided sufficient time is allowed for the reduction. This powder was shown to have the hexagonal structure, but had a strong tendency to be pyrophoric; and very special precautions were necessary for its subsequent examination.

Thus although Owen and Madoc Jones[2] concluded that for fine cobalt powders, the cubic form was preferred, it has been shown here that faulted hexagonal cobalt powder can be prepared with no detectable quantities of the cubic modification.

7.3 The influence of oxygen on the phase structure of cobalt.

It was shown that oxygen does not necessarily stabilise the cubic form of cobalt, for no cubic cobalt was detected in any of the oxidised hexagonal cobalt powders studied.

The finding of Kochanovska[3] that at a certain stage of milling, the cubic modification became stabilised could not be confirmed, and as reported by Hinnuber, Rudiger and Kinna[14] oxygen absorption during milling had no effect on the transformation.

Lassner[4] has proposed that during milling the oxygen content of cobalt powders decreases, but suggested no reasons for this. Indirectly this finding was confirmed in this work. It was stated in Chapter 4 that the initial oxygen content of the Hoboken cobalt powder was 1.16%, whereas the maximum oxygen content of any one of the milled cobalt powder samples was 1.05% (this maximum was, in fact obtained with the Hoboken powder). Similarly, on milling the very fine pure hexagonal cobalt powder, no continuous increase in loss in hydrogen values occurred with increasing milling time, and considerable scatter in the results was obtained.

This confirms that absorption of oxygen into the hexagonal close packed allotrope lattice did not take place. No cubic cobalt was detected in any of the milled hexagonal cobalt samples.

Thus in the milling experiments, oxygen exerted no influence on the cubic to hexagonal phase transformation.

7.4 The influence of titanium.

It was found that titanium exerted a negligible influence on the phase structure of cobalt at the level studied.

7.5 The influence of cobalt from different sources on the cobalt - tungsten carbide powder milling and compact sintering behaviour.

During the milling of tungsten carbide and cobalt powders preparatory to sintering, the cobalt agglomerates and the tungsten carbide grains appear to be beaten into these agglomerates. Thus the initial stages of agglomeration of the cobalt powder are of importance in determining the minimum amount of hard metal vibratory milling required for satisfactory densification to occur on sintering. This initial state of agglomeration explains why the Hoboken hard metal powders and the annealed materials required less milling for satisfactory sintering densification than the less agglomerated materials. Photo micrographs of the materials used were shown in Chapter 4.

It was also shown on hand mixed mixtures that the cobalt powders showing maximum agglomeration yielded the maximum densities on sintering.

Correct grinding is of major importance in determining the densification of hard metal alloys, although other factors such as whether the powder will press to yield a satisfactory green density are also of importance.

The carbide powders must not be agglomerated prior to adding the cobalt powder. In fact premilling of the carbide powder (which causes agglomeration) has been shown[5], [6] to result in poor sintering characteristics for the hard metal alloy.

Thus it may be concluded that poor sintering characteristics for the hard metal alloy powder will result if aggregates of cobalt or carbide are present before sintering. A thin film of cobalt must (as far as possible - depending on the cobalt content of the alloy) separate the carbide grains. These concepts are in agreement with the proposals of Dawihl and Mal[7] considered in Chapter 5.

In addition during grinding of the alloy powder mixtures, there is a continuous increase in the proportion of the ε (hexagonal close packed) cobalt allotrope; with this is associated a change in the coercivity of the material.

All indications in this work were that the cobalt containing higher proportions of hexagonal modification had a stronger tendency to agglomerate

than powders with a lower hexagonal to cubic ratio.

The equation derived by Exner and Fischmeister[8] which describes the speed of shrinkage during sintering of tungsten carbide-cobalt alloys takes account only of the carbide grain size, and not of any parameter (such as the coercivity) which describes the physical state of the cobalt, which, after all, is considered to be of importance in the first stages of sintering.

Factors which have not been considered in this work on the sintering reactivity of hard metal alloy compacts are:

(1) the influence of carbon content of the carbide on the sintering reactivity.

(2) apart from the examples described, the influence of strain in the carbide grains on the sintering reactivity.

(3) the influence of oxygen in the hard metal powder, which has always been assumed to lower[9] the sintering reactivity of metal powders.

(4) the influence of any inhomogeneity within the carbide grains.

In view of all the other variables involved, it would have been extremely difficult to introduce these as well. In the work reported in Chapter 6, however, it was shown that within the carbon and oxygen levels obtained, these parameters exerted little effect. Oxygen can, however, be both in physically and in chemically adsorbed forms in association with hard metal powders. In other metal powders, oxygen can

have beneficial or adverse effects on sintering reactivity.[9], [10]

Some explanation for the variation in the coercivity and specific surface area of a hard metal powder with milling time was given.

7.6 The relations between powder properties and sintered properties for hard metal alloys.

Although the cobalt in hard metal alloys becomes liquid during the sintering process, and the cobalt itself undergoes a phase change (as the binder in sintered compacts is always in the face centred cubic form, unless incorrect heat treatment has been used),[11] certain relations are evident between the powder and sintered characteristics, provided certain precautions are observed in the sintering procedures used. That there is some relationship between powder properties and sintered properties, is characteristic of powder metallurgical products, as opposed to those produced by casting or fusion, for example.

It is important to understand these relationships so that cemented carbide alloys may be tailored for particular applications. As discussed in Chapter 6, relationships between the parameters and their interaction effects represents the only way in which any type of model for the sintering of hard metal alloys may be built up, because of the large number of variables involved. The most significant of these

relationships is that between the specific surface area of the hard metal powder and the coercivity of the sintered product.

The finding that as the sintering conditions become less favourable for the attainment of ideal properties (e.g. 1480°C which is excessive for a 10% cobalt material, or a high dew point of the exit gases), the relations between the parameters become less satisfactory, is of significance in showing the importance of these variables in sintering. In a series of experiments,[12] where a series of milling trials were carried out, and the samples sintered under nominally identical conditions, but in different runs on different days over a two month period, a very poor linear correlation (correlation coefficient 0.38) was found between the coercivity of the powder and the coercivity of sintered compacts. Thus the sintered properties of hard metal compacts are considerably influenced by the sintering conditions used, and all indications are that a large statistical experiment, similar to the one described here, should be carried out on samples of the same material, but using the conditions of sintering, i.e. time, temperature, atmosphere and packing material, as the variables. An experiment of this type must be carried out to obtain a unified model for tungsten carbide. Evidence has been presented here of the marked influence of dew point of the exit gases on the

properties of the sintered product.

7.7 Conclusions.

As is well known, cobalt powders from widely different sources can have wide variations in proportions of the hexagonal and cubic allotropes present.[13]

Cobalt powders from different sources have been shown to be of importance in the milling of hard metal alloys in relation to the amount of milling required for satisfactory densification of the compacts during sintering.

The transformation from cubic to hexagonal cobalt can be regarded as a process of simple shearing, and even very slight cold working such as screening, can cause a partial transformation. There is a close structural inter-relationship between the face centred cubic and hexagonal close packed forms.

For cobalt required in powder form, the distinct phases can be prepared by control of the reduction temperature and time; however, there is a broad temperature range above the transition temperature where both phases can co-exist in varying proportions.

Thus all samples of cobalt powder can be considered as mixtures of the two allotropes depending on their previous thermal and mechanical history.[13]

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THE $\alpha \rightleftharpoons \varepsilon$ TRANSFORMATION IN COBALT WITH PARTICULAR REFERENCE TO THE USE OF COBALT IN CEMENTED CARBIDES

VOLUME (II)

The Grinding of Cobalt Metal Powders

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

G.J. Rees B.Sc (Hons) (Rand)

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.



G.J. Rees

August 1972

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PREFACE

Extensive research work was carried out on the $\alpha \rightleftarrows \varepsilon$ transformation in cobalt with particular reference to the use of cobalt in cemented carbides, which constitutes Volume I of this thesis. Following the change of the candidate's registration from the degree of M.Sc. (Eng.) to the degree of Ph.D. considerable additional work on the original project was carried out. The results of this further work are incorporated in this second volume, which is devoted mainly to the processes which occur during the grinding of cobalt metal powders.

THE α ⇌ ε TRANSFORMATION IN COBALT WITH PARTICULAR REFERENCE TO THE USE OF COBALT IN CEMENTED CARBIDES

VOLUME II

The Grinding of Cobalt Metal Powders

SUMMARY

Experimental evidence and theoretical considerations indicate that the behaviour on grinding of cobalt powders with different initial proportions of the hexagonal and cubic phases is governed primarily by the crystal structures of the two allotropes of cobalt. The importance of the presence of dislocations on the processes which can occur during the grinding of cobalt powders is discussed; it is suggested that "pile ups" of dislocations may be responsible for the "cold-welding" process. Some modifications to the grinding process can result from the presence of oxide films on the powder particles. Experimental evidence suggests that during grinding in commercial acetone the oxide films react chemically with the grinding fluid. It is suggested that several olefinic compounds are formed by the chemical reaction, and the compounds formed are adsorbed on the metal powder particles during the later stages of grinding.

The processes which take place during grinding are discussed in terms of the free energy changes which occur. It was found that several of these findings have important applications in the manufacture of hard metal alloys. A major limitation of the work is that it was not possible to study the internal structure of the cobalt metal particles.

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THE GRINDING OF COBALT METAL POWDERS

(1) INTRODUCTION

In Volume I it was shown that agglomeration of cobalt powder particles during wet grinding was an important requirement for satisfactory sintering characteristics of hard metal alloy powders. From the evidence provided by electron micrographs it was suggested that the brittle tungsten carbide grains become embedded in the cobalt agglomerates during hard metal milling.

Grinding studies on pure cobalt powders revealed that certain powders had a stronger tendency to agglomerate during the initial stages of milling than did others. Hard metal balls were used as the grinding medium, and acetone as the milling fluid. It appeared that the proportions of hexagonal close packed and face centred cubic allotropes of cobalt present in the initial powder exerted a significant influence on the agglomeration characteristics during the first stages of grinding. Cobalt powders with a higher proportion of the h.c.p. phase present (in the initial powder) showed an increased tendency to agglomerate during the initial stages of grinding compared with powders which were predominantly cubic in structure. The nature of the agglomerates formed in cobalt powders with different initial allotropic ratios was not discussed.

The aim of the present work was to assess the possible reasons for the agglomeration behaviour of different cobalt powders during grinding, and discuss the nature of the agglomerates formed. The earlier data are summarised, and the possible processes which can occur during the grinding of cobalt powders are discussed.

From a consideration of these processes and some additional experimentation, possible reasons for the different grinding behaviour of cobalt powders are suggested.

The ground powders were examined by electron microscopy; a Cambridge Stereoscan Microscope and a Philips EM 200 transmission Microscope were used. The X ray diffraction data obtained on the cobalt powders studied previously were re-examined, and some information was obtained regarding the occurence of dislocations.

2. SUMMARY OF PREVIOUS RESULTS

A number of fine commercial cobalt powders differing in initial specific surface area and in the proportions of the h.c.p. and f.c.c. phases were vibratory milled in a stainless steel ball mill of 800 ml. capacity. 300 ml. of chemically pure acetone was used in each case as the milling fluid, and 2 Kg of hard metal balls (6 mm in diameter) as the grinding medium.

The only significant impurity present in the acetone was water, which did not exceed 0.5 per cent by volume as determined using the Karl Fischer technique, which has been adequately described [1],[2],[3],[4].

Small samples (8g) of the ground cobalt powders were removed from the mill after various milling intervals. The samples were dried on a water bath under reduced pressure to remove the acetone.

The specific surface area of each ground sample was determined using a modified B.E.T. technique on a Perkin Elmer 212D Sorptometer. The proportions of the two allotropes of cobalt present in the samples were determined by X ray diffraction analysis using a Philips PW 1060 Diffractometer and application of the equation of Sage and Guillaud [5].

The variations in powder properties were plotted graphically against the milling time. For powders which initially consisted of a mixture of the two allotropes of cobalt it was found that the specific surface area decreased during the initial stages of grinding. Evidence for the occurence of agglomeration was provided by the Cambridge Stereoscan photomicrographs of the ground materials. The morphologies of the initial powders were also examined on the Scanning Microscope.

A study was made of the grinding of a fine cobalt powder prepared by hydrogen reduction of cobaltosic oxide at 400°C, which showed no traces of the cubic modification. On milling this powder a continuous decrease in specific surface area was noted up to 90 hours of grinding; after this period there was a steady increase in specific surface area of the ground metal.

The milling of two annealed powders which initially contained both allotropes of cobalt was investigated. These powders showed no decrease in specific surface area during grinding and a continuous increase in this powder property was noted with increasing milling time. The behaviour of the annealed cobalt powders may be seen by reference to Figure 4.17 of Volume I.

The X ray diffraction results on the ground powders showed that the proportion of the hexagonal phase increased with grinding time for those powders which initially contained a mixture of both allotropes. No cubic cobalt was detected in any of the ground samples of the fine powder which consisted solely of the hexagonal modification initially.

Table 2.1. summarises the initial properties of the cobalt powders together with the properties at the states of maximum agglomeration, and the grinding times necessary to achieve this condition.

TABLE 2.1

SUMMARY OF INITIAL COBALT POWDER PROPERTIES AND AT STATES OF MINI

COBALT POWDER NUMBER	INITIAL PROPERTIES				AGGLOMERATED PI		
	(1) S_S M^2/G.	(2) ALLOTROPIC RATIO	(3) O_2%	OBSERVATION ON SCANNING ELECTRON MICROSCOPE.	(4.) COERCIVITY OERSTED	(1.) S_S M^2/G.	(2) ALLOT RATI
CF — 6 POWDER	1·25	0·35	0·74	POWDER PARTICLES HAD RELATIVELY SMOOTH SURFACES & WERE GENERALLY ROUNDED IN SHAPE LITTLE EVI — DENCE OF SURFACE ROUGNESS A FEW AGGLOMERATES PRESENT.	150	0·90	2·6
HOBOKEN COBALT POWDER(GRINDING OF THIS POWDER WAS REPEATED)	1·53	0·70	1·16	LARGELY AGGLOMERATED IN THE INITIAL CONDITION, ELEMENTARY PARTICLES APPEARED TO CONSIST OF LONG FILAMENTS.	130 (125)	1·05 (1·25)	2·1 (2·0
FINE H.C.P POWDER PREPARED AS DESCRIBED IN VOLUME I	2·82	NO CUBIC PHASE DETECTED	1·63*	VERY FINE POWDER WITH PARTICLES LESS THAN ½ μ IN SIZE PARTICLES GENE — RALLY ROUNDED. DISPERSION DIFFICULT BECAUSE OF FINE PARTICLE SIZE.	261	0·97	NO CL COBA OR C OXIDE TECT
ANNEALED HOBOKEN COBALT POWDER.	1·07	0·77	0·62	POWDER WAS MORE AGGREGATED THAN THE UNAN — NEALED MATERIAL FILAMENTARY NATURE OF ELEMENTARY PARTICLES CLEARLY VISIBLE	NO EVIDENCE OF ANY GRINDING.		
ANNEALED CF — 6 POWDER.	0·96	0·45	0·41	POWDER PARTICLES SEVERELY AGGREGATED TO FORM LARGE GENERALLY ROUND UNITS. SOME PARTICLES SHOWED EVIDENCE OF THERMAL SINTERING DURING ANNEALING.	NO EVIDENCE OF ANY AG		
CF—10	1·32	0·22	0·53	THIS POWDER WAS FINER THAN THE CF-6 POWDER, POWDER PARTICLES HAD SMOOTH SURFACES AND WERE GENERALLY ROUNDED IN SHAPE.	184	1·20	3·9

NOTES :—

1. SPECIFIC SURFACE AREA AS MEASURED ON PERKIN ELMER 212D SORPTOMETER.
2. RATIO OF HEXAGONAL TO CUBIC PHASE PRESENT.
3. OXYGEN CONTENT OF POWDERS.
4. COERCIVITY MEASURED AS DESCRIBED ON PAGE 77 OF VOLUME I

* LOSS IN HYDROGEN VALUE

TABLE 2:1

POWDER PROPERTIES AND AT STATES OF MINIMUM SPECIFIC SURFACE AREA

	AGGLOMERATED POWDER PROPERTIES.				GRINDING TIME TO REACH MINIMUM S_S (HRS.)
ON ON SCANNING I MICROSCOPE.	(4) COERCIVITY OERSTED	(1) S_S M^2/G	(2) ALLOTROPIC RATIO	OBSERVATION ON SCANNING ELECTRON MICROSCOPE.	
ARTICLES HAD RE MOOTH SURFACES ENERALLY ROUN- PE LITTLE EVI — SURFACE ROUG - W AGGLOMERATES	150	0·90	2·60	EVIDENCE OF COLD WEL- DING, SOME EVIDENCE OF FINE PARTICLES EM-- BEDDED IN THE AGGLO- MERATES	20
GGLOMERATED IAL CONDITION, Y PARTICLES AP- CONSIST OF MENTS.	130 (125)	1·05 (1·25)	2·10 (2·05)	THE TYPE OF AGGLOME- RATES FORMED WAS NOT EXAMINED	10 (10)
POWDER WITH LESS THAN ITICLES GENE — UNDED DISPER- ULT BECAUSE OF CLE SIZE	261	0·97	NO CUBIC COBALT OR COBALT OXIDE DE- TECTED.	OBSERVATIONS WERE MADE AFTER 10, 20 & 30 HRS. OF GRINDING SOME EVIDENCE FOR COLD WELDING AFTER 10 & 30 HRS. CONSIDERABLE EVIDENCE OF INDIVIDUAL PARTICLES PRESENT IN THE AGGLOMERATES ESPECIAL- LY AFTER 20 HRS GRINDING	90
AS MORE AGGRE- IN THE UNAN — TERIAL FILAMEN- RE OF ELEMEN- GLES CLEARLY	NO EVIDENCE OF ANY AGGLOMERATION DURING GRINDING.				—
RTICLES SEVERE- TED TO FORM ERALLY ROUND E PARTICLES VIDENCE OF SINTERING NNEALING.	NO EVIDENCE OF ANY AGGLOMERATION DURING GRINDING				—
DER WAS FINER CF-6 POWDER; PARTICLES HAD URFACES AND ERALLY ROUNDED	184	1·20	3·90	AFTER 50 HRS. GRINDING PARTICLES HAD SMOOTH SURFACES FINE PARTICLES WERE EVIDENT AFTER 70 HRS. OF GRINDING.	30

IN ELMER 212 D SORPTOMETFR.
IT.

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Observations on the morphologies of the initial and agglomerated conditions are also summarised in the Table.

Noteworthy from these data is that the ease of agglomeration during the initial stages of grinding appears to be associated with a high ratio of hexagonal to cubic allotropes present in the initial powder. A correlation between ease of agglomeration and initial oxygen content is also discernible. This is discussed further later.

After agglomeration the specific surface area increased with further milling in a manner similar to that shown by the grinding of many "real crystal" materials.[6]

With the exception of the powder supplied by Societe du Metallurgie du Hoboken the scanning photomicrographs revealed that the original powder particles were rounded and had smooth surfaces.

The presence of fibrous particles in the Hoboken Cobalt suggested that this cobalt had been prepared by the hydrogen reduction of cobalt oxalate, on the basis of previous work.[7] The tendency of cobalt oxalate to yield fibrous particles on hydrogen reduction was confirmed by reducing 100 g of B.D.H. chemically pure cobalt oxalate at 400°C for four hours. This powder contained no traces of the f.c.c. modification.

The powder was examined on the Stereoscan Microscope; a considerable number of fibrous particles were evident; two samples of this powder are shown in Figure 2.1. and Figure 2.2. It is suggested therefore that the process of reduction proceeds through different mechanisms in the case of cobalt oxalate from that in cobalt oxide. Hydrogen reduction of cobalt oxide yields rounded smooth metal powder particles, with no fibrous particles.

The agglomerated ground Cobalt powders were examined on the Stereoscan Microscope: a number of smooth surfaces indicative of the occurence of "cold welding" (this term is discussed in detail later) were evident in the agglomerates; in addition a number of areas were visible where smaller particles had become bonded to one another. After extended milling periods the scanning photomicrographs revealed that considerable size reduction had occured and the individual metal particles had very smooth surfaces.

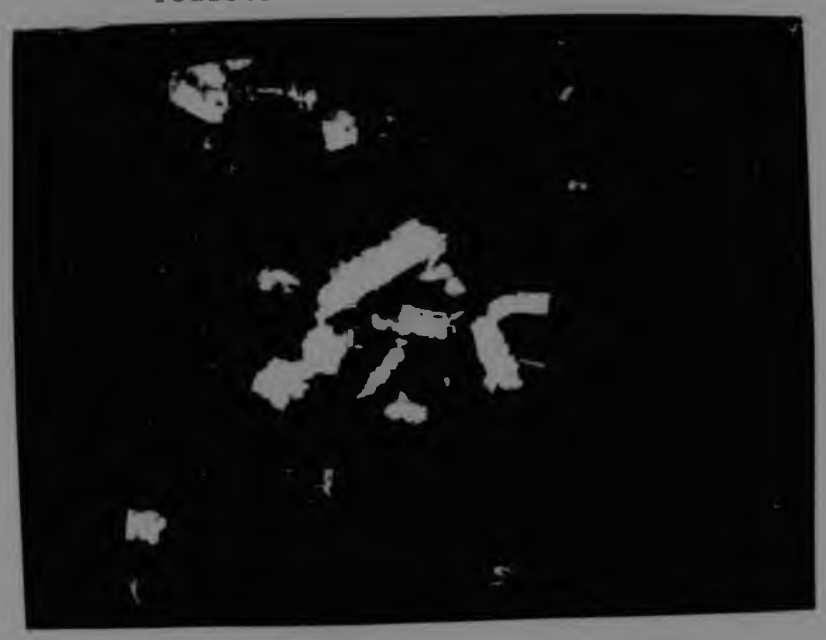
It was suspected that chemical reaction between the metal powder particles and the acetone occured during grinding. For the one powder thoroughly studied the carbon content of the ground material increased with increasing milling time. In addition, studies with a Stanton thermobalance suggested that a residue was present in the ground powders after vacuum drying. This residue could be removed by heating in hydrogen.



x 1000

FIGURE 2.1.

Cobalt metal powder prepared by reduction of cobalt oxalate



x 2000

FIGURE 2.2.

Cobalt metal powder prepared by reduction of cobalt oxalate

The major part of the weight loss on heating in hydrogen occured in the temperature range 20° to 200°C. This finding considered together with other evidence on the reduction of cobaltosic oxide suggested that the weight loss was not due to the reduction of oxide; it was suggested that the weight loss could be due to the desorption of strongly bound acetone or other chemical compound or due to the loss of free carbon from the metal powder in the form of a hydrocarbon with the cobalt metal acting as a catalyst.

A detailed X ray study using a line breadth technique was carried out on a number of ground samples arising from the same initial cobalt powder after different milling times. The cobalt metal powder consisted initially of a mixture of the f.c.c. and h.c.p. phases. The results showed that a rapid increase in stress occured during the first 30 hours of grinding. The cyrstallite size of the cobalt decreased as grinding proceeded. The stacking fault probability in the h.c.p. phase was found to be a maximum after 10 hours of grinding. After this period further milling resulted in a decreased probability for the occurence of stacking faults in the h.c.p. phase. Some erroneous conclusions were drawn from these X ray data; this is discussed later together with an analysis of the value of the information that can be obtained from X ray diffraction studies of powders.

The oxygen content of the ground samples increased with increasing milling time, but considerable scatter was evident in the experimentally determined results.

No oxides of cobalt were detected in the ground materials using X ray diffraction analyses. The limit of detection using the technique applied is about 4 %.[8] The oxygen levels of the ground samples were all considerably below this detection limit; however, since cobalt is a strongly electropositive metal it is likely that some oxides of cobalt were present in the powders after grinding. Although the presence of oxygen was found to exert no influence on the cubic to hexagonal allotropic conversion occuring during grinding, oxide films present on the metal particles could reasonably be expected to exert some influence on the grinding process; it is therefore necessary to consider the possible influence of these oxide films on the grinding behaviour.

In general the variations in surface area during grinding may be summarised as follows:-

(a) For the commercial cobalt powders - the specific surface decreased during grinding with the grinding time necessary to obtain the minimum specific surface area generally correlated with the allotropic ratios of the initial powders, i.e. the predominantly hexagonal powders reaching this minimum specific surface area after a shorter grinding time than the predominantly cubic powders.

After the minimum specific surface area had been reached, further grinding resulted in an increase in specific surface area. The annealed cobalt powders also showed this behaviour; the annealing treatment decreased the specific surface area and caused the powders to agglomerate; on milling these powders no further decrease in specific surface area was observed - a continuous increase in specific surface area with grinding time was obtained.

(b) For the fine powder which showed no traces of the cubic modification a decrease in specific surface area up to 90 hours of milling was observed.

Some noteworthy differences in the nature of the agglomerates were evident in the different ground powders; in the agglomerates originating from a predominantly cubic cobalt powder (e.g. CF - 6 O_2 0.74 %, allotropic ratio $I_{(10\bar{1}1)}/I_{(200)}$ 0.38, shown in Figures 4.5 and 4.6) there is little evidence of particles within the agglomerate of sizes similar to those present in the initial powder (Figure 4.7), whereas the agglomerates produced during grinding of fine hexagonal cobalt powder (O_2 1.63 %, Figure 4.14) show considerable evidence of fine particles within the agglomerates. The probable reasons for this behaviour are discussed later. The predominantly cubic cobalt powders yielded agglomerates which were "coherent" with no evidence of fine particle boundaries. In the previous volume it was shown that agglomeration of the cobalt powder was a necessary requirement for achieving satisfactory sintered hard metal compact densities.

The data shown in Table X of Chapter 5 indicated that the most agglomerated cobalt yielded the highest compact density in a series of compacts which were prepared by hand mixing. This fact together with the results of the other investigations suggested that the superiority of predominantly hexagonal cobalt powders in yielding higher sintered compact densities compared with predominantly cubic cobalt powders was connected with the interaction between the cobalt and carbide particles during grinding, and was not connected in any way with the behaviour of the cobalt during heating to the sintering temperature. In other words, the previous work suggested that the superiority of predominantly hexagonal cobalt powders was connected with its ability to become more intimately dispersed around the asperities of the carbide grains in a shorter grinding time than predominantly cubic cobalt powders.

Recently, Jung (9) has shown that on heating a pressed hard metal compact to the sintering temperature all the cobalt in the compact has transformed to the f.c.c. form at a temperature of 600°C during the heating cycle. This evidence confirms that the conclusively proved superiority of hexagonal cobalt powder in reducing the grinding time required for satisfactory sintering-densification is not connected with the behaviour during sintering, but must become manifest during the grinding process itself. This suggests that hexagonal powders become more intimately dispersed throughout the carbide powder during milling than is the case with predominantly cubic cobalt powders.

3. SURVEY OF METAL PARTICLE COMMINUTION

3.1. INTRODUCTION

The main aim of the present work was to explain the findings described in the previous section; in particular the reasons were sought for the differences in agglomeration characteristics of different cobalt powders during the initial stages of milling. Some explanation for the type of bonding in the agglomerated cobalt powders was required.

During grinding the particles of the material being comminuted are subjected to a variety of forces, e.g. compressive, impact and torsional forces. In addition the particles are abraded against one another. Thus consideration of the mechanical properties of the material being ground is important. The influence of crystal imperfections in the material must be considered. The adhesional characteristics of the metal powder being ground would influence the course of milling. Contaminant films on the surfaces of the particles could exert an effect on the grinding behaviour. The role of the grinding fluid must be considered. In addition the factors which can operate in systems of very fine particles must be described and evaluated.

A number of the physical processes which can occur during comminution are influenced by the temperature of operation within the grinding mill.

The temperature distribution within a mill during grinding may be approximately evaluated by measurement of the outside wall temperature of the mill and consideration of a heat transfer model. The calculations are shown in Appendix 1. The model is somewhat idealised in that it is assumed that the grinding balls are confined to a cylindrical region about the centre line of the mill, and that the cylinder containing the balls constitutes a heat generating source. It is assumed that an annulus of acetone surrounds the heat generating source, within which there is an annulus which contains the cobalt powder. Convective heat transfer is assumed in the acetone, and conductive heat transfer within the cobalt powder. The temperature distribution is assumed to be symmetrical about the horizontal centre line of the mill. The calculations shown in Appendix 1 indicate that the temperature at the edge of the heat generating source is approximately 134°C; the cobalt powder is at a temperature of approximately 91°C, and the mill wall temperature is about 60°C. The model indicates that 8210 calories (34,48 k joule) of heat are transferred to the ambient atmosphere per hour.

It is not possible to carry out calculations to see whether the temperature distribution within the mill derived in Appendix 1 is realistic.

In the case of rotary ball mills, Davis[10] has developed equations which describe the motion of the balls within the mill, and a relationship between the number of ball collisions and the time of grinding was obtained. In the case of a vibratory ball mill the path of motion of the ball charge within the mill is thought to be very complex and is not well understood[11]. No relation for the number of collisions which occur in unit time within a vibratory ball mill has been derived. Ivensen et al[12] have derived an approximate expression for the distance that a hard metal ball moves up the wall of the mill before it is forced away from the wall. Using this expression the calculations shown in Appendix 2 indicate that a grinding ball moving away from the side of the mill will collide with a stationary ball at the lowest point in the mill with a velocity of 114.60 cm/sec. Using this velocity the energy dissipated in a ball collision may be evaluated; as shown in Appendix 2 the energy dissipated in such a collision is 8.12×10^{4} ergs ($8,12 \times 10^{-3}$ joules or 1.95×10^{-3} calories). However the number of ball collisions in unit time cannot be evaluated and thus it is not possible to compare the total energy dissipated in ball collisions with the heat flux derived in Appendix 1. As was discussed in Volume I[13], it is usually assumed that the grinding time required to achieve a given specific surface area in a powder in a vibratory mill is about 1/6th of that required in a rotary mill (assuming that the milling is carried out in the same fluid in both cases).

However it is not possible to compare a vibratory ball mill with a rotary ball mill operating at a very high rotational speed, as no increase in the milling rate in a rotary ball mill occurs if the rotational speed is increased above a certain value unless the gravitational constant is also increased[14]. In a conventional rotary mill, a primary limitation of the obtainable milling rate is that the gravitational constant cannot be increased.[14] Thus although vibratory and rotary ball mills may be approximately compared with respect to the rates of surface area generation, it is not possible to compare the rates of energy dissipation. The motion of the grinding balls within a vibratory ball mill is not clearly understood, and for this reason the validity of the total heat flux passing through the mill walls, as shown in Appendix 1, cannot be evaluated.

During grinding the metal powder particles are impacted by the balls, and in order to understand the deformation behaviour of the metal powder, some idea must be derived of the order of magnitude of the shear stresses acting on the cobalt metal particles. The pressure generated at the instant of impact between two bodies in an elastic collision may be calculated by the Hertz equations[15]. Appendix 3 indicates that the pressure generated by two impacting hard-metal balls (one stationary, and the other moving with a velocity of 114.60 cm/sec.) is approximately 2.3×10^{11} dynes/cm^2 (i.e. $2,3 \times 10^{10}$ N/m^2), assuming the Hertz relation.

The pressure generated in a collision where there is permanent plastic deformation (e.g. collision between a cobalt powder particle and a hard metal ball) cannot be calculated by the Hertz equation, because two assumptions of the Hertz theory are not fulfilled, namely:

(i) The material in collision is isotropic and homogeneous.

(ii) There must be no plastic flow of either of the colliding bodies.

However Tabor [16] has extended the Hertz theory to cases where a collision results in permanent plastic deformation of the bodies. In order to apply Tabor's theory, the dynamic flow pressure of cobalt must be known. This has apparently not been reported in the literature and thus in Appendix 3, where Tabor's equation is applied to an impact between a cobalt particle and a grinding ball, a value of 50,000 p.s.i. (i.e. $3,448 \times 10^8$ N/m^2) has been assumed for the dynamic flow stress of cobalt, which is similar to the values reported for a number of other ductile metals [17]. Tabor's tneory shows that the pressure on a cobalt particle is approximately 10^{15} dynes/cm^2 (10^{14} N/m^2). Comparison of the pressure generated at the instant of impact between two colliding grinding balls and the pressure given by Tabor's method with the reported compressive yield strength for cobalt of 2.95×10^9 dynes/cm^2 [18] indicates that plastic deformation of the cobalt will result from particle-ball collisions during grinding.

The inability to resolve the doublet during X ray diffraction analysis of the cold worked powders, noted in the previous work,[19] confirms that plastic deformation occurs during grinding. Due to the plastic deformation, it is not possible to calculate with any accuracy the shear stresses acting on the individual cobalt particles during grinding. In subsequent calculations therefore, where the order of magnitude of the shear stress is required, it has been assumed that the applied shear stress is approximately one half of the applied pressure generated by the colliding balls, i.e. $\sim 1 \times 10^{11}$ dynes/cm^2 (1×10^{10} N/m^2). In view of the uncertainty of the dynamic flow pressure for cobalt, the pressure given by Tabor's theory has not been considered further.

During grinding, it is probable that a very complex stress distribution is exerted on the powder particles. The stress distribution would probably vary with position within the powder mass. The variation of the stress distribution would be difficult to evaluate unless a simple model with restraints differing considerably from a practical situation were assumed. Stress unloading and reloading processes will occur while the particles are in contact with one another which are additional complications.

The important conclusion is, however, that the stresses generated by the impacting grinding balls are of sufficient magnitude to cause irreversible plastic deformation within the cobalt particles, by conversion of the kinetic energy of the balls into a permanent distortion of the structure of the metal particles. A certain proportion of this converted kinetic energy will remain stored within the metal powder particles, as is shown later.

Thus with the approximate temperature distribution in a mill during grinding established, together with an approximate value of the applied shear stress, it is possible to review the factors which could explain differences in milling characteristics of different cobalt powders.

3.2. DEFORMATION AND FRACTURE CHARACTERISTICS OF METALS AND THE MECHANICAL PROPERTIES OF THE ALLOTROPES OF COBALT

One feature characterises all the types of fracture that can occur in metals: the nucleation of fracture arises as a result of inhomogeneous plastic deformations in regions of microscopic dimensions. (20)

In the case of low temperature brittle fracture, the inhomogeneity can arise from twinning or slip band formation; with fatigue fracture, deformation becomes localised to a few slip bands as a result of the strain hardening process occuring under cyclic loading.

For the ductile mode of fracture, the localisation of plastic deformation either at non plastic particle inclusions, or in heavy deformation bands initiates the fracture process. Fracture processes which result from very rapid deformations e.g. adiabatic shear fracture and effects produced by compression waves[21], are unlikely to occur during comminution and need not be considered further. A number of mechanisms have been proposed for different fracture processes in various metals and alloys. A survey of the literature indicates considerable disagreement as to the exact mechanism by which the various characteristic fracture patterns are nucleated in different materials.

The predominant type of fracture mechanism which occurs in cobalt has not been specifically discussed in the literature. From general consideration of the characteristics of cobalt, it would be expected that low temperature brittle fracture, ductile fracture and fatigue fracture could occur under various conditions.

F.c.c. cobalt in common with other f.c.c. metals has theoretically 12 possible operative slip systems which permit deformation under an applied load. However it is likely that the slip which occurs during deformation will be chiefly associated with the 3 primary glide systems[22], as a consequence of the low stacking fault energy.

In hexagonal cobalt, three slip systems are possible theoretically; the chief mechanism operative at a low temperature will be slip on the basal plane i.e. (0001) $\langle 11\bar{2}0 \rangle$.[23] This single slip system is predicted theoretically at room temperature by the anisotropic elasticity theory of dislocations,[24] and is expected in h.c.p. cobalt because the c/a ratio of 1.623 is close to the value of 1.633 which is predicted for ideal h.c.p. stacking,[23] and for which only basal slip is anticipated. This single slip system in h.c.p. cobalt provides for limited slip behaviour and therefore deformation. In practice therefore f.c.c. cobalt has 3 operative slip systems, and h.c.p. cobalt has only a single slip system.

According to the von Mises' criterion,[25] 5 independent slip systems are required for crystal to undergo general plastic deformation by slip. When a polycrystal is deformed, a grain within it is constrained to deform generally. If 5 independent slip systems are not available, other modes of deformation may become operative. Apart from fracture and slip, twinning is a favoured mode of deformation, more especially where the number of glide systems is limited, as is the case in both allotropes of cobalt.[26]

The tendency towards deformation twinning increases with decreasing stacking fault energy.[27]

Jaswon and Dove's[28],[29],[30] inequality procedure predicts that twinning should occur on the {111}, {100} and {101} planes of f.c.c. metals, with the closest packed {111} planes having the minimum twinning shear, namely $|s| = \frac{1}{2}$ and in addition requiring no atomic shuffles for twinning. In practice twinning on {111} of f.c.c. metals is observed but not on the other two planes. In h.c.p. cobalt the observed twinning planes are $\{10\bar{1}2\}$ with $|s| \neq 0.138$ and the $\{11\bar{2}2\}$ and $\{11\bar{2}4\}$ both with $|s| = 0.112$.[27]

The mechanism for the nucleation and growth of twinned structures in different metals does not appear to be well understood. Several mechanisms for twinning have been proposed, and the following summarise the important conclusions regarding this mode of deformation:

(1) Energy considerations indicate that spontaneous nucleation of twins in f.c.c. structures would be unlikely.[27]

(2) Cotrell and Bilby's[31] theory of twinning, which is so successful in explaining twinning in b.c.c. structures can explain twinning in f.c.c. structures only if a thick ($\sim$ 50 atom) twin nucleus is assumed to be initially present.

(3) Although Venables[32] has developed a theoretical mechanism by which twins can be nucleated from a single stacking fault, it is thought that in practice twins do not form from a single stacking fault.[27]

Although the existence of a critical stress for twinning is doubted by some workers,[27] the critical stress for twin nucleation according to Venables' theory[32] would be

$$\sigma_c = \gamma_{sf}/b$$

where σ_c is the critical stress for twin formation

γ_{sf} is the stacking fault energy

b is the Burgers vector

σ_c is also the critical stress required for the formation of a stacking fault.

(4) Oliver[58] has suggested that macroscopic twinning arises from twin nuclei introduced during crystal growth processes i.e. twins cannot result solely from deformation processes.

(5) In general terms previous plastic deformation is a necessary requisite for twinning, and the energy to form a twin must come from an aggregate of slip dislocations.[27]

(6) When twinning is caused by an external stress, it is necessary that the applied stresses do work during the formation of the twin, i.e. the shear stress across the twinning plane and resolved in the shear direction should be positive. It is thought that the magnitude of the critical shear stress for twinning varies with the purity and perfection of the crystals.[27]

(7) O'Neill[34] originally noted that the majority of metals which exhibit low temperature brittle fracture also deform by mechanical twinning. He suggested that twin deformation might be responsible for crack nucleation, i.e. a form of twin induced crack nucleation might be operative.

There is some evidence that for certain metals local cracks may be induced in areas of twin termination, but there is no conclusive evidence that complete fracture arises from twin formation.[27] It is probable that the stresses required for twin nucleation are of the same magnitude as those required for crack initiation.[27]

(8) As discussed later and as a consequence of the characteristics of dislocation motion in cobalt, twins provide sites for dislocation pile ups and consequently for fracture nucleation.[20] In addition, intersection of glide dislocations with twin boundaries may produce "twinning dislocations" thus propagating deformation by twinning.[27]

(9) The literature on twinning, although fairly extensive, suggests no conclusive mechanism for twin formation. Deformation twinning is expected in both allotropes of cobalt because of the limited number of operative glide systems.[26]

The situation during the grinding of metal powders is very complex because of the non uniform direction of application of the stresses. Deformation may occur by slip, twinning or fracture depending only on which crystallographic direction is most favourably oriented relative to the stress direction, and on the resistance to the various mechanisms.[35]

In order to thoroughly understand the deformation and fracture characteristics of the allotropes of cobalt, it is necessary to consider the importance of the dislocations initially present in the reduced cobalt metal powders, and the behaviour of these dislocations under the influence of the applied stresses, which arise during the milling of the powders. The importance of dislocations introduced during grinding must also be assessed.

The cobalt powders used were prepared by hydrogen reduction of oxide at elevated temperatures, followed by rapid cooling to room temperature. As a result of the quenching process the powder particles may contain more vacancies at room temperature than the thermal equilibrium concentration.[36] The vacancies may also yield stacking fault tetrahedra arising from the collapse of vacancy discs.[37] Electrical resistivity[38],[39] and magnetic after effect measurements[40],[41] on cobalt specimens indicate that these vacancies may have considerable mobility at low temperatures (< 200°K). Annihilation of distant Frenkel pairs, and divacancy formation were thought to be the chief processes arising from the low temperature mobility of vacancies.[38] A certain proportion of dislocations will also be present in the reduced powders. These dislocations can adsorb vacancies and new dislocations can be generated from interaction of the vacancies with the dislocations. In particular Bardeen-Herring vacancy sources[42] would be expected to nucleate a number of dislocation loops; the vacancies exert a force of approximately $\mu b/10$ on dislocations, where μ is the shear modulus of the metal and b is the Burgers vector of the dislocation.[43]

A thermodynamic method has been evaluated by Mc Lennan [44], by which the energy of formation of monovacancies in metals may be calculated. The calculated values are in good agreement with those derived experimentally using electrical resistivity, thermal emf, specific heat and magnetisation techniques for a number of metals. A calculation shown in Appendix 4 indicates that the energy required to form a monovacancy in cubic cobalt is 23.3 k cals/g atom (97,86 k joules/g atom), assuming published values of Young's modulus and Poisson's ratio. However anisotropic values of the energy of formation of a monovacancy would be expected in f.c.c. cobalt, as in common with other f.c.c. metals, Young's modulus is a maximum in the <111> direction, and a minimum in the <100> direction [45].

In addition in the Mc Lennan calculation [44], there are uncertainties in f (the fraction of the volume of the solid per atom) and r_a (the atomic radius). In spite of these uncertainties, the thermodynamic method should yield values for the energy of formation of a monovacancy, which are of the correct order of magnitude, in view of the agreement between predicted and experimental values found for other metals. No experimental values for the energy of formation of a monovacancy are available for cobalt in the literature. The values calculated here compare favourably with chose derived using Mc Lennan's theory for Copper (27.4 k cals/g atom) and Nickel (36.7 k cals/g atom) [44].

The calculations shown in Appendix 4 indicate the energy required for the direct formation of monovacancies in cobalt, and the energy released when a monovacancy is annihilated. In view of the large energy of formation of a monovacancy, the direct introduction of vacancies during grinding would be unlikely. Vacancies could be produced from dislocation interactions as discussed later.

In Volume 1 it was suggested[46] that the volume change which occurs during reduction from oxide to metal resulted in deformation of the metal powder, and as a consequence stacking faults were produced in the metal powders. X ray diffraction analyses of the powders provided conclusive evidence that stacking faults were present in the reduced powders. The proportions of growth and deformation stacking faults in the h.c.p. phase could, however, not be separately determined because of the overlapping of certain of the X ray diffraction lines, but it was suggested that deformation stacking faults would be predominant. These stacking faults would be surrounded by very stable partial dislocations[47]. The stacking fault energy in both allotropes of cobalt is particularly low; in f.c.c. cobalt at room temperature the stacking fault energy is about 30 ergs/cm2 (3×10^{-2} joules/m^2).

This energy is about twice that of a twin boundary which has been found to be about 12.7 ergs/cm^2 (1,27 x 10^{-2} joules/m^2) for f.c.c. cobalt.[49] The central force bond model of a metal[50] predicts that the stacking fault energy should be twice the twin boundary energy. Thus in the case of f.c.c. cobalt good agreement between theoretical and experimental values exists. For f.c.c. cobalt the stacking fault energy drops to 24.5 ergs/cm^2 (2,45 x 10^{-2} joules/m^2) as the temperature is raised to 150°C[49]. In h.c.p. cobalt the stacking fault energy is also about 30 ergs/cm^2 (3 x 10^{-2} joules/m^2) at room temperature.[48] These stacking fault energies are particularly low compared with those of other metals; e.g. aluminium has a stacking fault energy of 200 ergs/cm^2,[51] and copper has a stacking fault energy of 73 ergs/cm^2.[52] Stacking fault energies are difficult to determine experimentally where the values are low; certain workers are of the opinion that the values cannot be accurately determined if the stacking fault energies are less than 60 ergs/cm^2.[53],[54]

Thus certain proportions of vacancies, dislocations and stacking faults will be present in the cobalt powders prior to grinding. The X ray diffraction results described in the previous volume suggested that the individual metal particles had mosaic structures with small crystallites of both hexagonal and cubic cobalt present in the individual metal particles.

The exact significance of the experimentally measured crystallite sizes is discussed later.

Dislocation loops usually have a mixed character, being neither of the pure edge nor of the pure screw types.[55] However in both allotropes of cobalt, it is probable that edge character of the dislocations will predominate, since in cobalt, as will be clear later, cross slip is difficult; cross slip is a favoured motion of screw dislocations.[56] Any screw dislocations would thus be virtually trapped. Edge dislocations can move only in their slip planes. X ray diffraction analyses, the details of which are given in Section 5.5, show that the dislocation densities in the cobalt powders are relatively high, and of the order of 10^{11} cm^{-2}, compared with values of 10^5 to 10^6 cm^{-2} in well annealed metal crystals.[22]

When stress are applied to crystals dislocations glide away from their original positions on their slip planes The minimum stress for dislocation glide is given approximately by:[22]

$$\sigma \text{ min} = \frac{b\mu N^{\frac{1}{2}}}{2\pi}$$

Where σ min is the stress required for dislocation glide

b is the Burgers vector of the dislocation

μ is the shear modulus of the metal

N is the dislocation density

Substitution of values in the above equation indicate that applied external stresses of the order of 10^9 dynes/cm^2 (10^8 N/m^2) are required for dislocation glide in cobalt. During milling of the cobalt powders therefore the external stresses exerted by the grinding balls are sufficient to cause dislocation glide. If a dislocation encounters an obstacle such as a twin boundary, stacking fault, impurity centre or another dislocation during glide, it tends to cross slip onto a lower resolved shear plane.[57] Once past the obstacle the dislocation tends to cross slip back onto the original glide plane. The ability to cross slip is closely related to the stacking fault energy. In metals of very low stacking fault energies, the very wide splitting of the partial dislocations surrounding the stacking faults will impede cross slip.[22] In both allotropes of cobalt therefore glide of dislocations will result in their piling up at the obstacles after only small glide displacements from the dislocation sources in the crystal. A very non uniform dislocation distribution is therfore expected in deformed cobalt, with little evidence of the dislocation "cell structure" described by Swann[58] and Howie.[59] In the ground powders the dislocations will be arranged in complex networks or coplanar arrays, with little evidence of tangling. The Lomer Cottrell locks will be widely extended.[22] In view of the expected dislocation distribution in deformed cobalt a polygonisation process such as that, which occurs in aluminium at room temperature,[22] is unlikely during grinding of the cobalt metal powders.

A polygonisation process has been reported for cobalt,[60],[61] which is thought to involve vacancy mobility. However the minimum temperature required for this process is about 200°C. The maximum average temperature in the mill during grinding is about 135°C; thus the reported polygonisation process is unlikely.

Dislocation pile ups at grain boundaries would be expected to exert a significant influence on the progress of agglomeration during grinding of cobalt powders. The leading dislocation of a pile up is acted upon not only by the applied stress but also by the interaction forces with the other dislocations in the pile up.[62] As a result of the large stress concentration, and the plastic and elastic incompatibility at the boundary four processes may result from pile ups:[63]

(i) Slip can be initiated in an adjacent adhering grain if the leading dislocation is forced through the boundary. The broken boundary regions would then have the properties of additional dislocation pile ups.

(ii) Fracture nucleation at the grain boundary may occur.

(iii) Stepped boundaries may be formed.

(iv) The pile up may activate a Frank Read source in the adjacent grain.

In both allotropes of cobalt little blunting of the pile ups will occur, because of the low stacking fault energies, and a further consequence of the low stacking fault energy is that the dislocation at the rear of the pile up will be effectively locked, and little relaxation of the pile up will occur when the applied stresses are removed; thus very large forces may be exerted on the leading dislocation of the pile up. The behaviour of dislocation pile ups at grain boundaries is not thoroughly understood, but the four processes mentioned are thought to occur under various conditions. Stroh has suggested that fracture will result when the two leading dislocations of a pile up are forced within a distance b of one another, where b is the average Burgers vector of the dislocations in the pile up.

Single dislocations are also attracted to grain boundaries and their energy decreases monotonically with decreasing distance as they approach the boundary. Single dislocations reaching the particle boundaries will be effectively pinned at the boundaries. However pinned single dislocations may result in the grain boundary becoming kinked or stepped.

Climb of dislocations in the ground cobalt powders will probably not occur.

Dislocation climb is thought to be a thermally activated process[22] and several workers are of the opinion that temperatures of approximately 0.5 Tm are necessary for dislocation climb (where Tm is the melting point of the metal in degrees absolute). An activation energy similar to that required for atomic self diffusion must be supplied before dislocation climb can occur. Cold working does not appear to lower the temperature at which dislocation climb can occur[68]; thus although Silcox and Whelan observed dislocation climb in deformed aluminium at 190°C (i.e. 463°K), this temperature is approximately half the melting point of aluminium on the absolute scale (933°K). During the grinding of cobalt metal powders the maximum average temperature achieved within the mill is only about 0.23 Tm; thus the occurence of dislocation climb is unlikely.

The vacancies which are initially present in the powders occupy less space than atoms, and thus have an associated strain energy[55]. These vacancies therefore tend to migrate to vacancy sinks in order to lower their free energy. Theoretical calculations of the dynamic lattice vibrations of crystals[69] indicate that vacancies will be attracted to a free surface (i.e. sinks) with a force that varies inversely as their distance from the surface. The vacancies arising from rapid cooling of the powders after reduction may therefore be annihilated at grain boundaries, dislocations, other vacancies and impurity atoms as a result of vacancy migration under the applied stresses.

Furthermore a certain proportion of vacancies will be produced during deformation as a result of certain dislocation reactions. The nature of these reactions is difficult to predict as reactions producing vacancies which result from cross slip or climb are not expected during the grinding of cobalt metal powders. However the following reactions discussed by Seitz [70] and Cottrell [71] and which do not involve climb or cross slip could produce vacancies during deformation of cobalt:

(i) local heating at a dislocation

(ii) dislocation annihilations

(iii) coalesence of edge dislocations of opposite sign

These reactions are thought to be possible at room temperature. [71]

Apart from the stacking faults present in the powders prior to grinding, which arise from deformation during the reduction process, additional stacking faults are introduced during grinding. The following theory indicates that the introduction of stacking faults by milling is probable from energy considerations. A dislocation line passing between the A and B planes of the cubic structure can split into two partial dislocations, i.e.: [72]

$$\frac{1}{2}\,a\,\{101\} \rightarrow \frac{1}{6}\,a\,\{21\bar{1}\} + \frac{1}{6}\,a\,\{11\bar{2}\}$$

Since the energy of a dislocation (neglecting the core energy) is approximately proportional to the square of its Burgers vector, it is clear that the addition of the squares of the Burgers vectors in the above example indicates that this dissociation is very favourable, as the total energy would be reduced by dissociation.[72] The dissociation leads to the introduction of a stacking fault which results in a local change in structure from the f.c.c. to h.c.p. forms.

The stress required to form a stacking fault may be derived from the formula given earlier for the stress required to nucleate a twin. The shear stress required to introduce a stacking fault is approximately 10^9 dynes/cm^2 (10^8 N/m^2) in both allotropes of cobalt. As the shear stresses operative during milling are of the order of 10^{11} dynes/cm^2, (10^{10} N/m^2) stacking faults may be readily produced in both allotropes of cobalt during grinding.

The partial dislocations surrounding the stacking faults would probably bow out to assume an equilibrium configuration under the influence of the applied stress; however due to their stability it is unlikely that the partials will be torn apart by the applied stresses.[73]

Crystal imperfections interact directly with the localised stress fields present in metals.

The localised stresses are related not only to the applied stress but also to the stress fields caused by the presence of other dislocations and vacancies. As the kinetics of dislocation motion are not simply a function of the applied stress, but are also related to local interactions, the kinetics cannot be readily evaluated, and the expected types of crystal imperfections can only be discussed in general terms.

The effects of plastic deformation would be expected to be evident, throughout the particles, and not only on the surfaces of the particles. In view of previously published findings [74], [76], [78] differences in the dislocation density between the surface regions and the interior of a particle might be anticipated. Furthermore non uniform deformations could arise in different particles of a powder, because of different local cross sectional areas arising from the powder particle size distribution.

During grinding the applied stresses will result in an homogeneous shear in the <11$\bar{2}$> direction on the {111} planes of the cubic structure, changing the f.c.c. material to the h.c.p. form [77]. The small volume change [78] (-0.003 %) arising from the phase transformation during grinding could also be expected to influence the density and distribution of the dislocations present. It has been suggested that the internal stresses arising from volume changes of this type can be reduced by plastic flow or twinning [79].

As noted earlier grinding results in a variety of different types of forces being applied to the metal particles. Most studies on the influence of deformation on the motion of dislocations have been carried out by the direct observation (in an electron microscope) of thin foils subject to tensile stresses.

Experimental observations indicate that tensile deformation produces the following changes in thin foils of h.c.p. cobalt single crystals:[80],[81] During the initial stages slip results in the edge dislocations being arranged in stress free dipole layers. Certain of the edge dislocations become arranged in multipole layers. Further applied stresses result in deformation twinning on $\{11\bar{2}2\}$ and $\{11\bar{2}4\}$ in regions highly disturbed by slip or in areas of high internal stress. A significant increase in work hardening was noted, which was attributed to twin formation, as the applied stresses were increased. Dislocations associated with non basal slip were not observed. The thin foil results were explained by the work hardening theory of Seeger et al.[82] It is noteworthy that twinning on $\{10\bar{1}2\}$ was not observed in this study, although twinning on this plane has been reported elsewhere.[83] A thin foil study of f.c.c. cobalt has not been reported in the literature.

Thus although cross slip is more difficult in f.c.c. cobalt than in other f.c.c. metals with higher stacking fault energies, greater deformation before fracture is expected in f.c.c. cobalt as compared with

h.c.p. cobalt, since the von Mises' criterion is more readily accomodated in the f.c.c. allotrope. Thus when cobalt metal particles become trapped between two grinding balls (or between a ball and the mill body) the f.c.c. cobalt would be expected to exhibit more ductile properties (i.e. greater deformation before fracture) than the h.c.p. allotrope H.c.p. cobalt would exhibit a fracture, much more characteristic of the "semi-brittle" type compared with the f.c.c. allotrope. Similarly fatigue fracture would be expected to occur after a shorter grinding time in h.c.p. cobalt compared with f.c.c. cobalt.

As noted earlier, the cross slip, conjugate and critical glide systems of the f.c.c. form will be unstressed, and the 3 glide systems of the primary can slip during deformation. In h.c.p. cobalt, on the other hand, there is only one single slip system in the basal plane on which the dislocation glide can occur. These expected differences in deformation behaviour between h.c.p. and f.c.c. cobalt are consistent with two sets of experimental observations:

(1) Polycrystalline h.c.p. metals exhibiting basal slip do not deform plastically to the same degree as do the f.c.c. and b.c.c. metals.[84] (This observation was not made specifically for cobalt, but was a general summary of the fracture and deformation behaviour of a number of hexagonal and cubic metals).

(2) The ductilities of the two allotropes of cobalt have been measured experimentally:[85] the ductility of f.c.c. cobalt was much higher than that of the h.c.p. allotrope.

Basal glide in h.c.p. metals is insufficient therefore to allow deformation in a general way by slip.

These overall differences between h.c.p. and f.c.c. in their slip behaviour can, of course, be modified by the presence of stacking faults in both phases. The influence of stacking faults on the structure of the f.c.c. and h.c.p. phases was discussed in Volume 1.[86]

Deformation twinning is expected in both allotropes of cobalt. This is a consequence of the low stacking fault energy and the limited number of operative glide systems.

A very non uniform dislocation distribution will arise from deformation in both the allotropes of cobalt. In particular dislocation pile ups, stacking faults and twinned areas will arise. The exact dislocation interactions which occur during grinding cannot be accurately predicted. The prominent dislocations in h.c.p. cobalt will be those associated with the basal plane.

In f.c.c. cobalt the important dislocations, which will influence the deformation process, will be those of the close packed {111} planes.

A number of features associated with the grinding of different cobalt powders can be explained using the deformation and fracture behaviour of the two allotropes of cobalt described in this section.

3.3. THE OXIDES OF COBALT AND THEIR PROPERTIES

It was noted earlier that the cobalt metal powders contained oxygen, the amount in general depending on the grain size of the metal particles. The nature of this oxygen was not discussed in the previous volume; it was suggested,[87] however, that the oxygen was associated with the surfaces of the metal powder particles, and its presence was not due to incomplete reduction of cobaltosic oxide during preparation of the metal powders. The oxygen could be present in both physically and chemically adsorbed films on the surfaces of the metal powder particles.[87] It was noted that fine hexagonal cobalt powder prepared by reduction at low temperatures tended to be pyrophoric, and cobaltosic oxide was present on the surface, the presence of which was detected by X ray diffraction analysis.

Experimental work described later shows that some chemically bonded oxygen is present on the surfaces of the metal particles, and electron diffraction analysis suggests that the oxide present is cobaltosic oxide (i.e. Co_3O_4). A simple calculation shown in Appendix 5 indicates the manner in which the thickness of the oxide film on the particles surfaces may be evaluated. The calculation is probably over-simplified because the thickness of the oxide film will vary with the surface free energy which is theoretically anisotropic in both allotropes of cobalt, as a consequence of the anisotropy of the shear moduli.[88] Boas and Mc Kenzie[88] have described experiments which demonstrated that the extent of tarnishing of Copper varied with crystallographic direction in the metal sample. Appendix 5 includes calculations of the oxide layer thickness on the cobalt metal powders, the grinding characteristics of which were described in Chapter 4 of the previous volume. Neglecting anisotropy, oxide film thickness of the order of 100°A are expected.

Despite the crystal parameters being different for the oxide (Co_3O_4) and the metal, the relative positions of the metallic atoms, in an oxidised metal sample, were similar for the metal and for the oxide, i.e. on hexagonal cobalt it was found[89] that (111) (Co_3O_4) // (0001) (Co).

Theoretical calculations have shown that the differences in lattice parameters in oxide and metal result in the oxide film on the surface of the metal being in a stressed condition, [90], [91] and the presence of dislocations in surface cobalt oxide films have been observed. [92]

Cobaltosic oxide has been described as an ionic conductor, [93] and also as a metal deficient semi-conductor, with vacant cation sites. [89] It has been suggested that the oxide layers form on the metal as a result of the outward diffusion of cations and electron holes from the metal surface. [94] Porosity has been detected by different workers [89] in oxide scales of various thicknesses. In view of the probable mode of formation of oxide scales, it is thought that the electrons of the metal oxygen bonds are displaced towards the oxygen atom, which gives rise to a dipole layer. [95] Such oxides in contact with a fluid will have a negative zeta potential, which has been experimentally measured for a number of metal oxides. [96] Thus it is important to realise that the oxide surfaces on the metallic particles will probably be negatively charged. A zeta potential between the oxide surface and the limited number of ions dissolved in the water in the acetone will probably exist, but it will exert no influence on the grinding behaviour because the particles are in constant motion; during sedimentation of charged particles it has been observed that the particles tend to become [97]

detached from the diffuse electrical double layer; thus during grinding it is very probable that the double layer will be removed from the oxide films. (No zeta potential between the metal particles and the water in the acetone will arise as there is no preferential charge distribution in the metal).

Oxide films are unlikely to exhibit the same ductility as metals because of differences in bonding mechanisms in the two materials.[98] In metal crystals the bonding is due to electrostatic attraction between the valency electrons and the positive ion cores. The electrons are not however localised at the sites of their parent atoms. The non localised electrons in metals enhance the occurence of plasticity during deformation, and thus lead to ductile properties. In oxides the electrons are localised in electron shells of the ions.

The mechanical characteristics of cobaltosic oxide films have not been studied. Cobalt (II) oxide scales have been shown to possess a certain plasticity at elevated temperatures;[99] the plasticity was found to increase with increasing deviations from stoichiometry as reflected by an increase in the number of vacant cation sites. Differences in plasticity due to stoichiometric effects could be expected for Co_3O_4. No specific results have been reported concerning the adhesional characteristics of the oxides to cobalt metal, although certain observations have been reported for nickelous and ferric oxides.[100]

Some general observations indicate that oxide scales formed on cobalt at temperatures higher than 700°C were brittle and friable;[89] oxide on metal formed at lower temperatures adhered to the metal and showed no evidence of cracking. Chattopadhyay and Neasor[92] have confirmed that the mechanical stability of oxide films formed on f.c.c. cobalt may be poorer than that of scales formed on h.c.p. cobalt. These authors[92] found that greater strains and higher dislocation densities were present in scales formed on f.c.c. metal compared with the h.c.p. form. Cobaltosic oxide was found to predominate in scales formed on h.c.p. cobalt with about 50 % Co_3O_4 in the scales formed on f.c.c. metal, the balance being CoO. It was reported at a much earlier[89] time that the h.c.p. allotrope oxidised more readily than the f.c.c. form. In general, however, the nature of the oxide scales formed on cobalt metal (and no results on the oxides on cobalt metal powders have been reported) has received little attention; the mechanical properties of these oxides could exert an important influence on the grinding of cobalt metal particles.

The structure of Co_3O_4 has been thoroughly investigated[93] because of its ferromagnetic properties. Co_3O_4 is thought to have the same structure as magnetite, but it does not have a permanent magnetic moment. There is a dominant negative exchange between the Co^{2+} ions in the tetrahedral sites and the $(Co^{3+})_2$ groups (associated with oxygen as $((Co^{3+})_2O)$) in the octahedral sites.[93]

The oxygen parameter (v) has been determined to be 0.388 at room temperature, indicating that Co_3O_4 is not a completely ideal spinel.[93] Certain catalytic properties of spinels have been reported.[101]

On removal of a fine cobalt metal powder from a reduction furnace to the atmosphere, it is probable that van der Waals forces result in physical adsorption of oxygen on the surfaces of the metal particles in the first instance. However the affinity between fine cobalt particles and oxygen is such that chemisorption eventually occurs and a layer of Co_3O_4 up to several hundred angstrom units thick may be present on certain areas of the metal particles prior to grinding. The possible importance of these films on the course of grinding cannot be ignored. It has been pointed out[102] that adsorption of water vapour can occur on metal and metal oxide particle surfaces, so that in addition to oxide some hydroxide films may also be present.

Parravano[103] suggested that metal powder particles could be bonded together by the presence of a common oxide film which was chemically bonded to both the metal particles. The importance of this type of bond in cobalt powders is discussed later in connection with the experimental results.

Roscoe[104] originally found that surface oxide films on cadmium crystals raised the critical shear stress of the metal.

He suggested that molecules of oxide sealed up surface cracks and strengthened the surface layer of the metal. The oxide was thought to fill the cracks and reduce their ability to concentrate surface stress.

In studies on zinc crystals Harper and Cottrell[105] confirmed Roscoe's observations on the ability of oxidised surfaces to increase the shear stress of the crystal. The influence of surface oxide films on mechanical properties of metals has also been mentioned by Nabarro et al.[22]

Thus surface oxides may raise the critical shear stress of metals. The metal particles were however ground in a liquid where the Rehbinder effect is also operative. This is discussed in the following section.

3.4. THE ROLE OF THE GRINDING FLUID

On purely mechanical grounds it is difficult to see any great difference in fundamental principles between wet and dry grinding. The effect of the liquid on the motion of the ball charge would be practically negligible. However, it has been found in practice that the nature of the medium in which comminution occurs exerts a profound influence on the energy input necessary to achieve a given specific surface area. It is well known in practice that certain "additives" can be used in grinding to bring about a reduction in milling time necessary to obtain a certain degree of fineness.

Rehbinder and his coworkers carried (106),(107),(108) cut a number of experiments on the influence of surfactants (i.e. "the additives") on the resistance of solids to stress and rupture. Both minerals and metals were studied in these investigations; the findings may be summarised as follows:

(1) The cohesive forces between atoms on solid surfaces are decreased on adsorption of the surfactant; adsorption probably occurs in the first instance at structural defects or microcracks.

(2) A weakening of the material occurs at the structural defects; this was ascribed to a decrease in the surface free energy of the material resulting from adsorption. Thus the resistance to rupture is reduced.

(3) A wedging pressure arises in the cracks from the film of surfactant adsorbed on the surface.

(4) The effect of the adsorbed film was to keep the cracks open once they had been formed.

These phenomena collectively are known as the Rehbinder effect.

According to Rehbinder's theoretical treatment the probability P of the formation of rupture cracks at "weak spots" on the surfaces of metals is given by:

$$P = C_m \exp - \left[\frac{P^s_{s/l} \delta^2_m}{kT} \right]$$

Where C_m is a constant characteristic of the metal

$F^s_{s/l}$ is the surface free energy of the solid liquid interface

k is the Boltzmann constant

T is the absolute temperature

δ_m is the distance between structural defects

Dislocations can alter the adsorption characteristics, since dislocations influence the surface stress distribution.[109]

Since it is known that the energy requirements for wet grinding are (with other factors being equal) approximately 20 % less than for dry grinding to achieve a certain specific surface area,[110] there are good reasons to suspect that milling fluid might be adsorbed at structural defects, thus facilitating comminution, at least in the case of brittle friable materials. For most materials the liquid solid interfacial energy is lower than the gas-solid interfacial energy;[111] thus theoretically it would be expected that grinding in the presence of a liquid would require a lower energy than dry grinding to achieve a given specific surface area.

The hypothesis that milling fluid could promote cracking in brittle materials must be modified for ductile metals,[112] since as has been pointed out, in ductile metals most of the energy required to propagate a crack is used up in plastic deformation at the crack tip, and is about 30 times larger than the surface energy created by propagation of the crack.

Thus on milling ductile metals the lowering of the surface free energy of the metals by adsorption of liquid should make little difference to their friability.

However, the experiments of Harper and Cottrell[105] suggest that the Rehbinder effect is operative when metal crystals with surface oxide films are strained in a liquid medium. These workers noted that the ability of surface oxide films to raise the critical shear stress could be dramatically altered by carrying out the experiments in a number of liquids. The general effect of the liquid medium was to lower the critical shear stress compared with the values obtained in air. A certain time delay was noted before the Rehbinder effect became operative; it was found that the response time was related linearly to the viscosity of the liquid in which the experiments were carried out. Mobile agents such as kerosene or alcohol produced a much more rapid lowering of the critical shear stress than did viscous paraffins. It was concluded that the Rehbinder effect was operative by liquids penetrating the oxide films presumeably through cracks.

Thus during comminution of cobalt powders, the Rehbinder effect is not likely to assist in comminution of the metal powder particles, but it may contribute to the ultimate fracture of oxide scales on the metal particle surfaces.

It has been suggested[113] that for extensive comminution of metals to occur on wet grinding, there must be a chemical reaction between the metal and the liquid. Standard works of reference[114],[115] list no chemical reaction between cobalt metal or cobalt oxide and acetone. The oxide of cobalt are reported to be insoluble in acetone.[114] Cobalt being a strongly electropositive metal acts as a reductant towards aldehydes which also contain the C = O carbonyl group which is present in acetone:[116] a secondary alcohol does not result from the reaction of cobalt with acetone, although other reducing agents can result in the formation of this produce from acetone.[116]

Acetone does not exhibit keto enol tautomerism to any extent, and only minute traces of the enol form have been detected.[117] Thus condensation reactions between the enolic form and methyl groups in other acetone molecules are not expected.

Acetone does however undergo intermolecular condensation reactions in the presence of certain compounds.[116] Evidence presented later indicates that there is a chemical reaction between cobalt and acetone during milling, and, on the evidence of the organic compounds isolated from the reaction mixture, it is possible to give an outline of the chemical reaction that occurs.

3.5. FACTORS RESPONSIBLE FOR AGGLOMERATION OF FINE POWDERS

It can be anticipated that a system of fine particles dispersed in a liquid may be in a thermodynamically unstable state, because any free energy associated with the large interfacial area between the dispersed phase and the continuous phase can decrease by the aggregation or coalesence of the dispersed particles of fine powder. In fine particle systems, the free energy may be positive and the fine powder particles may constitute a lyophobic dispersion. Rather than remain in contact with the liquid the particles aggregate or coalesce with one another.

The formal theory of coagulation of particles of fine powder was developed by von Smoluchowski.[118],[119] According to this theory the rate of disappearance of primary spherical particles, due to collision following diffusion of the particles towards each other, is related to the diffusion coefficient D of the particles through the liquid, to the number n_1 of the primary particles per cm^3 and the collision radius of the particles $\underline{R}$, is expressed by:

$$\frac{-dn_1}{dt} = 8\pi D\underline{R}n_1^2$$

The original theory assumed that every collision was effective in removing two of the primary particles from the system if the centres of the particles approached to within the collision radius $\underline{R}$.

In practice each collision will in effect remove only one particle from the system since there were two particles before collision and only one afterwards.[111] Hence if n is the total number of particles within the system, the above equation should be written in the form

$$\frac{-dn}{dt} = 4\pi D\underline{R}\, n^2$$

This equation integrates to

$$\frac{1}{n} - \frac{1}{n_o} = 4\pi\, D\underline{R}t$$

Where t is the time of agglomeration.

The diffusion coefficient D may be derived from Einstein's formula:

$$D = \frac{kT}{6\pi\eta a}$$

Where k is the Boltzmann constant

T is the absolute temperature

η is the viscosity of the medium

a is the radius of the particles in the disperse system.

The Einstein formula is valid provided the powder particles are large in size compared with the mean free path of the molecules in the continuous medium.[111]

$\underline{R}$ is approximately equal to 2a, i.e. the particles must just touch before collision can occur.

In practice many particle systems are stable for longer periods than predicted by the above equations due to an energy barrier W, which makes many of the collisions elastic, i.e. the particles are repelled away from each other without agglomerating. Thus as a first approximation:

[111]

$$\frac{1}{n} - \frac{1}{n_o} = 4\pi D\underline{R}t \exp - \frac{W}{RT}$$

Where R is the gas constant

T is the absolute temperature

The above theory predicts that the potential well responsible for cohesion is infinitely deep, i.e. two particles having touched do not separate. This is approximately valid for suspended particles of colloidal metals.

[111]

Thus it can be seen that all fine particles have a natural tendency to agglomerate; the tendency being more pronounced the finer the particle size since D increases with decreasing particle size.

Having established that fine powder particles dispersed in a liquid tend to reduce their surface free energy by agglomerating, it is appropriate to try to estimate whether f.c.c. or h.c.p. cobalt powder has the larger surface free energy. Some idea of the values of the surface free energy of metals may be obtained in the following ways:

(1) Gogate and Kothari[120] obtained the following relation theoretically by considering the free electrons of a metal confined to a two dimensional thin film:

$$\gamma \propto (A/p)^{-4/3}$$

Where γ is the total surface energy

(A/p) is the atomic volume

Where A is the atomic weight of the metal

p is the density of the metal

Smith[121] established the relation:

$\gamma \propto (A/p)^{-1.41}$, for a number of metals. Thus the theoretical predictions of Gogate and Kothari[120] were practically confirmed by the earlier experiments of Smith[121], with the exception that the exponents were not identical.

Since the density of hexagonal cobalt is slightly higher than that of f.c.c. cobalt, the atomic volume is lower for the h.c.p. form. On this basis therefore, h.c.p. cobalt would be expected to have a larger surface free energy than the f.c.c. form, although the difference would be small because the volume difference between the two forms per unit weight is only 0.003 %.

(2) Leadbeater[122] by considering surface tensions, melting temperatures and heats of sublimation of metals showed that for a number of metals the total molar free energy is proportional to $(A/p)^{2/3}$.

Thus according to this relation h.c.p. cobalt should have a lower surface free energy than f.c.c. cobalt.

(3) Kuczynski[123] has derived the relation

$$\gamma = \frac{\mu\delta}{8}$$

where γ is the surface free energy of the metal

δ is the interatomic distance in the crystal

μ is the shear modulus

If the interatomic distances for both allotropes of cobalt are assumed to be the same and of the order of 3 or 4 ^{o}A, γ should depend on μ. Koster's[124] data indicate that Young's modulus (and hence μ) of cobalt decreases as the temperature is raised (i.e. as the temperature is increased from the h.c.p. stable region to the f.c.c. stable region). Thus on this basis γ should be lower for the f.c.c. form compared with the h.c.p. allotrope. However, because both phases are anisotropic γ would also depend on the crystallographic direction in the crystal.

Thus it appears that theoretical methods do not enable a prediction to the made as to which allotrope of cobalt would have the higher surface free energy.

A survey of the literature indicates that for most metals the surface tension measurements (on which the surface free energies are based) have been made at or near the temperature of melting of the metal, and no data are available for lower temperatures. The relation between surface free energy and temperature may be shown by the following formal thermodynamic argument:

The Gibbs-Duhem equation[125] for a single homogeneous phase in reversible equilibrium may be written in the form:

$$SdT - VdP + Ad\gamma + \sum_j n_j d\mu_j = 0 \qquad (1)$$

where S is the interfacial entropy

V is the relative volume of the phase

A is the interfacial area

γ is the interfacial free energy

P is the pressure

$$dG = \sum_j n_j d\mu_j \qquad (2)$$

Where dG is the classical Gibbs free energy associated with the temperature T.

Dividing equation (1) by A and expressing the results in terms of the interfacial free energy gives:

$$-d\gamma = S_s dT - \Delta t\, dP + \Sigma_j \theta_j d\mu_j \qquad (3)$$

Where S_s = S/A which is the entropy per unit area of interface

$\theta_j = n_j/A$ is the number of moles of the j th component per unit area of interface

Δt = V/A is the average thickness of the interface phase

For a single component system of equilibrated interfaces where there are boundaries, the chemical potential can be considered to be esentially constant, and therefore $d\mu_j = 0$ and the summation over j in equation (3) will be zero. In addition since the interface has a thickness Δt which must be of the order of a few interplanar spacings $\Delta t dP$ must be very small, and in practice can be neglected.

Therefore $-d\gamma = S_s dT$

Therefore $\left(\frac{d\gamma}{dT}\right) = -S_s$ _____ (4)

Equation (4) therefore expresses the fact that the interfacial free energy will have a negative temperature coefficient since entropy is always positive.

Apart from proving that the surface free energy increases as temperature is reduced, the above analysis should hold for any general boundary; equation (4) should hold for a boundary such as a stacking fault. Equation (4) therefore probably describes formally the reason for the decrease in stacking fault energy as the temperature is raised, which was described in Section 3.2. of this volume.

The interfacial entropies of the allotropes of cobalt have not been reported, although the entropy of solid cobalt has been evaluated.[126] H.c.p. cobalt is stated to have an absolute entropy of 7.18 cals/^{o}K g atom (30,16 joules/^{o}K g atom) at 298°K, whereas f.c.c. cobalt has an entropy of 13 cals/^{o}K g atom (54,6 joules/^{o}K g atom) at 720°K. Extrapolation of the value for f.c.c. cobalt to room temperature was not given in the data.

Thus a number of methods of analysis do not prove conclusively which allotrope of cobalt has the higher surface free energy. The surface free energy will certainly be anisotropic in both forms of cobalt. The thermodynamic analysis is in agreement with Kuczynski's analysis; both these methods predict that the surface free energy will be higher for the h.c.p. form compared with the f.c.c. form. The surface energy of cobalt has been determined to be 1970 ergs/cm^2 (1,97 joules/m^2) at 1354°C using the microcreep technique in an atmosphere of hydrogen.[49] Another value of 1740 ergs/cm^2 (1,74 joules/m^2) has been quoted in the literature.[127]

There a number of other special factors which can promote agglomeration of fine powder particles.

These are:

(1) ELECTROSTATIC FORCES: Frictional charging is only likely in dry grinding, and can only lead to significant particle agglomeration with systems of non conductors.[128] Both cobalt metal and the oxides are conductors and the grinding was carried out in a liquid. Thus it is unlikely that electrostatic forces could contribute to agglomeration of the cobalt metal particles.

(2) CAPILLARY FORCES: As soon as a fluid completely envelopes a system of solid particles agglomeration forces due to capillary bonding should disappear.[129] Agglomeration due to capillary forces will not occur during the grinding of the metal powders.

(3) MECHANICAL INTERLOCKING: The rounded shapes of individual particles in the cobalt powders studied suggests that agglomeration during grinding caused by mechanical interlocking is unlikely.

(4) THERMAL SINTERING: The lowest temperature at which cobalt metal particles can sinter together is about 400°C.[130] This temperature was not achieved for extended times during grinding. In the agglomerates examined there was no evidence of neck growth between adjacent particles, which is a feature of thermal sintering.

(5) MAGNETIC FORCES: Some time ago it was suggested (128) that magnetostatic forces could contribute substantially to the bonding of magnetite agglomerates. The exact bonding forces were not calculated however; since cobalt is a ferromagnetic material and cobaltosic oxide can exhibit induced magnetic properties magnetostatic forces could conceivably contribute to bonding in cobalt metal powder agglomerates.

There are a number of factors which prevent an exact calculation being made: during grinding the cobalt powder particles are not magnetically saturated nor orientated for maximum strength. Any model of magnetostatic bonding would be greatly simplified by the initial assumptions made, e.g. the particles have a uniform size, a uniform structure is present in the particles and that stray field effects are neglected. Furthermore applied stresses result in changes in the magnetic properties of ferromagnetic materials; (131) it is assumed that these changes arise from dislocations introduced by the cold working process. (129) Brown has interpreted changes in the magnetic permeability of cold worked ferromagnetic materials in terms of the dislocation density.

With the above limitations the model shown in Appendix 6 was derived to calculate the magnetostatic bonding forces in the cobalt powder agglomerates.

Substitution of the numerical values shows that the magnetostatic bonding energy is very small, namely $6,5 \times 10^{-36}$ joules. Even with the shortcomings of the model noted above, this result should give a value of the approximate order of magnitude of the magnetostatic binding energy. The energy dissipated in a collision between two grinding balls (derived in Appendix 2 as $8,12 \times 10^{-3}$ joules) is many orders of magnitude greater than the binding energy of an agglomerate due to magnetostatic forces. Thus it is unlikely that stabilisation of an agglomerate during grinding could occur due to magnetostatic forces, and magnetic forces do not contribute to agglomerate bonding in the absence of an applied magnetic field. In the calculation shown in Appendix 6 the magnetic moment has been taken to be 161 oersted per g. Allowance for the presence of the two allotropes of cobalt in an agglomerate could alter the binding energy slightly but insufficiently to alter the order of magnitude of the binding energy. Myers and Sucksmith[134] have shown that the magnetic moment at 293°K is 161.0 Oe/g ($1,280 \times 10^4$ amp turn/m g) for h.c.p. cobalt and 167.3 Oe/g ($1,330 \times 10^4$ amp turn/m g) for f.c.c. cobalt.

Cobaltosic oxide can exhibit induced magnetic properties; a film of this material is present around some fine cobalt metal powders prior to grinding.

A calculation shown in Appendix 7 indicates that the binding energy of an agglomerate of Co_3O_4 would only be $7,28 \times 10^{-54}$ joules.

Thus although Exner, Fischmeister and Lindelof[136] suggested that magnetic forces could promote agglomeration of cobalt powders, the model in Appendix 6 indicates that the binding energy due to magnetic forces is negligible.

(6) VAN DER WAALS FORCES: It has been suggested that van der Waals forces can contribute to the bonding of powder agglomerates.[128] Van der Waals forces of attraction between metal surfaces have been measured[136]; for chromium plates at a separation of 1μ the force of attraction was 0.01 dynes/cm^2 (10^{-3} N/m^2). Thus very weak forces of attraction between the metal particles are expected which are attributable to the van der Waals effect. These forces are effective over only very small distances and diminish with the 7th power of the distance between the particles. For particles with irregular surfaces therefore, these forces would be limited to very small areas around point contacts of the particles. Since acetone is a small molecule and therefore easily polarised, van der Waals forces between oxide layers and acetone could exist. Thus it may be concluded that van der Waals forces of attraction may occur during grinding, but the forces are small and effective only over very limited distances.

(7) THE INFLUENCE OF THE DIELECTRIC CONSTANT OF THE FLUID:

Kopelman and Gregg[137] noted that the electrical polarisability of the grinding fluid influenced the degree of dispersion; the turbidimetrically measured particle size of tungsten powder decreased with increasing dielectric constant of the liquid as the dielectric constant increased to 25; with dielectric constants greater than 25, the particle size remained constant. Acetone has a dielectric constant of 21.4 at room temperature[138]; thus some of the agglomeration noted in the cobalt powders could possibly be ascribed to the electrical polarisability of the acetone. However very different agglomeration tendencies were noted during grinding of different cobalt powders in the same liquid; thus this effect could not account for the differences in agglomeration characteristics observed. The physical reasons for the effect noted by Kopelman and Gregg are difficult to explain, and the following suggestion is made for this effect: As the dielectric constant ε of the fluid is increased so is its dipole character. With increasing ε the forces of attraction between the fluid molecules and metallic particles becomes greater than the van der Waals forces of attraction between the metallic particles themselves[139]; thus particles become detached from the aggregates and are removed to the bulk of the fluid.

It is evident that none of the physical effects discussed above can explain the agglomeration behaviour observed on grinding cobalt powders, and it is therefore necessary to consider in greater detail the motion of the powder mass and the balls in the mill during grinding.

3.6. PHYSICAL ADHESION AND COLD WELDING

When the metal powders are placed in the milling fluid prior to grinding, the analysis of the previous section indicates that the particles tend to diffuse towards one another, and agglomerate. Einstein's equation indicates that the finer powders should agglomerate together more rapidly than the coarser powders.

During milling the powder agglomerates are impacted by the grinding balls. Bradshaw (140) originally suggested that in addition to comminution, a "cold-welding" process could occur during grinding. Based on observations on fine nickel powders, Bradshaw suggested that "stable unions" of fine particles could be formed during grinding. Stable unions of large particles were thought to be unlikely, but no reasons could be advanced why very small particles could not "cold-weld' to the large particles.

Bradshaw suggested that the type of bond formed between the metal powder particles was similar to that formed in Bowden's experiments on sliding friction. In Bowden's work adhesion due to diffusion welding occured.[141] The phenomenon first noted by Bradshaw implies that when two metal particles are pressed together by an external force the particles yield to the applied force by adhering together, and a metallic bond is formed by diffusion.

From the Dupré[142] equation the force required to separate two adhering metal surfaces by a molecular dimension may be calculated, and is approximately 600 kg/cm^2 (5,88 x 10^7 N/m^2). In practice such high adhesive strengths are not obtained; usual values are about 30 kg/cm^2 (2,94 x 10^6 N/m^2).[143] This large difference between the values arises from plastic flow and is thought to be due to the existence of dislocations in the adhering surfaces.[144]

Soft metal surfaces adhere strongly to one another, since the adhesion is not opposed by elastic stresses in the solid.[145] Adhesion between metal surfaces may be reduced considerably by the presence of oxide films.[145],[146] However if the properties of the oxide are such that it may be easily ruptured marked adhesion between the metal surfaces may still occur.[145]

As has been discussed in several works the studies of adhesion and friction are closely interrelated, and depend on the same mechanical properties of the solids. When two solid surfaces are brought into contact under an applied load, the asperities of the two surfaces will contact and deform elastically and plastically until the applied load is supported. If while the two surfaces are adhering together, a tangential force is applied to one of the solids, a very definite force is required to move one solid over the other. This force is a function of the true surface area of contact, and of the shear strength of the material under the real contact area. The resistance to movement of one surface over the other is friction, and the applied tangential force is the friction force. Thus measurement of the coefficient of friction will yield information about the adhesional properties of solids.

The coefficient of friction is closely related to crystal structure.[147],[148],[149] The coefficient of sliding friction has been measured for single crystal specimens of hexagonal cobalt;[150] the coefficient of friction was 0.35. In the same series of experiments the coefficient of friction was measured for a single crystal of (f.c.c.) copper and was found to be 21.0.

These experiments showed that the friction coefficient for f.c.c. cobalt was slightly higher (0.40) than for the h.c.p. form, but the friction coefficient was not as large as that determined for copper. Of particular significance is that cobalt oxide films did not significantly reduce the measured friction coefficients compared with the values obtained for the oxide free metals studied in vacuum. In this respect the influence of cobalt oxides on the adhesional characteristics differs markedly from the behaviour of other metals with oxide surface layers, where a marked decrease in friction between metals is noted in the presence of an oxide film. [146], [151]

These differences in friction coefficients for the two allotropes of cobalt may be explained on the basis of the differences in mechanical properties described earlier; in particular the greater ductility of the f.c.c. form will permit greater ease of deformation under an applied load than is the case for h.c.p. cobalt. Thus a more marked increase in the true area of contact of the specimens will result in the f.c.c. cobalt compared with h.c.p. cobalt which leads to greater adhesion and an increase in the coefficient of friction.

It is generally believed that the presence of dislocations in the adhering surfaces will result in a decrease in the adhesion and thus friction.[144] The effect of the presence of dislocations would be to reduce the true area of contact between the adhering metal surfaces. This decrease in the true area of contact arising from the presence of dislocations in the surface may occur in two ways:

(1) Herring[152] has pointed out that surfaces subjected to an applied load tend to deform by slip of dislocations in atom layers which are just below the free surface. The surface thus acquires a structure in which lines of atoms are missing from the crystal face, giving rise to a surface layer of atoms with an "internal step".

(2) An "external step" can arise from a pile up of dislocations at a particle boundary. In addition a pinned dislocation at a surface can give rise to a kinked boundary. Both of these processes were discussed in Section 3.2.

Therefore the particles have a tendency to adhere to one another when placed initially in the grinding fluid.

When milling commences the agglomerates will be impacted together by the grinding balls. F.c.c. particles will exhibit greater physical adhesion than h.c.p. cobalt particles as a consequence of the differences in deformation characteristics expected between the two cobalt allotropes.

It is important to assess the physical processes which can occur when the particles are in intimate contact. From observations of agglomerates on the scanning electron microscope (e.g. Figures 4.5. and 4.6. of the previous volume) it appears that the aggregates have the appearance of large metallic particles. This implies that a type of "metallic bonding" is formed between the smaller particles.

Bradshaw (140) suggested that during grinding the metallic particles formed a "cold-welded" bond, and that atomic diffusion occured by atoms of one surface diffusing into the surface and along the grain boundaries of an adhereing surface. However a more detailed consideration of the "cold-welding" process suggests that Bradshaw's diffusion mechanism may not be entirely correct.

It is well known that the activation energy for atomic diffusion may be lowered in plastically deformed regions of a metal. (153) As discussed in 3.2. plastic deformation could introduce a large number of vacancies, which might be expected to enhance the rate of volume diffusion.

In addition plastic deformation could increase the so called "internal energy" of the metal. The presence of vacancies would be expected to lower the activation energy required for atomic self diffusion. Some theoretical calculations have shown that while the activation energy for self diffusion in copper by a direct interchange mechanism is about 2.05 eV ($3,28 \times 10^{-19}$ joules) the activation energy may be lowered to about 1.40 eV ($2,24 \times 10^{-19}$ joules) if diffusion occurs by a monovacancy mechanism.[154] As a monovacancy is one of the simplest defects which is thought to be introduced by cold working, empirical grounds might suggest that the presence of vacancies and a higher "internal energy" would lower the activation energy required for volume self diffusion. The cold worked condition is said to be in a thermodynamically mestastable state compared to the unstrained condition;[153] the higher "internal energy" or stored energy arises as a consequence of the "cold-working".

However, diffusion is a thermally activated process.[155] The calculations shown in Appendix 1 indicate that the average temperature within the mill is at maximum 135°C. The maximum temperature that can arise in a single collision between two colliding grinding balls cannot be explicitly calculated, because there is no rigorous theory for estimation of the time of the collision, and thus the rate of energy dissipation cannot be evaluated.

According to Tabor's theory[16] for impacts between a soft metal and non deformable colliding body in which permanent plastic deformation of the soft metal occurs, the duration of the impact is given by:

$$t = \frac{\pi}{2} \sqrt{\frac{m}{2\pi R p_o}}$$

Where t is the time of duration of the impact

R is the radius of the colliding sphere

m is the mass of the colliding sphere

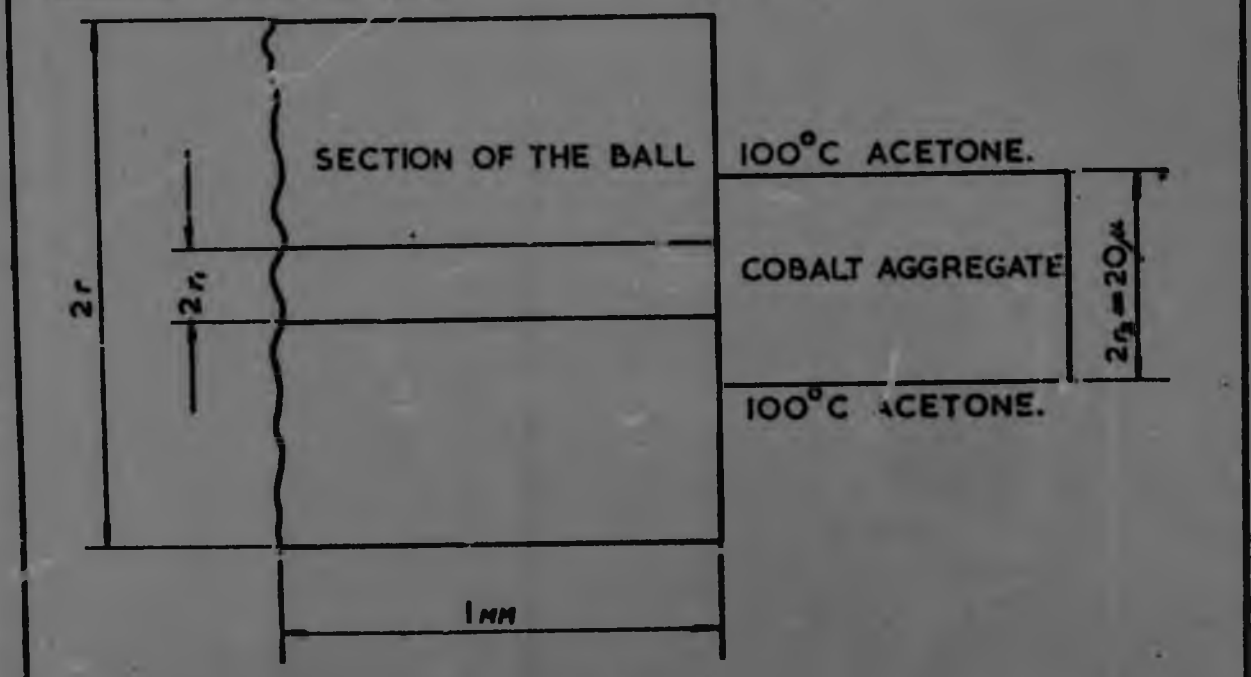
p_o is the dynamic flow pressure of the softer metal, which is plastically deformed in the impact

Solving this equation indicates that the duration of the impact between a 6 mm hard metal ball and a cobalt particle is 2.88×10^{-4} seconds. Consider a section of a hard metal ball adjacent to a cobalt powder aggregate as shown in Figure 3.6.1. Assume that the section of the ball is cylindrical with a diameter of 2r.

Assume that the heat generated is one half of that generated in a ball collision, i.e. 0.975×10^{-3} calories; Assume that the acetone at the edge of the agglomerate is at a temperature of 100°C. Assume that all the heat dissipated in a collision is used to maintain the acetone at a temperature of 100°C. Let the temperature at a distance r_1 from the centre of the section be t_1. Assume that the heat is dissipated in a cylindrical length of 1 mm.

FIG. NO. 3·6·1.

MODEL FOR EVALUATION OF MAXIMUM TEMPERATURE GENERATED IN A BALL COLLISION.



By the Fourier equation for heat conduction:[167]

$$t_1 - t_2 = \frac{q \ln (r_2 / r_1)}{2\pi k}$$

Where q is the heat flux

k is the thermal conductivity of hard metal, which is given as 0.06 cals/$^{\circ}$ cm sec.[168]

t_2 is the acetone temperature of 100°C

Thus solving this equation yields:

When $r_1 = 0.5\mu$ then $t_1 = 372^{\circ}C$

$r_1 = 0.05\mu$ then $t_1 = 582^{\circ}C$

$r_1 = 0.01\mu$ then $t_1 = 725^{\circ}C$

This inaccurate model indicates that the maximum temperature generated in a ball collision may result in the temperature at the edge of a cobalt agglomerate exceeding the allotropic transformation temperature of cobalt in localised areas. In practice repeated impacting by the grinding balls produces the low temperature h.c.p. phase; the high temperature f.c.c. phase is not produced. In this analysis the temperature at the edge of a powder agglomerate has been considered and not the temperature at the centre of an agglomerate. Heat would have to flow from the edge of the agglomerate to the centre of the agglomerate.

Therefore it may be concluded that direct impacting of the agglomerates by the balls may produce temperatures in excess of the allotropic transformation temperature in localised regions. The balls and powder are in constant motion within the mill and an exact solution of the heat transfer process is not possible.

Experiments have shown that the activation energy for self diffusion in unstrained cobalt at 1000 - 1400°C is approximately 62 to 67 k cals/g atom.[158],[159],[160],[161] (From the temperatures at which these experiments were carried out, it is presumed that the materials studied had cubic structures, although the structure was not specifically determined in any of the investigations). An empirical postulate of Van Liempt[168] states that the activation energy for bulk diffusion in a metal is given by 32 Tm, (where Tm is the melting point of the metal in degrees Kelvin). Van Liempt's postulate indicates that the activation energy for self diffusion in cobalt should be 56.48 k cals/g atom, which is in good agreement with the experimentally measured activation energies. In sintered cobalt specimens prepared from powders, the activation energy for self diffusion has been determined to be 38.5 k cals/g atom at 600 to 800°C.[163]

In a sintered metal powder compact, it is suggested that the activation energy is probably lowered compared with cast materials by the occurence of more extensive diffusion along the smaller grain boundaries, and as a result of other imperfections associated with a sintered product.

Diffusion of atoms along dislocations in low angle boundaries is a phenomenon that is known to occur;[164],[165] thus the presence of dislocations can enhance the apparent volumetric diffusivity. The activation energy required by a process of this kind is thought to be approximately half the activation energy required for volume self diffusion.[166],[167] In the case of cobalt an activation energy of approximately 30 k cals/g atom would be required.

Surface diffusion of atoms on cleaned metal surfaces requires a lower activation energy than bulk diffusion, and will occur in preference to bulk diffusion.[168],[169] Surface diffusion has been observed at 300°C in adhered copper - nickel surfaces in vacuum, but times of several hours were required to obtain marked diffusion.[170]

Thus it may be concluded that "red-heat" temperatures (600 - 800°) would be required for long periods to achieve appreciable "cold-welding" by diffusion of material between adjacent grains.

During grinding the maximum average temperature is about 135°C, and the maximum temperature generated by direct impacts must be approximately 700°C; the duration of the impacts is small. Thus there is little possibility that the extensive "cold-welding" observed (especially in f.c.c. cobalt) occurs as a result of volume diffusion. Very localised volume diffusion might occur, however. The surface diffusion characteristics of cobalt have not been reported in the literature, but in view of the very slow rate of surface diffusion noted for copper - nickel surfaces at 300°C it is improbable that surface diffusion could contribute to the "cold-welding" process.

(152)
Herring has developed an expression for the driving force for self diffusion between two adhering surfaces where the only motivating force for self diffusion is a concentration of vacancies between the surfaces and the interior of the solids. Using this expression for cobalt particles of radius 1μ, assuming that the surface free energy of cobalt is $\sim$ 2000 ergs/cm^2 and that the atomic volume of cobalt is 6.02 cc/g yields a driving force of 4.91×10^8 ergs/g atom (48,1 joules/g atom). The thermal energy at 300°K is approximately 2.53×10^{10} ergs/g atom. Thus the driving force provided by a concentration of vacancies is considerably less than the thermal energy of the system, and cannot motivate self diffusion between adjacent particles in physical contact with one another.

At the average temperature within the mill i.e. $\sim 100^{o}C$ therefore, a concentration of vacancies cannot motivate self diffusion.

Thus it does not appear that a diffusional mechanism can account for the "cold-welding" process even though vacancies and defects are present which could lower the activation energy. It does not seem possible that temperatures necessary for thermal activation of diffusion persist for sufficient time during grinding for "cold-welding" to occur by a diffusional process; thus another mechanism must be proposed for the "cold-welding" process. Dislocation climb cannot occur if the temperature does not exceed $700^{o}C$.

Bubble raft experiments have shown that slip can result in the bonding together of adjacent particles and no thermal activation is necessary. [171],[172],[173] Bragg and his co-workers have shown that the forces between uniformly sized bubbles of a plastic crystalline material on the surface of a liquid closely resembled those that were predicted to exist between metallic ions, and that rafts of bubbles would deform at a critical stress by the slip of dislocations. Bubble raft studies showed that geometric changes from the state of initial adhesion can be readily accomplished by slip deformation processes.

In both allotropes of cobalt pile up of dislocations at grain boundaries are expected, and thus slip processes between adjacent grains could occur. In order to study a process of this type consider the phys cal situation shown in Figure 3.6.2.; two adhering powder particles are in physical contact; both particles have been severely deformed during grinding and their surfaces can be represented by a series of terraces; one particle is represented by a flat plate the other by a cylinder. Suppose that a dislocation of Burgers vector b is nucleated in either surface by the slip of one terrace into another. The yielding of the second grain is caused by an unstressed pile up of dislocations at the surface of one of the particles. Consider that the boundary formed is a wedge shaped notch with a wedge angle θ as shown in Figure 3.6.3. If the slip plane of the nucleating dislocation is approximately normal to the surface of the plate the two surfaces will move towards each other by a distance approximately equal to their normal separation thereby annihilating a region of material approximately equal to the cross hatched region shown in Figure 3.6.3. The width of the strip of annihilated surface is approximately equal to the terrace width (or $b/\tan\theta$). The length is twice the radius of the dislocation loop.

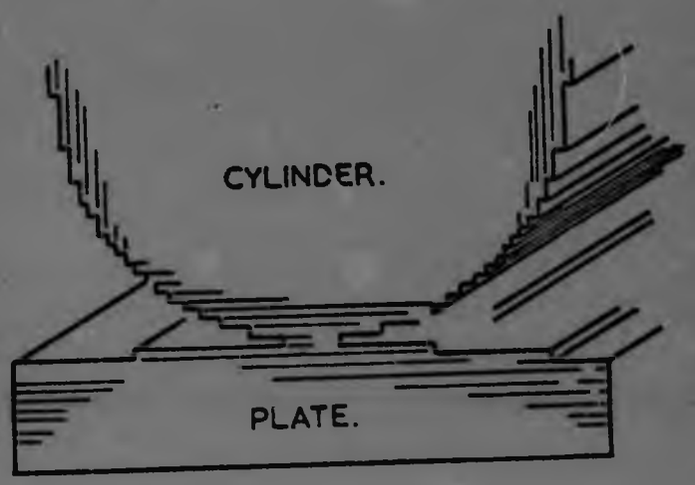


FIG. NO. 3·6·2.

INITIAL CONTACT BETWEEN TWO POWDER PARTICLES REPRESENTED BY A CYLINDER AND A PLATE (BOTH PARTICLES HAVE BEEN SEVERELY DEFORMED WHICH IS REPRESENTED BY A SERIES OF TERRACES.)

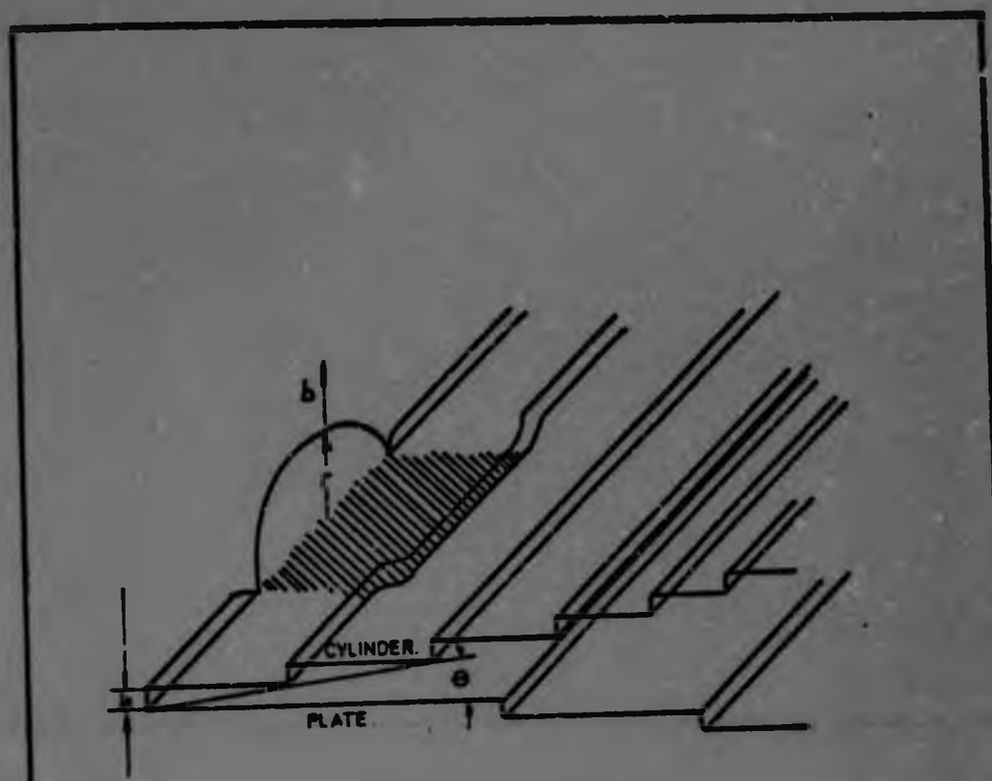


FIG. NO. 3·6·3.

NUCLEATION OF A DISLOCATION LOOP AT THE TIP OF A WEDGE SHAPED NOTCH.

Since two surfaces are annihilated, the free energy change is given by:

$$G_S = \frac{-4br\gamma}{\tan\theta}$$

Where γ is the surface free energy of cobalt

r is the radius of the dislocation loop

If two free surfaces contain grain or mosaic boundaries which are eliminated an additional negative free energy is introduced. Let this be G_B. By introducing a dislocation in the second grain, an elastic energy term has been introduced which (neglecting the core energy of the dislocation) is given by:(174)

$$G_D = \frac{\mu b^2}{4} \ln\left[\frac{r}{5b}\right] \text{ per unit length}$$

Where μ is the shear modulus of the metal

The total free energy change upon nucleation of the dislocation and annihilation of the interface is the sum of the interfacial, grain boundary, and elastic energy terms, i.e.

$$\Delta G = \pi r\mu \frac{b^2}{4} \ln\left[\frac{r}{5b}\right] - G_B - \frac{4\,br\,\gamma}{\tan\theta}$$

In the model considered no external work was involved, thus the free energy equation contains no additional terms. Also noteworthy is that no thermal activation is necessary for this process.

Consider the following specimen calculation:

The anisotropic elasticity theory (176) and a consideration of the stacking fault energy for cobalt indicates that the ratio r/b must be approximately 10, as the dislocations are widely extended:

Assume $\tan\theta = 0.01$ therefore $\theta \simeq 0.01$ radians $\simeq 0.6^{\circ}$

γ Cobalt $= 2000$ ergs/cm^2

b $= 3^{\circ}$A

$$\therefore \Delta G = \frac{\pi}{4}(3\times10^{-8})^3 10.0.798\times10^{12}.2.303\log 2 - G_B - \frac{4.10(3\times10^{-8})^2.2.10^3}{0.01}$$

$$= 12 \times 10^{-11} - 720 \times 10^{-11} - G_B \text{ ergs}$$

$$= -708 \times 10^{-11} - G_B \text{ ergs}$$

$$= -7{,}08 \times 10^{-16} - (G_B \times 10^{-7}) \text{ joules}$$

This simple process whereby slip occurs between two grains in physical contact yields a negative free energy; thus the process could occur spontaneously.

The model therefore suggests that dislocation interactions could exert a significant influence on the "welding" together of fine particles during grinding, and that the so called "cold-welding" process could result from slip deformation processes while the grains are in contact. With the evidence that dislocation interactions are probably responsible for "cold-welding", it is possible to make some suggestions as to the type of bond that is formed between metal particles during grinding. Cross slip and dislocation climb are not possible in the dislocation interactions.

Three sets of dislocations with three non-coplanar Burgers vectors are a prerequisite for the formation of a general grain boundary such as is present in a polycrystalline metal.[176] If three independent sets of dislocations are not present as is the case in both allotropes of cobalt only special types of boundaries can be formed.[176] In f.c.c. cobalt the only dislocations that need be considered are those of the {111} planes; in h.c.p. cobalt dislocations which can result in slip interactions are those of the basal plane. Thus the types of grain boundaries that can form are theoretically predicted to be unique tilt boundaries.[177] No other orientation is theoretically possible such that characteristic metallic bonding may occur. A unique tilt boundary consists of one set of edge dislocations;[177] the boundary angle would depend on the dislocation density as would the boundary energy.[178] Another property of the unique tilt boundary is that it has no long range stress field. This can be proved theoretically.[178]

In practice these theoretical predictions of orientation at grain boundaries are often not obeyed since the dislocations can interact with one another resulting in configurations with lower energy.[178] In the particular case of the allotropes of cobalt, a pile up of dislocations can generate very large stresses at the boundaries which can cause fracture or slip in an adjacent grain.

Hypothetically a grain boundary can move normal to itself by pure slip through motion of individual dislocation segments on their glide planes, provided none of the segments with edge dislocations has glide planes coinciding with the boundary. Theoretically this would require very high applied stresses.[178] Thus generally low angle grain boundaries are both immobile in glide and stable against dissociation. The unique tilt boundary is however a glissile boundary, which can advance normal to itself by glide on slip planes normal to the boundary plane. As the boundary advances the volume of one grain increases, in the same proportion as the volume of the other decreases. This forward boundary motion requires no net transport of matter to or from the boundary, but only exchange of matter between the dislocations in the boundary. Some segments in the boundary are thought to act as sources and others as sinks.[178]

Thus in so far as the dislocation motions in "cold-welding" are concerned the following is the proposed description of the process involved: agglomerated metal particles are impacted by the grinding balls, and dislocations are introduced which interact with the dislocations initially present. The impacting of the balls results in physical adhesion between the metal particles.

Stresses generated in the agglomerates by the balls result in slip processes between adjacent grains which can reduce the free energy of the system as shown in the model. In addition unique tilt boundaries can be formed by interaction of the {111} planes of the cubic and the {0001} planes of the h.c.p. structure. These unique tilt boundaries are mobile and, as they consist of sets of dislocations, it is likely that they could be attracted towards free surfaces i.e. boundaries of the particles. If these processes do occur the apparent size of the "coherent" metal particles can increase, and the "cold-welded" aggregates will consist, in appearance, of particles larger in size compared with the particles size of the powder before grinding. By the formation and migration of unique tilt boundaries, the free energy of the powder will be reduced by elimination of free particle surface. Further the energy of the dislocations will be reduced provided the dislocations in the boundary can be eliminated at free surfaces, and do not interact with other dislocations whereby the dislocations become sessile.(179) All these processes occur while the particles are in physical contact, but the migration of the glissile low angle boundaries can only occur under the influence of an applied stress. Slip between adjacent particles can occur while the particles are in physical contact in the absence of an applied stress provided a pile up of dislocations can break through the boundary.

More extensive slip can occur in the f.c.c. form compared with the h.c.p. form, and more extensive "cold-welding" is therefore expected.

In addition to the glide of the dislocations during grinding, the vacancies in the metallic lattices must be considered. The vacancies tend to be driven away from rigid boundaries under the influence of an applied stress, and are attracted towards the free boundaries such as dislocations and free surfaces.(69) If a vacancy is eliminated at a particle surface, the energy required for the formation of a vacancy is released, which is about 20 k cals/g atom.

Vacancies expelled from the metal particles would tend to reduce the number of defects in the adhering surfaces, and the effect of the removal of vacancies could be to increase the true area of contact between particles that are in adhesion. The concept of vacancy elimination reducing the number of steps on a surface has been proposed;(180) thus the energy released on the vacancy reaching the surface would probably reduce the free energy of the surface.

Twinned regions could be expected in certain areas of the "cold-welded" agglomerates, since twinning is an expected mode of deformation in both allotropes of cobalt.

The "cold-welding" processes described above cannot continue indefinitely, because of the increasing deformation of the particles (and hence dislocation density) which is introduced by continued impacts from the balls. Work hardening of the cold welded material will result in the slip processes being impeded, and fracture will result from large concentrations of dislocations at the mosaic and twin boundaries. After extensive deformation, certain of the dislocations may become sessile and act as obstacles towards further glide of dislocations. Cubic regions of the powder are transformed to the h.c.p. form by deformation; the h.c.p. form is more prone to brittle fracture. Small particles will therefore tend to become removed from the cold welded agglomerates. Certain of these particles may be rewelded to other agglomerates, but it is shown later that there is a chemical reaction in the grinding fluid by which certain compounds can be adsorbed on the powder particle surfaces, which can prevent metal -metal readhesion. A stage during grinding will be reached therefore where the rate of fracture exceeds the rate of re-adhesion and the agglomerates will decrease in size.

Several investigations have shown that f.c.c. metals work harden more rapidly than do the h.c.p. metals. *(181)*

Thus it might be expected that comminution of f.c.c. agglomerates would occur more readily than occurs for h.c.p. agglomerates. However the occurence of more extensive slip in the f.c.c. form compared with the h.c.p. form leads to more extensive "cold-welding" in the f.c.c. form.

The presence of grinding fluid would promote the occurence of physical adhesion between the metal surfaces in comparison with adhesion in air. This is predicted by the Stefan equation (182) which is shown in Appendix 8. (This equation was originally derived by Stefan in 1874, and has subsequently been derived by others (182)). According to this equation, physical adhesion increases with viscosity of the surrounding medium. The viscosity of air at room temperature is 0.018 centipoise compared with a value of 0.320 centipoise for acetone at room temperature (183). In addition the Stefan equation predicts that the forces of adhesion are much greater for flake shaped particles than for rounded particles.

Thus it is suggested that physical adhesion and "cold-welding" occur when the agglomerated particles are impacted by the grinding balls. The adhesion and "cold-welding" behaviour is governed primarily by the operation of the slip systems in the hexagonal and cubic allotropes of cobalt.

"Cold-welding" implies the formation of larger particles from smaller particles during grinding, such that the large particles appear to be virtually coherent. The formation of these aggregates by diffusional processes is rather tenuous, but as the temperature generated on impact of balls cannot be evaluated exactly, diffusional processes resulting in "cold-welding" cannot be entirely ruled out. Slip and dislocation interactions while the particles are in contact could also and probably do result in "cold-welding". During grinding of both allotropes of cobalt cross slip and dislocation climb processes are improbable. It has been suggested that low angle tilt boundaries are involved in the "cold-welding" process; it was suggested that these boundaries are formed on the {111} planes of the f.c.c., and the {0001} of h.c.p. cobalt.

The distinction between physical adhesion and "cold-welding" is very difficult. Physical adhesion implies that there should be some evidence of discrete particles in the aggregates. It is suggested therefore that during grinding of metallic particles both physical adhesion (with some evidence of individual particles in the agglomerate) and "cold-welding" (where the large aggregates appear to be "coherent") occur. Factors such as surface roughness of the particles may influence the extent of "cold-welding" and physical adhesion observed.

It is possible that during the comminution of cobalt metal powders both processes occur to varying degrees. Both "cold-welding" and physical adhesion depend on the same physical properties of the metal. The occurence of agglomerates of this type in the ground powders indicate that considerable adhesion occurs during grinding and the junctions are able to withstand the released elastic stresses.

As a consequence of the deformation characteristics of f.c.c. cobalt under an applied load, compared with those of h.c.p. cobalt much greater adhesion would be expected between f.c.c. cobalt particles than between h.c.p. cobalt particles. It was recorded earlier that oxide films on f.c.c. cobalt are thought to be under greater strain than those on h.c.p. cobalt; the strained oxide scales would be more susceptible to fracture. Furthermore the previous work showed that predominantly f.c.c. cobalt powder prepared by reduction at high temperatures had coarser grain sizes compared with the h.c.p. powder prepared at low temperatures; the oxygen contents of the f.c.c. powders were shown to be lower than those of the h.c.p. powders. It is likely therefore that if oxide films were present on the f.c.c. particles prior to grinding, they could be easily ruptured and increased adhesion between f.c.c. particles could occur.

Thus it must be concluded that the forces of adhesion between cobalt particles would decrease in the following order:

f.c.c. - f.c.c. > OF* - f.c.c. - f.c.c. > OF - f.c.c. - OF - f.c.c.> h.c.p. - h.c.p. ≈ OF - h.c.p. - h.c.p. ≈ OF - h.c.p. - OF - h.c.p.

In general terms it has been found that the less ductile a metal is, the lower will be its adhesion. Thus agglomeration due to forces of adhesion will be much lower for h.c.p. cobalt than for f.c.c. cobalt, but this does not mean that cold welding between h.c.p. metal particles cannot occur.

4. PROPOSED MECHANISM FOR THE GRINDING OF COBALT METAL POWDERS

Having described a number of effects which are operative during comminution of metal powders, it is possible to attempt to explain the grinding characteristics of cobalt powders, which initially contain different proportions of the hexagonal and cubic phases.

* OF represents an oxide film

The following points summarise the expected behaviour, and some of the experimental results:

(1) During the initial stages of grinding of cobalt powders, all powders (except the annealed powders) were found to agglomerate, irrespective of initial allotropic ratio. Evidence for the agglomeration is provided by the decrease in specific surface area, and direct observations made on the ground powders with the Stereoscan Microscope. It is not possible to predict theoretically which allotrope has the greater tendency towards natural agglomeration when a cobalt powder is placed in the grinding fluid.

(2) On theoretical grounds it would be expected that hexagonal cobalt could be comminuted more easily than cubic cobalt, and cubic cobalt would exhibit "cold-welding" during grinding more readily than hexagonal cobalt.

(3) On grinding, predominantly cubic powders tend to form large "cold-welded" agglomerates, whereas in the hexagonal powders, powder particles with sizes similar to the initial sizes are evident within the agglomerates. Some evidence for the occurence of "cold-welding" is present in the hexagonal powders, however.

(4) During the course of grinding of cubic cobalt, transformation to the hexagonal modification occurs, as a result of shear.

Complete transformation of all the cubic material present to the hexagonal modification does not occur during grinding, but a significant proportion of the initially cubic material is present in the hexagonal form after extended grinding. Thus on grinding a cobalt powder, initially predominantly cubic in structure, characteristics of the cubic structure would be expected; thereafter properties more characteristic of the hexagonal modification could be expected.

Thus in broad outline the following behaviour would be expected on grinding cobalt powders:

(a) The predominantly cubic powders would show pronounced evidence for adhesion and "cold-welding" during the initial stages of grinding. Transformation to the hexagonal form would be occuring concurrently with the adhesion process. The hexagonal form shows much reduced adhesional characteristics compared with the cubic form, and in addition less energy would be necessary to comminute the particles. Therefore the "cold-welded" aggregates could be broken up into smaller particles.

Thus it would be expected that the following changes in specific surface area would be observed during the grinding of a predominantly cubic cobalt powder: The specific surface area would decrease initially due to the adhesion of the cubic particles, but simultaneously small particles of hexagonal material would be formed.

However during the initial period, the strong adhesional characteristics of the cubic material prevent any increase in specific surface area being recorded even as a result of the hexagonal particles formed. The particles of the hexagonal cobalt which are produced have a small tendency to adhere to one another, but the measured specific surface area still decreases. However a stage will be reached at which the energy supplied by the grinding will exceed the forces of adhesion in the agglomerates. The aggregates will break down and the specific surface area will increase. Thus a slow decrease in specific surface area due to adhesion of cubic material and formation of hexagonal material will occur over an extended grinding period. Thereafter a marked increase in specific surface area will occur due to the poorer adhesional characteristics of the hexagonal material.

(b) Predominantly hexagonal cobalt powders would be expected to show some adhesional characteristics during grinding. This would result in a decrease in the measured specific surface area. However hexagonal material exhibiting "brittle" fracture characteristics could also be comminuted during the initial stages of grinding. The net effect during the initial stages of grinding must be that the adhesional process operates in preference to the comminution process.

A stage will be reached where energy imparted to the agglomerates by the grinding balls will exceed the forces of adhesion within the agglomerates, and small particles will be removed from them. Either through contamination from the grinding fluid or by some other means, which are discussed later, hexagonal particles removed from the agglomerates do not tend to readhere to one another and the specific surface area increases. Thus on purely mechanical grounds a predominantly hexagonal cobalt powder would show an initial decrease in specific surface area, followed by an increase in specific surface area. The grinding period during which the initial decrease in specific surface area occurs would be expected to be much shorter than in the case of predominantly cubic powders due to the reduced adhesion shown by hexagonal powders compared with cubic powders.

The above processes probably represent a very simplified picture of the processes which occur during the comminution of cobalt powders. A number of the processes mentioned are probably occuring simultaneously with one another, and may compete with each other.

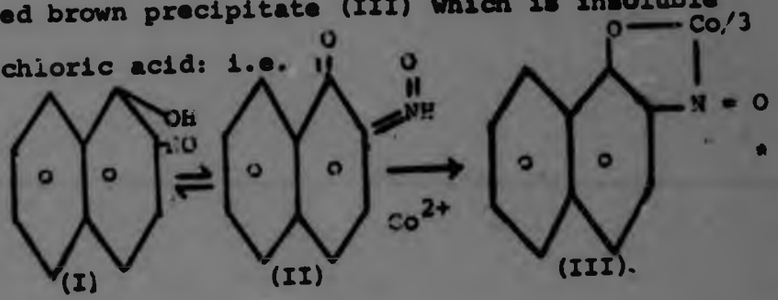
The mechanism proposed above for the comminution of predominantly hexagonal powders is not obeyed during the comminution of a cobalt powder, which consists solely of the hexagonal modification.

It was noted earlier that comminution of an ultrafine powder consisting only of the hexagonal form resulted in the minimum specific surface area being achieved after 90 hours of grinding. The probable reasons for this behaviour are described later in this section.

Metal powder particles could fracture during ball milling in the following way: Grinding in the cold works the metal powder particles and cold working makes the particles more reactive. The cold working of the particles is most severe in the sections of each particle caught between impacting balls (or between balls and ball mill wall) and this volume acquires a more positive free energy than the rest of the particle. On average the points of impact become thinner than the rest of the particle. The impacted regions of the particle are likely to be more reactive with respect to the ball milling medium than the rest of the particle which reacts with the milling fluid to a lesser degree. Eventual fracture of the particles probably occurs through these most heavily cold worked regions both because they are thinner (and thus weaker) than the remaining portions of the particle and because localised chemical reaction could produce effects which could assist the fracture process.

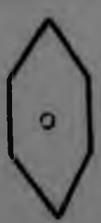
It is therefore necessary to discuss the possible role of the acetone in the comminution process. Evidence presented earlier suggested that the cobalt reacted with the grinding fluid during milling. A carbon pickup from the acetone was noted in the ground cobalt powders. After grinding cobalt powders for periods of about 70 to 100 hours the grinding fluid acquires a distinct yellow coloration. Using a spot test technique, it can be shown that this grinding liquid contains dissolved cobalt. The basis of the spot test is as follows: (184)

α - Nitroso - β napthol (I) reacts in its tautomeric isonitro-oxime form (II) with cobalt to give a red brown precipitate (III) which is insoluble in hydrochloric acid: i.e.



(I) (II) (III).

This spot test is positive with both di- and trivalent cobalt since the α nitroso β napthol reagent itself can act as an oxidising agent since it is an orthoquinoid compound, and a derivative of nitrous acid. (184) Thus it is not possible to be specific (without further experimentation) about the valency state of the cobalt in the acetone after grinding.



REPRESENTS A HYBRIDISED BENZENE RING

Nevertheless chemical reaction between the cobalt and the acetone must occur during grinding. Pure acetone not used for grinding exhibits a negative spot test.

It was noted earlier that no chemical reaction between cobalt metal and acetone has been reported in the literature, but reactions between basic oxides and compounds containing the carbonyl group were known. Thus it is suggested that the reaction observed during comminution might arise from the cobalt oxide rather than from the cobalt metal itself. It was noted that certain basic compounds could cause intermolecular condensation reactions, and it is conceivable that cobaltosic oxide could promote the condensation reaction. It is assumed therefore that it is through Co_3O_4 adsorbed on the surfaces of the metal powder particles that the condensation reaction results. In Co_3O_4 both di and trivalent cobalt ions are present, as was noted earlier.

Thus it is suggested that during grinding of cobalt powders, the behaviour expected from the crystal structures of the two allotropes of cobalt is modified by the presence of the acetone in the following respects:

(1) The acetone reacts with oxide films on the surface of the metal powder particles.

(2) The acetone promotes physical adhesion as predicted by the Stefan equation.

(3) For the reasons noted earlier the acetone is unlikely to influence fracture characteristics of the ductile metals as suggested by the Rehbinder theory.

(4) The acetone promotes limited agglomeration by its electrical polarisability effect.

Concurrently with particle fracture, it has been suggested that there is the competitive process of particle welding occuring during grinding. Particles of micron sizes dispersed in a liquid tend to stick to one another when they touch each other, (as was discussed earlier). Loose agglomerates of powder formed in this way could become "welded" to one another when caught between impacting balls (or between a grinding ball and the mill wall).

In general the smaller the particles the more readily they would be expected to stick to one another. As the particles grow by welding they could eventually reach an equilibrium size at which the rate of welding is equal to the rate of fracture.

Although some suggestions were made earlier for the mechanism of the "cold-welding" process, the detailed processes involved are difficult to explain, and it is difficult to suggest experimental techniques by which it may be investigated.

The technique which would be most suitable for the examination of this mechanism would be electron transmission studies on thin agglomerates of powder. No investigations of transmission studies on metal powders have been reported[185]; metal oxide powders have been studied in transmission and in a number of cases results have been obtained which cannot be explained satisfactorily and in some instances the anomalous results have been ascribed to the support technique used for the powder.[186]

The theory of electron penetration of solids is still incomplete, but thicknesses of the order of 1000°A are required for transmission studies.[187] Cobalt has the smallest relativistically corrected extinction coefficient of a number of metals.[188] Humphries[189] has calculated that 1.5 MeV microscopes are necessary for the satisfactory examination of metal sections 1μ in thickness for a metal of medium atomic weight (e.g. iron).

A number of techniques were used in this work in an attempt to study the internal structure of the cobalt particles:

(1) A number of cobalt powder particles were mounted on Cellofas lacquer and coated with carbon platinum. The lacquer was dissolved in water and the films placed on copper grids for examination in the EM200 unit.

Studies indicated that none of the particles were thin enough to obtain transmission results.

(2) Samples of the powder were treated with hydrochloric acid for various times. This treatment was found to increase the proportion of the f.c.c. form; in electrolysis it has been found[190] that a low pH favours electro-deposition of the f.c.c. form; the same effect could perhaps be operative during leaching. On examination of the leached powders no particles yielded electron transmission results. Another disadvantage of a technique of this type is the possible formation of etch pits on dislocations.[191]

(3) Some powders were mounted in a "Woods alloy"* (with a melting point of 95°C) but the alloy did not wet the cobalt particles, and only a mechanical bond between the particles and alloy was evident on micro-examination. A three phase structure (a eutectic composition of the Woods alloy and cobalt) was evident in these specimens which made electropolishing very difficult. These samples could be thinned to electro-transparency but the resulting foils were very brittle. The internal structure of the cobalt particles was not discernible however.

* Supplied by Cerro-tru Corporation - New York

(4) Similar experiments were carried out using a 91 % Sn 9 % Zn alloy (melting point 205°C) for mounting the particles. Similar difficulties to the use of Woods metal were encountered.

An alloy of low melting point must be used for mounting the powders, as the previous work [198] showed that the stacking fault probability was altered by heating powders to 300°C.

Thus the cobalt powders cannot be examined by direct transmission using 100 Kv which hampers a complete interpretation of the phenomenon of "cold-welding" and also the mechanism of the Co_3O_4 reduction process described in Chapter 2 of Volume 1. Howe [193] has found that cobalt foils 0.65μ in thickness may be examined at 750 Kv; thus it does not appear that the type of bonding present in cobalt powder agglomerates several microns thick can be examined even with very high electron accelerating voltages. Very high electron accelerating voltages would also be required for studying the detailed mechanism of the cubic to hexagonal phase transformation which occurs during grinding.

From the suggestions made above it is likely that the extent of transformation will be most marked in the sectors of the particles which are caught between impacting grinding balls.

The important question that has to be answered is the manner in which the transformation from one phase to the other occurs in the impacted regions, and the depth to which impact affects the structure and dislocation density. Without being able to examine the particles directly in transmission microscopy, the process of the transformation in powders, and the importance of prior faulting cannot be established. The mechanism of the cubic to hexagonal transformation in cobalt is well established in general terms, but the actual progress of the transformation does depend on the prior thermal and mechanical history of the material.(194) In particular surface effects could play a large role in the transformation in fine powdered metals. In a number of studies on single crystals it has been found that the slip processes near the surfaces of the specimens are different from those in the bulk of the materials.(22) Any chemical reaction with the grinding fluid could alter the properties of the surface compared with bulk material. Oxide films on the surface of the metal can affect the work hardening rate.(104),(105) None of these effects can be observed without the use of a microscope with very high accelerating voltages.

X ray methods are unsatisfactory for the examination of cold welded aggregates, in particular "cold welded" cobalt powders. It is shown later that the "cold welded" metal particles are porous in certain areas. This could lead to X ray line broardening and porosity is not accounted for in the formulae used. In cobalt powders which consist of both f.c.c. and h.c.p. modifications the (111) f.c.c. and (0002) h.c.p. profiles are practically coincident. Thus twinning on {111} of f.c.c. which is an expected mode of deformation for cubic cobalt cannot be quantitatively studied. Nabarro et al.(22) have pointed out that X ray methods are inadequate in resolution to provide a detailed structure of the cold worked state. In addition point defects such as vacancies have hardly any influence on X ray line breadth.(196) However as is shown later X ray diffraction can provide some information on dislocation densities and distribution. The effects which are actually measured in X ray diffraction are confined to a very limited depth at most approximately 10μ from the surface of the material.

Thus in the present case the only way in which the adhesional process can be studied is from observations on a Stereoscan Microscope.

Oxide films formed on fine cobalt powders would be expected to be non-stoichiometric in character for the following reasons: On exposure of a fine cobalt powder to air one or two molecular layers of oxygen could become bonded to the metal particles by van der Waals forces of adsorption; however, the character of the bond between the electropositive cobalt and electronegative oxygen changes in such a way that a chemisorbed film of cobalt oxide is formed on the surfaces of the metal powder particles. During this process of formation of the chemical bond and when a thin film is present, electrons can travel to the outer surface by the quantum tunnel effect.(196) Once these electrons arrive at the surface they could conceivably ionise adsorbed oxygen atoms and cause an electric field to be established between the surface of the oxide film and the metal surface. Cations from the metal could then be transferred from the metal through the film under the influence of the concentration gradient and the electric field. Studies of the oxidation of cobalt suggest that the oxide film grows by cation movements through vacant lattice sites, and that equilibrium is not established as the oxide scales contain a deficiency of cations.(89) Although no results have been reported for cobaltosic oxide, it was noted earlier that CoO scales exhibited greater plasticity the greater the deviation from stoichiometry with respect to the cations.

It was also noted that there were reasons to believe, from the coefficient of friction studies, that an oxidised h.c.p. surface showed no marked decrease in coefficient of friction compared with a "clean" h.c.p. metal surface. Thus adhesion between two oxidised h.c.p. surfaces would be expected to be comparable with that shown by two h.c.p. "clean" metal surfaces.

During the preparation of cobalt metal powders with different initial allotropic ratios, described in Volume 1, carbon dioxide gas was passed over the metal powder before exposure to the atmosphere, to prevent pyrophoricity. It was suggested that the CO_2 was physically adsorbed at certain sites, thus preventing further oxidation from the atmosphere. The CO_2 would be expected to be adsorbed at a certain number of preferential sites on the metal powder which would depend on topographical features such as surface roughness and grain size and shape. On exposure to the atmosphere, adsorption of oxygen would probably occur at the sites which were not occupied by CO_2 molecules. A scale of cobaltosic oxide could be formed at the CO_2 deficient sites, and the CO_2 could also interfere with the growth of scales at other sites. Due to the strong affinity between fine cobalt powders and oxygen there are reasons to suspect that oxygen could diffuse through the adsorbed CO_2 layers.

The barrier formed by the CO_2 could lead to greater deviations from stoichiometry in the scale than would be found in the absence of adsorbed CO_2 molecules. Thus in addition to the non-stoichiometry exhibited by Co_3O_4 under more normal conditions of formation, it is suggested that the particular circumstances present in fine cobalt metal powders could lead to very marked deviations from the stoichiometric composition. In addition surface oxidation is expected to be anisotropic as discussed in Section 3.3. It would be expected, therefore that cobalt powders (in particular fine hexagonal powders prepared at low reduction temperatures) would contain a non-uniform distribution of oxide scales with the cobaltosic oxide showing substantial deviations from the true stoichiometry. The calculations shown in Appendix 5, where spherical particles were assumed, indicate that in the case of the fine hexagonal powder the layer can be up to 200°A thick. In predominantly cubic cobalt powders with coarser grain sizes the layer of cobaltosic oxide would be expected to be much thinner. In addition it was noted that oxide films formed on hexagonal cobalt do not show the straining that is present in oxide layers formed on cubic cobalt. Thus although the oxide layer formed on hexagonal cobalt powders may be strongly bound to the metal, deviations from stoichiometry could occur for the above - mentioned reasons, and a non-uniform oxide distribution would also be expected.

The presence of dislocations on the surfaces of the metal powder particles could also lead to non-uniform adsorption.

With the above facts and the pronounced "stickiness" expected from very fine powders it is possible to suggest the processes which occur during the grinding of fine pure hexagonal cobalt powder: On adding the powder to the grinding fluid, metal powder particles will tend to adhere to one another. Particles loosely agglomerated together could, on being trapped between impacting balls, become welded to one another through the oxide films present on the particle surfaces. These oxide films, it was suggested, are susceptible to chemical reaction with the grinding fluid as milling proceeds. Although the oxide films could be expected to show a considerable degree of plasticity, the bonds formed between the oxide layers could not be expected to show the same adhesive strength as metal-metal bonds, because of the differences in the nature of oxide bonding compared with metallic bonding. A marked adhesion between oxide layers may however be evident. Due to chemical reaction with the acetone and further impacting by the grinding balls certain areas of the oxide may be removed to the grinding fluid, and severe strains and dislocations could be set up in other parts of the oxide layers.

These effects would be superimposed on a very non uniform and non-stoichiometric oxide scale. The two effects (oxide scale dissolution and deformation) could take place over a considerable grinding period and a long time may be necessary before these processes are completed. Removal of the oxide film will expose chemically pure hexagonal metal surfaces which (although the effect is not so strong as in cubic cobalt) could adhere to one another by the physical adhesion and "cold-welding" processes. Thus a further decrease in specific surface area may be anticipated with additional grinding. A stage will however be reached at which fracture of the agglomerates will exceed the extent of "cold-welding" and the net effect will be a further increase in specific surface area with increasing grinding time.

Thus it is suggested that the long period necessary to achieve the minimum specific surface area on grinding a pure hexagonal cobalt powder is due to the occurence of two adhesional or "cold-welding" processes. The proposed mechanism would account for the observations made on the agglomerates of hexagonal cobalt on the Stereoscan Microscope, namely that the agglomerates consist of a large number of small metallic particles bonded together, with other areas which show evidence of "cold-welding".

If it is assumed that the two adhesional processes take place over a very long grinding time, the continuous decrease in specific surface area over 90 hours of vibratory milling may be explained. The above proposed mechanism suggests that after very long grinding times, individual hexagonal cobalt particles should have rounded smooth surfaces similar to ground cubic cobalt particles which have been through a "cold-welding" process, followed by comminution of the "cold-welded" agglomerates.

Evidence of hexagonal particle surfaces presented later suggests that this is the case. The above mechanism assumes that oxide layers released by impacting balls are largely removed by dissolution in the acetone, or that their removal from the surfaces of the metal particles does not result in any net increase in specific surface area.

It was suggested earlier that on average particles removed from an agglomerate by comminution tend not to re-combine with one another on further impact from the grinding balls. Evidence that this must be the case, is provided by the continuous increase in specific surface area which is recorded after the minimum value has been measured. This process is noted in both the predominantly cubic and predominantly hexagonal cobalt powders.

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Observations made on cobalt powders after extended grinding periods (e.g. Figure 4.13 of Volume 1) show that the particles are generally rounded in shape and have smooth surfaces. Such particles therefore have the lowest surface area to volume ratio that is possible. The reasons for this lyophilic behaviour are not clear but the following may constitute a partial explanation: the surfaces of the rounded particles must be in a state of strain with a large number of crystal imperfections on the surfaces which have resulted from the cold working processes arising from grinding. In order to reduce the surface free energy, adsorption of acetone from the grinding fluid could occur with the surface imperfections acting as an "anchor". An analogy is provided by the way in which interstitial impurities segregate to dislocations and anchor them.[197] The individual rounded metallic particles could carry a "solvation sheath" of acetone molecules with them, and this state has a lower total free energy than any other state such as the adhesion (after a collision) of two metallic particles. This may be a rather idealised partial explanation for the observed behaviour. Unfortunately the adsorption of acetone from solution on metallic cobalt has not been reported in the literature, so no previous data are available to confirm this suggestion.

In addition measurements of the surface free energy of cobalt metal in acetone have not been made. The literature records no observations of differences in surface free energy of metals in solution arising from the cold working of the metals.

It was suggested earlier that reaction between cobalt metal and acetone during grinding was unlikely; thus there is little possibility of the presence of any reaction product (arising from interaction between cobalt and acetone) on the rounded metal particle surfaces, which would reduce the surface free energy and prevent adhesion between two rounded particles. However experimental evidence given later, indicates that the reaction of cobaltosic oxide and acetone results in the formation of some phorone, which is an unsaturated olefinic molecule. This compound could be adsorbed on the surfaces of the cobalt metal. This adsorption might be expected by analogy with studies in catalysis, where it has been found that transition metals with their unfilled $3d$ bands can cause adsorption and even polymerisation of olefinic molecules under certain conditions. Metallic cobalt with its $3d^7 4s^2$ band structure can show marked chemisorption and catalytic reactivity.

If the above suggestions are correct, cobalt powders which contain large amounts of oxide before grinding should exhibit lower adhesional characteristics, after the states of minimum surface area have been achieved, than cobalt powders which contain lower quantities of oxygen initially. Ideally the lowest adhesional characteristics, after the states of maximum agglomeration have been achieved, should be exhibited by pure hexagonal cobalt powders for the following reasons:

(a) In hexagonal powders a large amount of oxygen is present initially which would result in the formation of a considerable quantity of phorone by reaction of cobalt oxide and acetone. The phorone would be adsorbed on the cobalt metal particles.

(b) Hexagonal powder particles exhibit basal slip and thus are easily fractured compared with other cobalt powder which still contain some of the cubic modification after the state of maximum agglomeration (i.e. minimum specific surface area) has been achieved.

The above discussion will have indicated that complex physical and chemical effects may probably occur during the comminution of different cobalt powders.

In general the results in Chapter 4 of Volume 1 indicate that the following behaviour is recorded on grinding commercial cobalt powders with different initial allotropic ratios:

(1) Predominantly hexagonal powders (hexagonal fraction greater than 30 % by weight) show a rapid decrease in specific surface area to a certain minimum value during the first stages of grinding after which the specific surface area increases.

(2) Predominantly cubic powders show a much slower approach to the condition of minimum specific surface area, after which the specific surface area increases.

Powders of type 1 would not be expected to show the adhesional characteristics of powders of type 2. In powders of type 1 adhesion is the major process and the state of minimum surface area is reached relatively quickly. In powders of type 2 there is adhesion of the cubic phase but also conversion to the hexagonal form, and a much longer time is required to reach the state of minimum specific surface area.

It is very likely that several of the above mentioned processes are occuring simultaneously and in competition with each other.

In commercial cobalt powders it is clear that factors such as method of preparation, oxygen level, degree of prior mechanical working (e.g. the introduction of stacking faults by screening) and the allotropic ratio can interact with each other in a complex manner during grinding and lead to very different specific surface area variations. A special mechanism has been proposed for ultrafine hexagonal cobalt powders. Thus cobalt powders can be effectively graded into 3 categories according to their behaviour, on grinding in acetone.

A further complication in the interpretation of the results arises from the fact that the materials are polycrystalline. One single particle of cobalt powder consists of many single crystals. The particle is not composed of one phase and regions of both cubic and hexagonal modifications will be present in the same particle.

It was noted earlier that no formal theory is known which can be used to study the collision process between a grinding ball and a cobalt powder particle or agglomerate, because of the plastic deformation that occurs in the cobalt. Because of this incomplete knowledge, it is also not possible to gain any quantitative idea of the factors which determine the maximum size to which an agglomerate can grow.

Fracture of the metallic particles by fatigue mechanisms has been neglected in the above analyses. Repeated impacting of the metal particles by the grinding balls must lead to a fatigue fracture mechanism for some of the particles. The capacity of the f.c.c. form of cobalt to absorb more plastic deformation before fracture occurs, suggests that this modification would be less prone to a fatigue fracture mechanism than would be the case for the h.c.p. form. However as noted in Section 3.2. deformation of the f.c.c. phase by twinning could increase the possibility of fatigue fracture in the f.c.c. material.

In Chapter 5 of the previous work, it was shown that agglomeration of cobalt was an important requirement for achieving a satisfactory sintered density of hard metal powder compacts after a minimum grinding time. The main function of milling is to achieve a uniform dispersion of cobalt around the asperities of the carbide grains. The dispersed cobalt promotes uniform and regular shrinkage during sintering. The presence of any large cobalt particles devoid of carbide grains in the pressed compacts results in porosity in the sintered structures. It was shown that a predominantly hexagonal cobalt powder was preferable to a predominantly cubic cobalt powder for achieving a given sintered density after a minimum grinding time.

Suggestions must therefore be made as to the type of agglomerate and its bonding that would be most desirable in this particular use of cobalt metal powders. Type 1 cobalt powders were preferable to those of type 2, while the most satisfactory was an ultrafine hexagonal powder.

It was suggested that aggregates of cobalt were formed, and the finer carbide particles initially became embedded in the agglomerates. As grinding proceeded the agglomerates were broken down in size and also a rolling into thin foil like shapes occured during hard metal milling. The foils were thought to envelop the carbide grains and promote the initial stages of sintering. It was thought that the foil like particles were produced by the cutting of the cobalt aggregates by the carbide grains in the presence of the hard metal grinding balls.

It is very likely that fine brittle tungsten carbide grains impacted against a cold welded agglomerate consisting of predominantly ductile f.c.c. cobalt could become embedded in the binder metal agglomerate. The cobalt agglomerate would be plastically deformed by the impact and some conversion to the hexagonal modification would occur. The impact of a carbide grain large in size in relation to the size of an f.c.c. cobalt agglomerate would produce fracture of the carbide grain with perhaps some of the fractured material adhering to the binder metal.

On the other hand, impact of a large carbide grain against a more brittle oxygen bonded agglomerated hexagonal material would probably result in both fracture of the carbide and the fracture of the binder metal aggregate, with areas from the agglomerated cobalt adhering to the fractured carbide. Repeated impacts and collisions of this type would result in a much more rapid dispersion of cobalt throughout the tungsten carbide grains than would be the case with the more ductile aggregate of predominantly cubic material. There is little likelihood of a ductile f.c.c. agglomerate being fractured by impact; the agglomerate would plastically deform under the influence of the applied stresses. The only way in which the ductile material could be broken down and become dispersed uniformly throughout the carbide grains would be by a "cutting" process.

Thus it is suggested that the mechanism previously discussed for combination of cobalt and tungsten carbide during hard metal milling was perfectly correct for a predominantly cubic cobalt powder. However some modification to the proposed mechanism is necessary for a predominantly hexagonal cobalt powder which does not exhibit such pronounced metal-metal adhesion within the agglomerates.

Therefore during hard metal milling using a predominantly hexagonal powder, it is suggested that weak metal-metal and oxide-oxide adhesion occurs resulting in the formation of an agglomerate. The cobalt agglomerates and the carbide grains are fractured on impact with some of the binder metal agglomerate adhering to the fractured carbide. In the regions where hexagonal 'cold-welding" has occured, the mechanism operative during hard metal milling is presumeably similar to that which was suggested for cubic cobalt.

It is important to emphasise that during hard metal milling adhesion between carbide and cobalt must occur. The only way in which this can be achieved is through an agglomeration process followed by a fracture process. Very poor sintering characteristics result from a powder compact in which the cobalt powder particles are merely dispersed in a tungsten carbide matrix, no matter how fine or however well the binder metal particles are dispersed. Successful sintering only results when adhesion of the cobalt to the carbide has occured, and the cobalt must be uniformly dispersed around the edges of the carbide grains.

An experimental programme was therefore formulated to test some of the suggestions made earlier:

(1) The grinding of a completely cubic cobalt powder was not studied in the previous work.

A powder of this type could be expected to show marked initial adhesion.

(2) Considerable emphasis was placed on the role of adsorbed oxygen films in the grinding of predominantly hexagonal cobalt powders. A number of the observed effects were attributed to the presence of the oxide films. These films must be detected.

(3) The inability of metal particles to adhere to one another after the state of minimum specific surface area has been reached, and certain effects associated with the grinding of hexagonal cobalt powders were attributed to a chemical reaction occuring during grinding. Thus it is necessary to study the nature of this chemical reaction.

(4) In order to confirm the behaviour of different cobalt powders, it would be useful to extend the grinding tests to other milling fluid systems.

(5) The dislocation density and dislocation distribution can be determined using X-ray techniques on the powders studied previously and reported in Chapter 4 of the previous work.

(6) The differences in appearance between hard metal powders prepared with hexagonal and cubic cobalt powders can be investigated in greater detail.

5. EXPERIMENTAL PROGRAMME

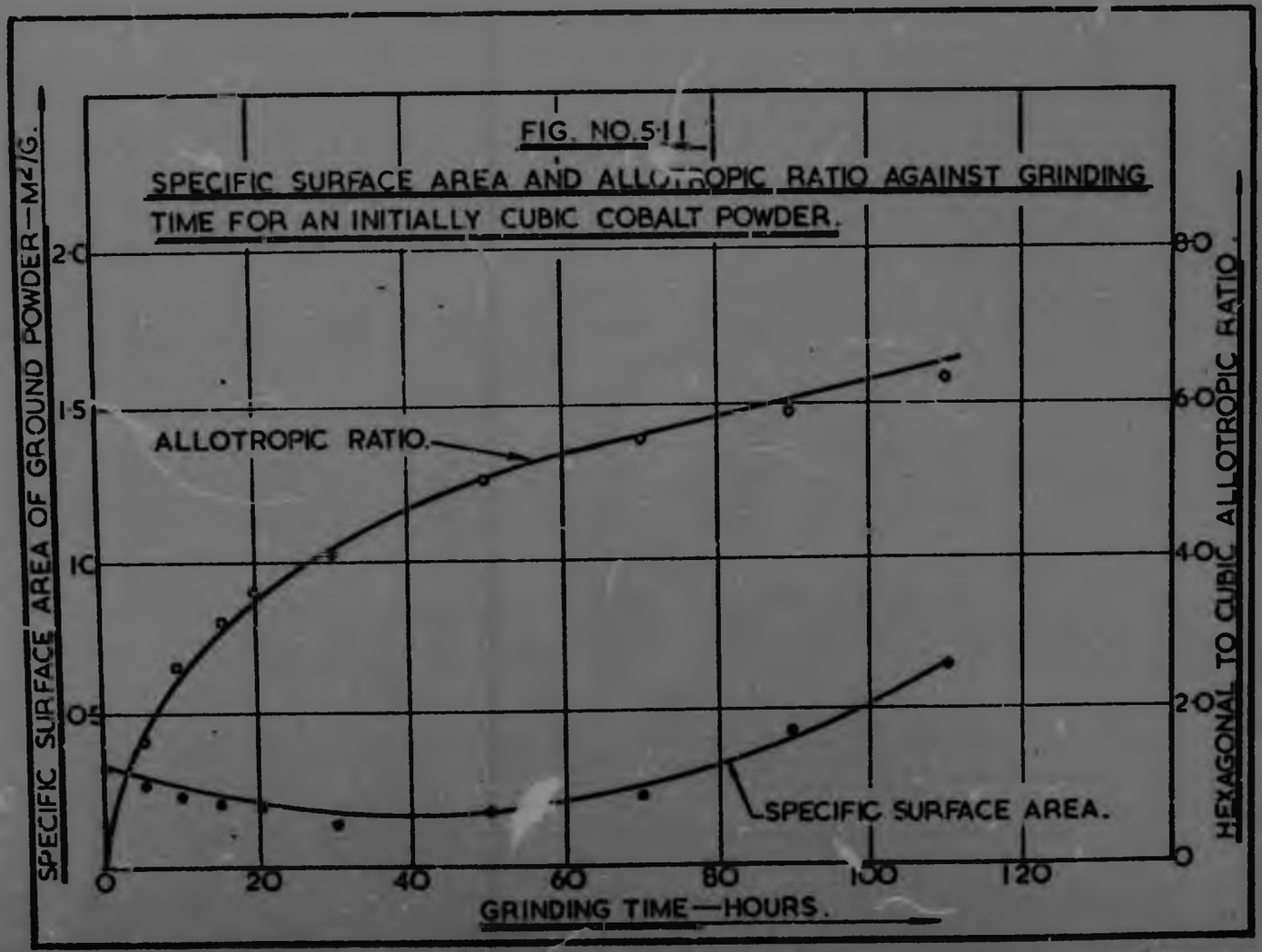
5.1. THE GRINDING OF CUBIC COBALT POWDER

As the grinding of a cobalt powder which showed no traces of the hexagonal modification had not been studied in the previous work, a powder was prepared by hydrogen reduction of cobaltosic oxide at 850°C for 6 hours. X-ray analysis showed that this powder contained no detectable proportion of the hexagonal modification. The oxygen content was 0.03 %, and the measured specific surface area was 0.32 m^2/g.

500 g of this powder was ground in a 800 ml. mill in the same manner as the powders that were studied previously. Small samples were removed after 5, 10, 15, 20, 30, 50, 70, 90 and 110 hours of grinding. The samples were dried under vacuum to remove the grinding fluid and the specific surface areas were measured on the Perkin Elmer 212D Sorptometer. X ray diffraction patterns were taken from the powders. Figure 5.1.1. shows the variations in powder properties with grinding time. There was a continuous decrease in specific surface area from the inception of grinding to the state of maximum agglomeration.

FIG. NO. 5·11

SPECIFIC SURFACE AREA AND ALLOTROPIC RATIO AGAINST GRINDING TIME FOR AN INITIALLY CUBIC COBALT POWDER.



A number of samples of the powder were examined on the Cambridge Stereoscan Microscope. A sample of powder after 5 hours of grinding is shown in Figure 5.1.2. (x 1960). The small cube of metal shown in this figure suggests that some "cold-welding" has occured after this grinding time, as does the appearance of some of the other aggregates. Figure 5.1.3. (x 1960) shows the powder after 10 hours of grinding, and the extent of adhesion can be seen to be much increased compared with that observed after 5 hours grinding. The appearance of the small cubic particle is noteworthy. As grinding was continued further, adhesion occured although there were a number of fine particles evident in the powder. Figure 5.1.4. (x 4940) shows a small sample of the powder after 15 hours milling. An agglomerate exhibiting the occurence of "cold-welding' is visible but a considerable number of very fine powder particles are also evident in this photograph. Figure 5.1.5. (x 9880) shows a single "cold-welded" agglomerate after 15 hours grinding. In this agglomerate there appears to be a basic structure onto which successive layers of cobalt have been "flattened" by the action of the grinding balls. During the period from 15 to 30 hours of grinding the specific surface area continued to decrease indicating the continuance of the process of adhesion during this period. Figure 5.1.6. (x 980) shows a typically "cold-welded" aggregate after 30 hours of grinding.

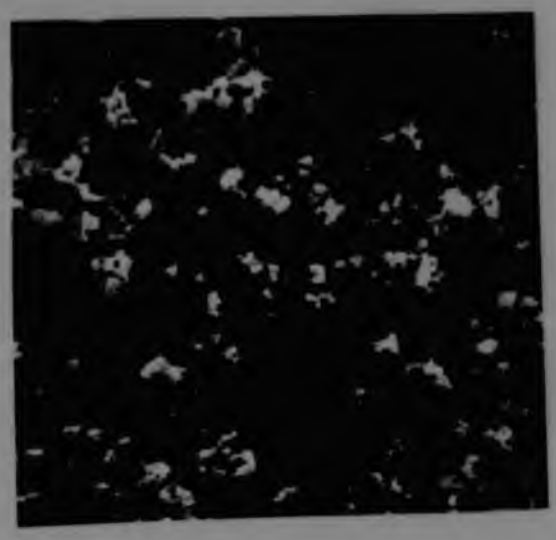


FIGURE 5.1.2.

Sample of cubic cobalt powder

after 5 hours grinding (x 1960)

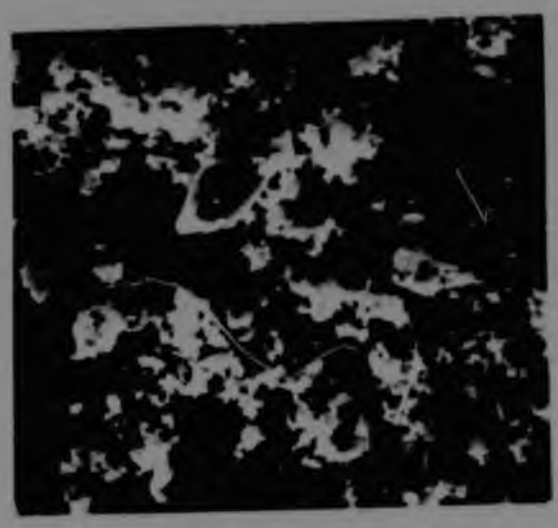


FIGURE 5.1.3.

Sample of powder after 10 hours

grinding (x 1960)



FIGURE 5.1.4.

Sample of powder after 15 hours milling (x 4940)



FIGURE 5.1.5.

Single cold welded agglomerate observed after 15 hours grinding (x 9880)

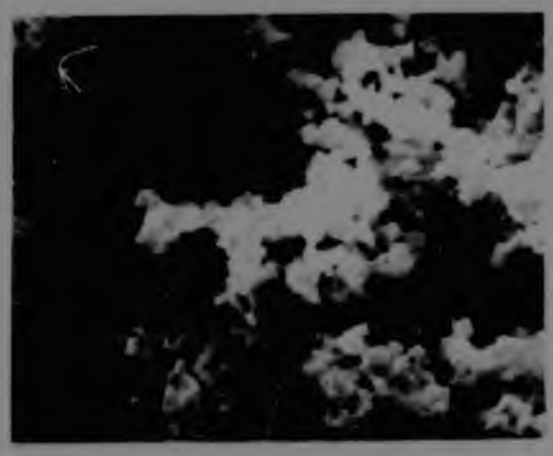


FIGURE 5.1.6.

"Cold-welded" aggregate observed after

) hours of grinding (x 980)



FIGURE 5.1.7.

Cube particle observed after 30

hours grinding (x 100)

After 50 hours of grinding typically "cold-welded" areas were evident. During the period 10 to 50 hours it was apparent that a number of "glistening" metallic cube and flake particles were being formed by grinding which were visible, because of their "glistening" appearance to the naked eye. A typical example of a cube particle is shown (x 100) in Figure 5.1.7., which was observed after 30 hours of grinding. This cube was approximately 0.20 mm in size. A small flake with an adhering cold welded region is shown (x 980) in Figure 5.1.8.

The above photomicrographs show that considerable adhesion of particles occured during grinding and in certain areas quite large unions of smaller particles must have been formed. This is confirmed by the decrease in specific surface area. However in all the powders examined although there was considerable evidence for the occurence of "cold-welding" some fine particles (as for example in Figure 5.1.4.) were always present in the ground powders. The non-adhering fine particles could have been cubic cobalt or alternatively could have been fine particles consisting predominantly of the hexagonal modification which had been removed from the aggregates by the action of the grinding balls. A low magnification photograph of the powder after 10 hours of grinding is shown (x 500) in Figure 5.1.9. Although there is considerable evidence of adhesion some particles are visible in the range less than 1 μ.

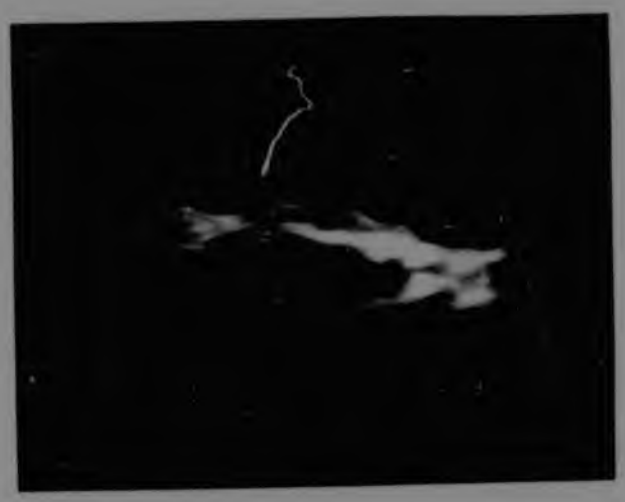


FIGURE 5.1.8.

Cobalt flake observed after 30 hours of grinding (x 980)



FIGURE 5.1.9.

Sample of powder after 10 hours grinding (x 500)

Fine particles less than 1μ in size are also visible in Figure 5.1.10 (x 500) which shows the powder after 15 hours of grinding. A particle union which would probably result from further grinding in the formation of a cubic "cold-welded" aggregate is shown in Figure 5.1.11. (x 9880). This union was observed after 5 hours of grinding. It appears from this figure that small particles of cobalt of initially irregular shape have been forced together and become "welded" to one another by the forces of the grinding balls. The shapes into which the original particles were forced by the grinding balls during the adhesion did not result in the elimination of porosity. However the "tail" of the particle at the top of Figure 5.1.11. seems to indicate that a large union of smaller particles has been formed and there is no evidence of the initial particles within this tail.

The cobalt powder initially in the cubic form after 70 hours of grinding is shown in Figure 5.1.12. (x 4940). Some evidence of agglomeration is present after this grinding time, but in general breakdown of the large agglomerates formed during the earlier stages of grinding has occured. Figure 5.1.13. (x 4940) shows some individual particles after 110 hours of grinding. The particles are seen to have smooth surfaces.

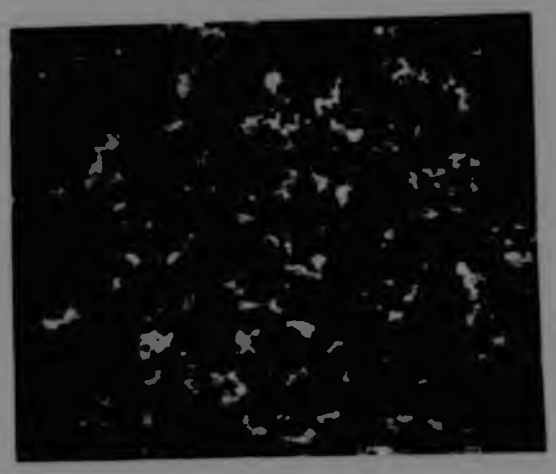


FIGURE 5.1.10.

Sample of powder after 15 hours grinding

(x 500)



FIGURE 5.1.11.

Particle union observed after 5 hours grinding

(x 9880)

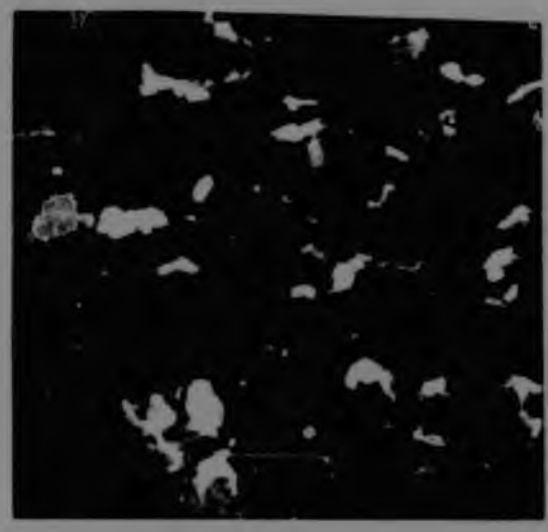


FIGURE 5.1.12.

Initially cubic cobalt powder ground

for 70 hours (x 4940)

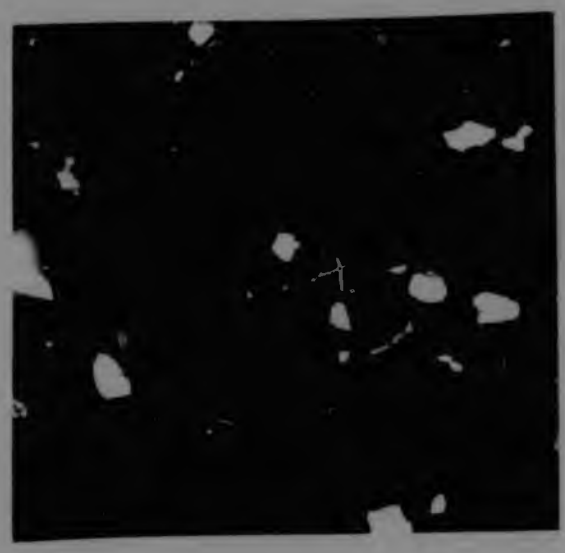


FIGURE 5.1.13.

Initially cubic cobalt powder

ground for 110 hours (x 4940)

Figure 5.1.1. shows that the cubic to hexagonal phase change proceeds with grinding, with an initially rapid increase in the hexagonal to cubic allotropic ratio, with a slower increase during the later stages of grinding.

It is suggested therefore that the f.c.c. cobalt particles "cold-weld" to one another during the initial stages of grinding. Adhesion between the individual cobalt metal particles appears to be such that contiguous units are formed in which the shape of the initial particles becomes unrecognisable in the milled aggregates. It was suggested earlier that "cold-welding" occured through processes involving dislocations. The adhesion is so strong that the surfaces are not "peeled" from one another when the impacting force provided by the grinding balls is released. The "peeling" (which is observed with less ductile metals) arises from the release of elastic stresses. *(198)*

The formation of the cube and flake shaped particles during grinding of f.c.c. cobalt is of interest. The presence of these flakes in some hard metal powders has long been known in industry, and their mechanism of formation has been a matter of speculation. Flaky glistening particles of cobalt are sometimes evident on the surfaces of hard metal compacts, in the green state after preheating.

The presence of such particles can cause "pull-outs" during the forming operation, which can eventually lead to porosity in the sintered surface. Alternatively the particles can melt during the sintering operation by the formation of a eutectic composition with carbon, and the resulting liquid can be drawn into the interior of the compact. The final result is again porosity on the sintered surface. It was anticipated in the previous work (Volume 1, Chapter 5) that some evidence for the occurence of flakes of cobalt would be seen in the various mixtures and compacts. No obvious examples of the occurence of flakes were noted however. This was probably because all the batches fabricated were made with cobalt powders that contained initially greater than about 20 % of the hexagonal modification. The cube shaped particles observed on grinding cubic cobalt were too small to be individually mounted in an X-ray goniometer for determination of their structure. Attempts were made to prepare cube shaped particles with sizes larger than 0.2 mm (which was approximately the maximum size detected). Several experiments were carried out using 3 kilos of hard metal grinding balls and varying powder charges of initially cubic cobalt powder with grinding times varying by hourly intervals up to total grinding times of 30 hours. Although cube shaped particles were detected in a number of these grinding experiments, the cube aggregates produced were too small in size for X ray examination of the individual units.

5.2. THE PRESENCE OF OXIDE FILMS ON THE SURFACES OF THE METAL POWDER PARTICLES

In Section 4 it was suggested that oxide films must be present on the surfaces of the hexagonal cobalt metal powders in order to explain the observed behaviour of these powders on grinding. It was suggested that these films must participate in the grinding process. It was known from the reduction studies reported in Chapter 2 of Volume 1 that the oxygen content of fine hexagonal powders is some 10 to 12 times greater than the oxygen content of the predominantly cubic powders prepared by reduction at high temperatures.

For various reasons discussed in Section 4 it was suggested that these oxide films would be non-stoichiometric in character and be non-uniformly dispersed on the powder particle surfaces.

It was decided therefore to see whether these oxide films could be directly observed. A fine hexagonal cobalt metal powder was prepared by hydrogen reduction of cobaltosic oxide at 400°C for four hours. X ray diffraction showed that only the hexagonal phase was present.

The oxygen content of the powder was 1.91 %. The initial powder was examined on the Stereoscan Microscope. A typical sample of the powder is shown in Figure 5.2.1. (x 1000). A sample of the powder was placed on Cellofas lacquer, and coated with carbon-platinum using an Edwards high vacuum coating unit. The Cellofas was dissolved in water and placed on a copper grid for examination in a Philips EM 200 Electron Microscope at 100 kV. Figure 5.2.2. (x 96000) shows the presence of a film of material around the cobalt metal particles which was more permeable to the passage of electrons than the metal particles. Around the greater part of the periphery of the metal particles the film is between 100 and 200 ^{o}A in thickness, with the thicker film joining the adjacent metal particles approximately 1000 ^{o}A across; one or two small metal particles are embedded in this thicker film. A sliver of material appears to have become detached from the metal particles. In the film joining the two particles there appears to be little evidence of porosity. It was not however possible to observe the fields of force arising from dislocations in the adsorbed film. Figure 5.2.3. (x 40000) shows a larger area of the metal powder particles from which the photograph shown in Figure 5.2.2. was taken.

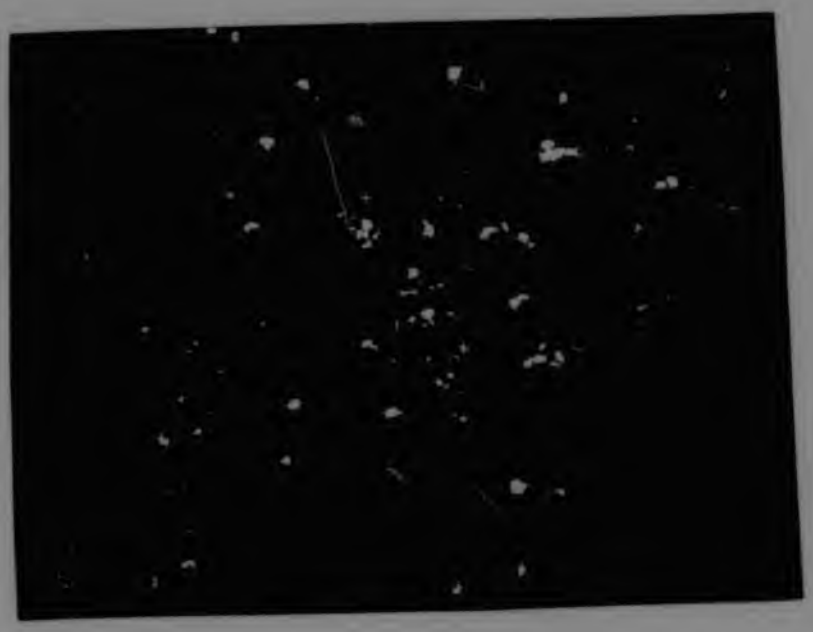


FIGURE 5.2.1.

Fine hexagonal powder after reduction (x 1000)



FIGURE 5.2.2.

Oxide film surrounding fine hexagonal cobalt (x 96000)



FIGURE 5.2.3.

Hexagonal cobalt metal powder (x 40,000)

Films that are non-uniform in thickness can be observed surrounding the metal particles.

Figure 5.2.4. (x 10000) shows a similar structure and some of the film material has become detached from the metal powder particles.

It was not possible to obtain electron diffraction patterns of the film in direct contact with the metal particles. The reasons for the non-correspondence of the area observed and the diffraction pattern obtained have been discussed by Marsh and Quarrell.[119] However it was found possible to obtain a diffraction pattern from a small region of scale material which had become detached from the metal powder particles. The film material was approximately 1200°A in diameter. The diffraction pattern of this material showed a pattern similar to that which would be expected from Co_3O_4. The (511), (440), (620), (642), (822) and (662) reflections were positively identified, although the intensities were not the same as they would be in a Debye-Scherer pattern. The absence of fine structure in the electron diffraction pattern tended to suggest that the oxide scale was polycrystalline. The fact that a spotted pattern was obtained indicated that very little refraction occured, and also tends to indicate that the surface of the oxide was relatively rough, as the electrons must have entered the material at large angles of incidence.[119]

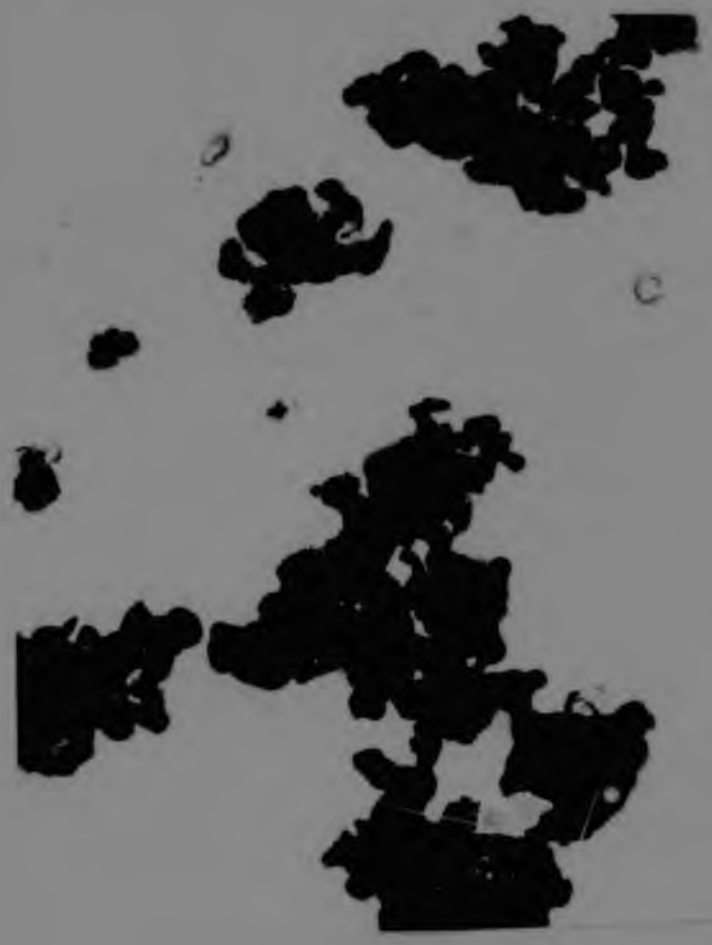


FIGURE 5.2.4.

Hexagonal cobalt (x 10000)

A number of other patterns were obtained from other pieces of scale; all closely but not exactly corresponded with the patterns expected for Co_3O_4. It is suggested therefore that the film surrounding the metal particles was an oxide of cobalt, which either due to non-stoichiometry or experimental difficulties associated with electron diffraction was not definitely characterised as Co_3O_4 but had a similar structure. The most convincing evidence that Co_3O_4 is present on the surfaces of the metal particles is provided by the detection of Co_3O_4 using X ray diffraction on fine pyrophoric hexagonal cobalt powder. This was discussed in Chapter 2 of Volume 1.

The metal powder with the surface oxide films was then ground in acetone using the same procedures as were detailed earlier, and samples were removed after various milling intervals. Some special precautions were taken during sampling of this batch in order to minimise the occurence of additional oxidation during sampling. Sampling was carried out under a large polythene container from which the air had been previously displaced with carbon dioxide gas. The ground powders were then dried under vacuum and examined on the Stereoscan Microscope. Figure 5.2.5. (x 2000) shows the powder after 5 hours of grinding. There is evidence for some adhesion after this grinding time. Figure 5.2.6. (x 9400) shows a very small agglomerate after 5 hours of grinding.

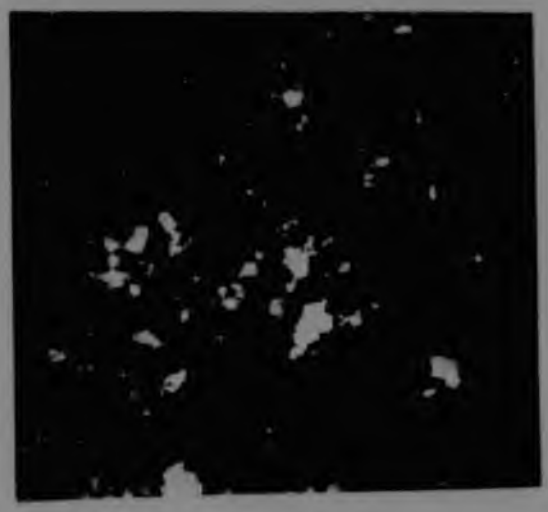


FIGURE 5.2.5.

Hexagonal powder after 5 hours grinding (x 2000)

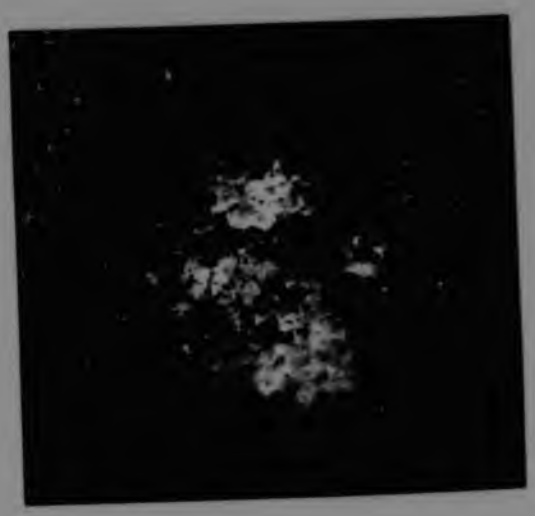


FIGURE 5.2.6.

Small agglomerate in hexagonal powder after 5 hours of grinding (x 9400)

The agglomerate is approximately 5 μ across and there is some evidence in this photograph for the occurence of "cold-welding" in the material. The state of the powder after 10 hours of grinding is shown in Figure 5.2.7. (x 2000). There is more evidence for the occurence of adhesion compared with that observed after 5 hours grinding. Very much greater "cold-welding" is noted after 20 hours of grinding as shown in Figures 5.2.8. and 5.2.9. (both x 2000). Although "cold-welding" has occured in the powder, there is considerable evidence for the presence of some ultra-fine particles within the agglomerated structures. This is in complete contrast with the behaviour noted earlier (5.1) with the cubic powder. More physical adhesion is noticeable after 30 hours of grinding. Powder samples after 30 hours of grinding are shown in Figures 5.2.10., 5.2.11. and 5.2.12. (all x 2000).

Thus physical adhesion and "cold-welding" can occur in hexagonal powders during grinding, but the effect is not so great as in cubic cobalt powders.

The powder after 70 hours of grinding is shown in Figure 5.2.13. (x 2000). Agglomerates are still visible but a number of the agglomerates have started to break down. The breakdown of a single agglomerate is shown in Figure 5.2.14. (x 2000). In this case it appears that material has been removed from the centre of an agglomerate.

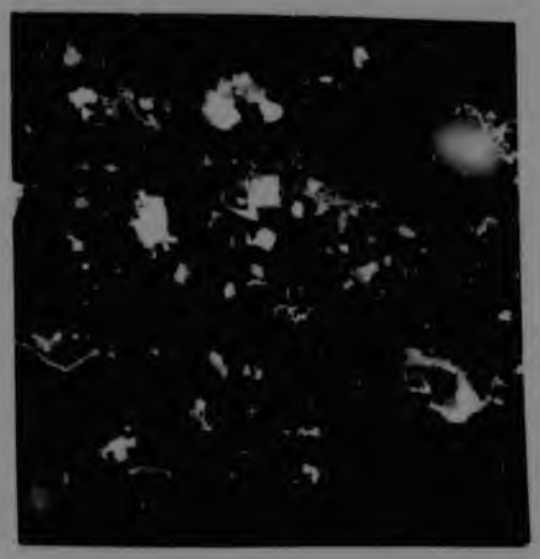


FIGURE 5.2.7.

Initially hexagonal powder after 10 hours of grinding (x 2000)



FIGURE 5.2.8.

Initially hexagonal powder after 20 hours of grinding (x 2000)

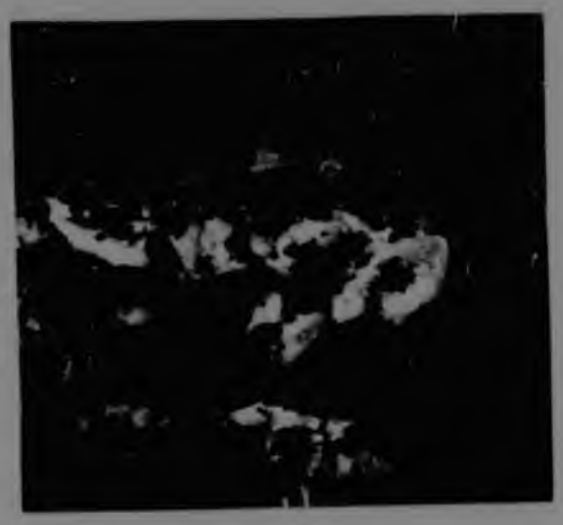


FIGURE 5.2.9.

Initially hexagonal powder after

20 hours of grinding (x 2000)

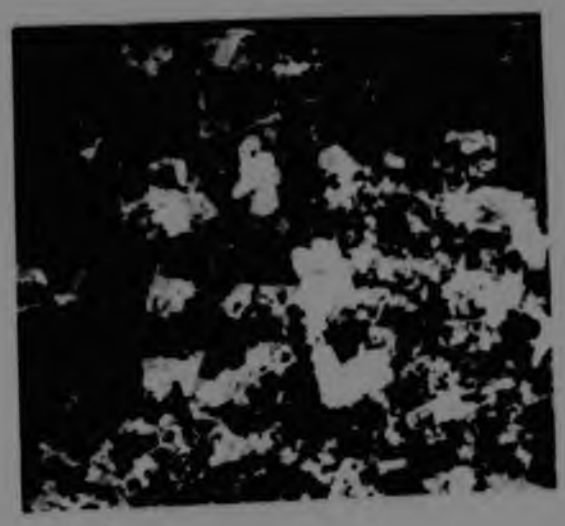


FIGURE 5.2.10.

Initially hexagonal powder after 30 hours

of grinding (x 2000)

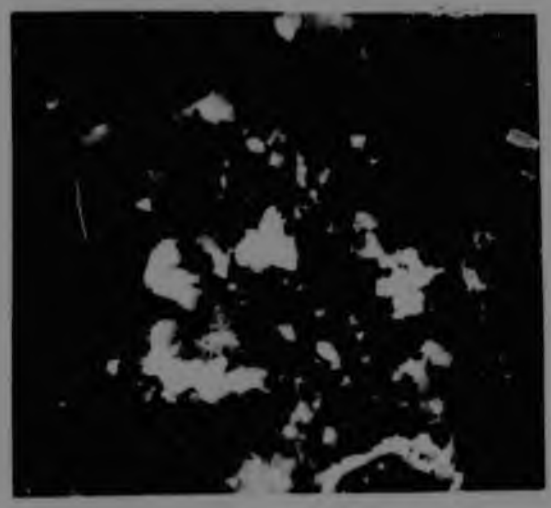


FIGURE 5.2.11.

Initially hexagonal powder after 30 hours of grinding (x 2000)



FIGURE 5.2.12.

Initially hexagonal powder after 30 hours of grinding (x 2000)

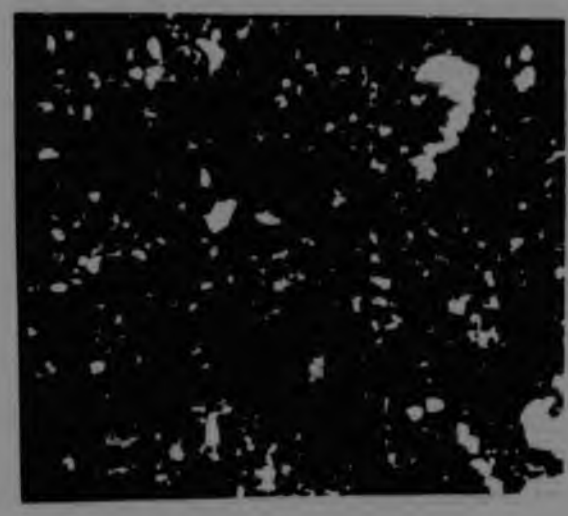


FIGURE 5.2.13.

Hexagonal powder after 70 hours grinding

(x 1000)

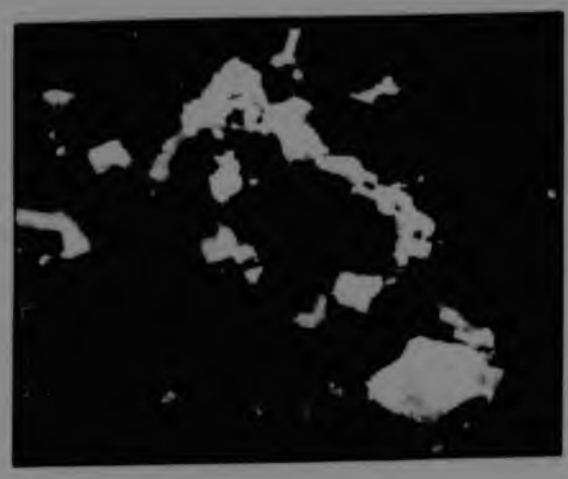


FIGURE 5.2.14.

Single agglomerate after 70 hours of

grinding (x 2000)

Further comminution occurs with additional grinding, e.g. Figure 5.2.15. (x 4940) which shows the powder after 110 hours of grinding. Comparison of Figure 5.2.15. with Figure 5.1.13. shows that after very long grinding times initially hexagonal powder appears similar to an initially cubic powder, which has been ground. Both powders have rounded particles with smooth surfaces.

Evidence of the metal particles shown in Figures 5.1.13. and 5.2.15. tends to confirm the supposition made earlier that the particles do not tend to reweld to one another after a minimum specific surface area has been attained during grinding.

The direct observation technique using the Philips EM 200 microscope was applied to a number of the ground hexagonal cobalt metal powders. Figure 5.2.16. (x 39000) shows a region where a number of metal powder particles have been forced together with oxide films linking the metal particles in certain cases. In this example the powder had been ground for 5 hours. An example after 10 hours grinding is shown in Figure 5.2.17. (x 64000). Figure 5.2.18. shows a sample of powder after 110 hours grinding (x 64000). There is very little evidence of oxide films around the peripheries of the individual metal particles but a flake of oxide can be seen which has become detached from other metal particles, and is freely dispersed within the powder.

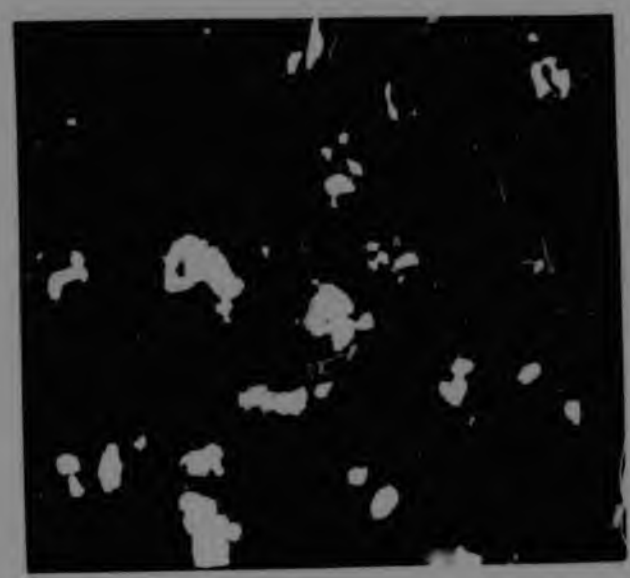


FIGURE 5.2.15.

Hexagonal powder after 110 hours of grinding (x 4940)



FIGURE 5.2.16.

Electron Micrograph of adhering metal powder particles (x 39000)

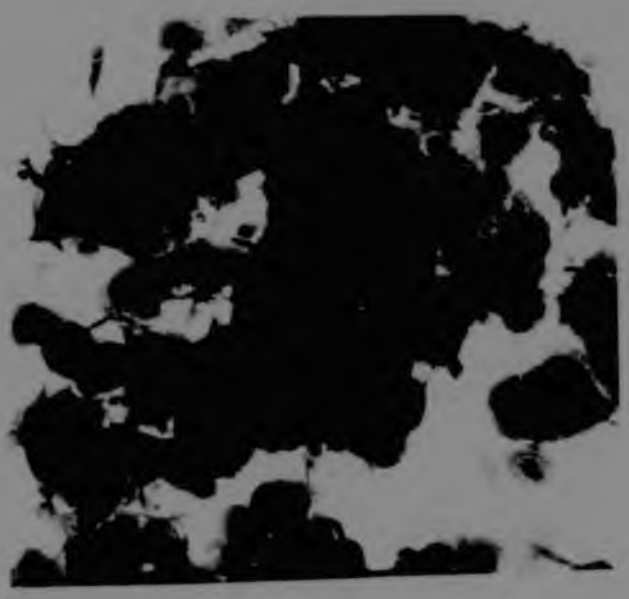


FIGURE 5.2.17.

Electron micrograph of adhering metal powder (x 64,000)



FIGURE 5.2.18.

Sample of powder after 110 hours of grinding (x 64,000)



FIGURE 5.2.19.

Isolated oxide particle (x 140,000)

A larger thicker oxide scale is shown in Figure 5.2.19. (x 140,000). Even at this magnification it is not possible to resolve the fine internal structure of the oxide.

As was mentioned earlier very little is known about the mechanical properties of oxides. It is generally recognised that oxide scales fail mechanically by a "spalling" process, discrete oxide particles being removed under the influence of mechanical forces. (200)

It was suggested that oxide films would not be expected to exert an influence during the grinding of predominantly cubic cobalt powders, for with these materials the particle size is coarser and much less oxygen is present than in a predominantly hexagonal cobalt powder.

Several samples of the powder that was initially cubic in structure referred to in 5.1. were examined in the Philips EM200 microscope.

Photographs of this material shown in Figures 5.2.20, 5.2.21, and 5.2.22. indicate that little oxide is present on the surfaces of the metal particles.

The experimental results indicate that the calculations of the oxide film thicknesses shown in Appendix 5 are meaningless; the metal powders are not surrounded by an oxide layer that is uniform in thickness prior to grinding.



FIGURE 5.2.20.

Electron micrograph of a sample of cubic cobalt. Small particles observed in sample of cubic cobalt prior to grinding. There is little evidence for the presence of oxide films (x 24000)



FIGURE 5.2.21.

Electron micrograph of a sample of cubic cobalt after 10 hours of grinding (x 64000)



FIGURE 5.2.22.

Electron micrograph of a sample of cubic cobalt (x 96000) after 30 hours of milling. The oxide films appear to be very thin. Noteworthy is the evidence for "cold welding" and the presence of porosity within the cold welded areas.

The oxide is unevenly distributed, which may be a consequence of both the stabilisation technique used and the anisotropy of the surface free energy of the metal.

Lassner (201) has shown that the oxygen content of cobalt powders decreases with increasing grinding time. In the previous work (202) it was noted that there was much scatter in the variations in oxygen content of the ground powders and grinding time. It is suggested that some of this variability in oxygen content with grinding time could be associated with the presence of chemically bonded oxide films on the surfaces of the metal powder particles; some areas of scale become detached during grinding, whereas other scales are firmly adhering to the metal. It could be anticipated that these effects superimposed on non uniform reoxidation during examination of the powders after grinding could lead to a very scattered relationship between oxygen content and grinding time.

The appearance of the metal powder shown in Figure 5.2.2. tends to confirm Parravano's (103) suggestion that metal powder particles may be bonded together by a common oxide film.

5.3. THE CHEMICAL REACTION OCCURING DURING THE GRINDING OF COBALT METAL POWDERS

5.3.1. OUTLINE OF POSSIBLE REACTION IN ACETONE

The following evidence, described earlier, is indicative that there is a chemical reaction during the grinding of cobalt powders in acetone:

(a) The carbon content of the milled metal powders increases with increasing grinding time.

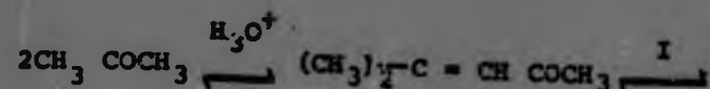
(b) Using a spot test with α nitroso β napthol reagent, acetone used as the grinding fluid can be shown to contain dissolved cobalt.

It is known (203) that acetone (I) undergoes the aldol condensation in the presence of basic hydroxides to form diacetone alcohol (II):

$$2CH_3\,COCH_3 \xrightarrow{Ba(OH)_2} (CH_3)_2\text{—}C(OH)\,CH_2\,COCH_3$$

(I) (II)

(II) is formed in small quantities in the above reaction. When acetone is treated with a solution containing H_3O^+ ions, mesityl oxide (III) and phorone (IV) are formed (203).



(I) (III)



(IV)

These products have the following properties: (203)

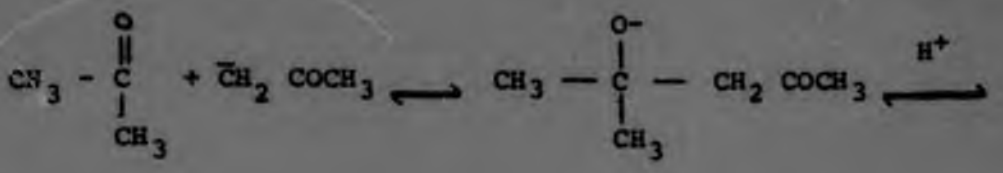
(II) is a colourless liquid with a boiling point at 760 mm Hg pressure of 164°C. On heating, it readily eliminates water to form (III). (III) is a liquid b.p. 130°C with a peppermint smell. (IV) is a yellow crystalline solid m.p. 28°C b.p. 198°C.

The mechanism of the aldol condensation is considered to be as follows: (203) in the presence of the base one molecule of the ketone forms a carbanion (V):

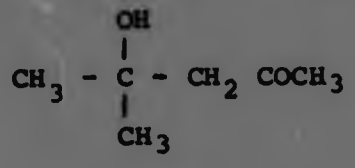


(V)

The carbonyl group in the other ketone molecule involved in the condensation is thought to undergo the electromeric effect in the presence of the carbanion which is a nucleophilic reagent, i.e.



(VI)



(II)

The proton necessary to complete the reaction is thought to be supplied by the dissociation of water molecules. *(203)*

5.3.2. EXPERIMENTAL

The 300 ml. of acetone used as grinding fluid for a batch of commercial cobalt powder, which had been ground in a vibratory mill for 110 hours, was carefully separated from the ground cobalt powder by filtration through a Millipore filter (the pore size of which is claimed to be 0.22 μ). The acetone had a slight yellow coloration, and the smell of the liquid indicated that some reaction had occured for the smell was not that of pure acetone. A positive spot test for the presence of dissolved cobalt in the used grinding fluid was obtained.

100 ml. of used grinding fluid was placed in a simple distillation flask and gently heated over a Bunsen burner.



A reduced pressure was applied to the contents of the flask by means of a water pump. The distillate was collected in a water cooled round bottomed flask. The greater volume of the liquid distilled over at 30 - 35°C which appeared to be relatively pure acetone. At this stage only about 5 cc of liquid remained in the distillation flask. The round bottomed flask used for collection was replaced by another. Heating was continued to about 75 - 80°C when a colourless fraction started to flow down the side arm of the distillate receiver. The round bottomed flask was again changed and heating continued. At 115 - 120°C the yellowish liquid remaining in the flask finally distilled over to the collection vessel. The heating of the distillation flask was continued until there was no liquid remaining to be distilled. A small quantity of an oily tar remained at the bottom of the distillation flask. A little acetone was added to this fraction and a positive spot test for the presence of dissolved cobalt was obtained.

The fraction which distilled over at 75 - 80°C (approximately 2 cc) was placed in a boiling point tube and heated in a liquid paraffin bath over a Bunsen burner. The boiling point at atmospheric pressure for this fraction was found to be 110 - 112°C. This liquid had a slightly peppermint smell and was distinctly lacrimatric.

The boiling point of the second fraction (approximately 1.5 cc) was found to be 165 - 167°C at atmospheric pressure.

After carrying out the boiling point test the liquid was placed in a small beaker, and cooled to below room temperature in a refrigerator, to see whether the material would crystallise and form a solid. After standing for several weeks a yellowish oily liquid remained which showed no tendency to form a solid.

On the basis of this evidence it is suggested that the lower boiling fraction corresponded to an impure form of mesityl oxide and that the higher boiling fraction was an impure phorone. It is suggested that diacetone alcohol may have been formed in the reaction during grinding, but none of this compound was isolated in the separation, probably because of its decomposition to mesityl oxide.

Three further 100 ml volumes of used grinding fluid were fractionally distilled; no diacetone alcohol was isolated from any of the separations. The mesityl oxide fractions were found to have boiling points in the range 107 - 116°C. After cooling in a refrigerator it was found that two of these phorone fractions yielded oily yellow solids. It was difficult to experimentally determine the melting points of the solid compounds isolated; one of the solids became completely liquid at 25°C, and the other showed no defined temperature of melting. The boiling points of these compounds were in the range 160 - 169°C. One of the solids isolated was recryetallised from fresh acetone, and was found to melt at 24 - 26°C.

It is suggested that although it was not possible to isolate very pure forms of mesityl oxide and phorone from the used grinding fluid that both these compounds are formed by reaction during grinding.

The water content of the acetone prior to grinding was determined and found to be 0.48 % by volume.

The possibility of the above reactions occuring during grinding must be considered; also the presence of the cobalt ions dissolved in the acetone must be accounted for.

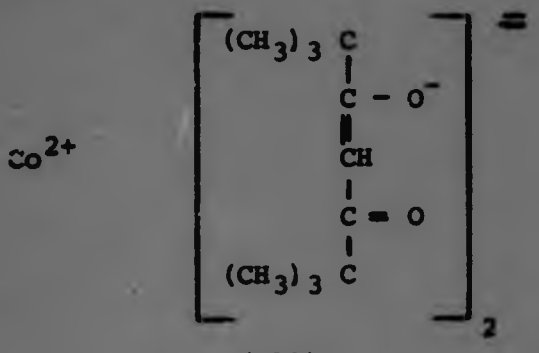
The first point to establish is the origin of the hydronium and hydroxyl ions which can promote the formation of mesityl oxide and phorone in the acetone. The oxide layers released from the cobalt metal are non stoichiometric for the reasons described earlier; there is a deficiency of cations on one side of the scale; the higher oxygen content on the one side could possibly promote adsorption of water from the acetone possibly in the form of ions. Co_3O_4 is reported to be insoluble in acetone or water;[204] the oxide is amphoteric and claimed to be hygroscopic.[204] Co_3O_4 is claimed to form a number of hydrates, (which are also claimed to be amphoteric) none of which are well characterised, nor have their solubility products been established.[204]

Water adsorbed on the metal powder from the atmosphere during a removal from the reduction furnace could result in the formation of hydroxyl groups on certain areas of the scales although hydroxides were not detected by electron diffraction. The solubility of the hydroxides (although low) in water would probably be greater than the solubility of the oxides. $Co(OH)_2$ could form from the tetrahedral groups in Co_3O_4. The solubility product of this compound in water is 2.16×10^{-16} at room temperature[205]; thus some solubility of this compound in water is expected, although the solubility will be low. Co^{3+} ions (derived from the $\{(Co^{3+})_2O\}$ groups in the octahedral sites of Co_3O_4) would be very unstable in water, being reduced to Co^{2+} and the water oxidised to hydrogen and oxygen.[205]

All of these factors together with the small size of oxide particles released on grinding would suggest that the small amount of water present in the acetone might be ionised yielding H_3^+O and OH^- ions. It is not possible to calculate the requirements of H_3^+O and OH^- necessary for the formation of phorone, mesityl oxide and diacetone alcohol, because it appears that the ions promote the reactions in catalytic manners. However there is the possibility that H_3^+O and OH^- ions can be formed in a mill during grinding which can promote reactions in the acetone.

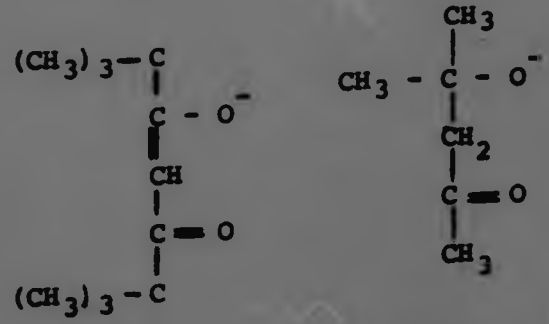
It was suggested that the diacetone alcohol could be formed during grinding but was unstable during the extraction process, probably forming mesityl oxide.

Co^{2+} ions can form inner salt complexes containing chelating ligands e.g. Vll. The properties of these compounds have only been cursorily examined. (205)



(Vll)

Compound (Vll) is known to have a tetrahedral structure and is very stable. It is formed by the reaction of Co^{2+} and the sodium salt of the ligand in ethanolic solution. The chelating ligand shown in (Vll) is similar in structure to the intermediate (Vl) thought to be involved in the formation of diacetone alcohol, i.e.



Ligand of (Vll) (Vl)

The presence of the olefinic linkage in the ligand of (VII) (which is absent in (VI)) would probably contribute to the stability of the tetrahedral complex with cobalt ions by π bonding within the ligand.[205] It is suggested that (VI) could form a compound of limited stability with the Co^{2+} ions, and that the Co^{2+} - $(VI)_2$ compound is soluble in the acetone. It is suggested that the oily tar compound which contained cobalt that remained after the distillation was a decomposition product of Co^{2+}-$(VI)_2$.

Diacetone alcohol (II) is a tertiary alcohol. Several of these compounds can be dehydrated with the formation of an olefine, but the temperatures required for this are high (> 400°C) and thus olefine formation during grinding is improbable.[206] Mesityl oxide is formed from (II) instead. Well defined olefine transition metal complexes are known, but are mainly characterised by metals with filled d shells, e.g. copper and palladium.[207] Cobalt with its $3d^7$ structure is therefore unlikely to form a well defined olefine-metal compound. However because of the unfilled d band in cobalt chemisorption of compounds with olefinic linkages is likely, since it is thought that the π orbitals of the double bond in an olefine can donate electrons to the metal.[208]

It may be concluded therefore that (111) and (1V) which both contain olefinic linkages could be adsorbed on the cobalt metal particles during grinding.

The presence of the carbon in the ground cobalt metal powders may be accounted for in the following manner: Both mesityl oxide and phorone have relatively high boiling points. During vacuum drying following grinding of the cobalt powders, the water bath temperature does not exceed 60°C. This temperature (even with the reduced pressure) may be insufficient to remove any mesityl oxide, phorone and diacetone alcohol formed by reaction during grinding. Thus although the acetone is removed during vacuum drying, the three compounds of higher boiling point would remain entrained with the dried metal powder. These compounds could contribute to the increase in carbon content of the ground metal powder.

The initial carbon content of the cobalt powder used in the first fractional distillation experiment to determine the organic compounds formed during grinding was 0.06 %. After 110 hours of grinding, the carbon content was 0.35 % indicating a carbon pick-up during grinding of 0.29 %.

Assuming that the increase in carbon arising from grinding was contributed equally by compounds (II), (III) and (IV), 0.48 g carbon in the 500 g metal powder was contributed by diacetone alcohol. The molecular weight of diacetone alcohol is 116 g of which 72 g are carbon. Thus the calculated weight of diacetone alcohol in the 500 g cobalt metal powder was 0.77 g. Assuming all the diacetone alcohol formed a chelated compound (based on VI) 0.19 g Co^{2+} would be required in the solution. The oxygen content of the cobalt powder prior to grinding was 1.08 %, meaning that 5.40 g oxygen were present in the 500 g powder. If half this oxygen was present as Co_3O_4, 7.45 g cobalt could be present in association with the oxygen as an oxide. Thus quite sufficient cobalt (as oxide) would be present to react with the calculated quantity of diacetone alcohol.

However the solubility product K_{SP} for $Co(OH)_2$ in water is given by:

$$K_{SP} = 2.16 \times 10^{-16} = (a_{Co^{2+}})(a_{OH^-})^2 = (C_{Co^{2+}})(C_{OH^-})^2$$

where the C's refer to the molar concentrations of the ions, and the activity coefficients are neglected (which is justified)[20]. K_{SP} indicates that only 512×10^{-16} mg of Co^{2+} could be present in the solution, assuming that the cobaltosic oxide dissociated through $Co(OH)_2$.

By using the method of chemical analysis given in Appendix 9, the amount of cobalt dissolved in 300 ml grinding fluid was found to be 6.0 mg.

This indicates the following, either:

(a) It is unlikely that all the calculated quantity of diacetone alcohol was found in a chelated compound with Co^{2+}.

(b) The Co_3O_4 does not dissociate through $Co(OH)_2$ into solution but probably through another hydrate which has an enhanced solubility in water compared with that of $Co(OH)_2$.

The observations made in the previous work[210] when a ground cobalt powder was heated in hydrogen in a Stanton thermobalance can now be explained: On reduction in hydrogen in the presence of a finely divided cobalt powder (acting as a catalyst in a similar manner to that of Ranay nickel[211]) mesityl oxide could yield 2 methyl-n-pentane, as could diacetone alcohol. Phorone on reduction could yield 2, 6 dimethyl-n-heptane. 2 methyl pentane boils at 60°C and 2, 6 dimethyl-n-heptane boils at 132°C[212]. These reduction products could therefore be expected to be easily removed on heating in hydrogen, and the weight loss occuring in the temperature range 20 to 200°C shown in Figure 4.18 could be satisfactorily explained.

It is important to assess whether sufficient of the organic reaction products was produced such that a layer of organic material could exist on the cobalt metal particles and prevent readhesion after the state of minimum specific surface area had been reached during grinding.

In the above example it was assumed that in 500 g cobalt 0.48 g carbon was contributed by phorone and 0.48 g carbon was contributed by mesityl oxide. Therefore the weight of phorone in 500 g ground cobalt

$$= 0.48 \times \frac{138}{109} \text{ g}$$

$$= 0.48 \times \frac{138}{109 \times 138} \text{ moles}$$

$$= 0.48 \times \frac{138}{109 \times 138} \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 2.66 \times 10^{21} \text{ molecules}$$

Therefore the weight of mesityl oxide in 500 g cobalt

$$= 0.48 \times \frac{98}{72} \text{ g}$$

$$= 0.48 \times \frac{98}{72 \times 98} \text{ moles}$$

$$= \frac{0.48 \times 6.02}{72} \times 10^{23} \text{ molecules}$$

$$= 4.04 \times 10^{21} \text{ molecules}$$

Thus the total number of molecules that could be adsorbed on the cobalt would be 6.70×10^{21} molecules. Studies of surface films and x ray data indicate that a paraffinic chain has a cross sectional area of $21 \times 10^{-16} \text{cm}^2$. (313)

Therefore surface area of organic compounds that could be adsorbed on the cobalt = $6.70 \times 10^{21} \times 21 \times 10^{-20}$ m^2 equal to 1410 m^2.

After grinding for 110 hours the cobalt powder had a specific surface area of 1.62 m^2/g. Therefore surface area of ground cobalt = 500 x 1.62 m^2 = 810 m^2.

This approximate calculation indicates that there is sufficient mesityl oxide and phorone in the cobalt to form a monolayer, which could prevent readhesion of the metal particles; in addition it was possible to isolate small quantities of phorone and mesityl oxide from the used grinding fluid; thus more than sufficient for monolayer formation was present. Furthermore the assumption has been made that the organic molecules are not adsorbed lengthwise but are adsorbed normal to the direction of the carbon chains. Thus in practice considerably more than one monolayer can be adsorbed on the cobalt particles.

Thus during the course of grinding of cobalt powders in acetone, it is suggested that three organic compounds are formed in varying amounts, namely diacetone alcohol, phorone and mesityl oxide. Free energy data for these compounds are not available to assess whether the suggested reactions are thermodynamically favourable. It appears that the cobalt oxide present on the cobalt metal powders prior to grinding can promote the formation of these compounds.

It was suggested that Co^{2+} ions are present in the acetone after grinding due to the formation of a chelated compound, but only small quantities of this compound can be present.

If the suggestions above are correct there should be a correlation between the amount of oxygen present as cobaltosic oxide in the powders prior to grinding and the extent of reaction during grinding as determined by the carbon content of the ground powders and the amount of cobalt present in the acetone after grinding. Unfortunately the amount of cobalt oxide present in a cobalt metal powder prior to grinding cannot easily be determined, and the total oxygen content must be taken as a measure of the oxide present.

In order to test this hypothesis ten cobalt powders differing in allotropic ratio and oxygen content were prepared by reduction of cobaltosic oxide in hydrogen as described in Chapter 2 of Volume 1. The precaution of stabilisation with carbon dioxide gas prior to exposure of the powder to the atmosphere after removal from the reduction furnace was observed.

The powders were ground in 800 ml vibratory mills using 300 ml acetone for 110 hours.

The acetone for the different metal powder batches was selected from the same container, the water content of which was determined by the Karl Fischer method and found to be 0.51 % by volume.

After grinding the greater volume of the fluid was decanted and filtered through the Millipore filter. The ground powders were dried under vacuum on a water bath. Small samples were assayed for total carbon. The cobalt dissolved in the grinding fluid was determined using the method outlined in Appendix 9.

Table 5.3.1. summarises the oxygen and carbon contents of the cobalt powders and the cobalt contents of the fluid used for milling.

Figure 5.3.1. shows the determined cobalt content of the grinding fluid plotted against the initial oxygen content of the powder. Figure 5.3.2. shows the relation between the carbon increments of the ground powders and the initial oxygen contents, and Figure 5.3.3. shows the relation between the percentage of hexagonal cobalt in the unground powders and the carbon increments of the powders after grinding.

TABLE 5.3.1.

Summary of carbon increments in cobalt powders on grinding, and the dissolved cobalt content of the grinding fluid

Reduction Condition for Cobalt Powder	Initial Carbon Content %	Initial O_2 Content %	Allo-tropic ratio H/C +	Initial Spec. Sur. Area m^2/g	Carbon Content after Grinding %	Carbon Increment %	Cobalt Dissolved in Grinding Fluid ≠
850°C 2 hrs	0.04	0.03	C	0.46	0.12	0.08	1.9
750°C 1 hr	0.03	0.41	0.18	0.79	0.14	0.11	3.6
650°C 2 hrs	0.03	0.76	0.72	1.24	0.15	0.12	5.1
500°C 4 hrs	0.05	0.88	1.02	1.51	0.17	0.12	5.6
450°C 2 hrs	0.04	1.09	1.59	2.00	0.20	0.16	8.1
450°C 4 hrs	0.06	0.99	H	1.91	0.25	0.19	7.2
400°C 1 hr	0.05	1.98	H	2.76	0.30	0.25	13.4
400°C 2 hrs	0.04	1.41	H	2.24	0.27	0.23	10.2
350°C ½ hr	0.04	3.79	X	3.02	0.49	0.45	19.1
300°C ½ hr	0.05	10.69	X	4.79	0.69	0.64	45.0
Commercial Powder	0.06	1.08	0.47	1.36	0.35	0.29	6.0

≠ Amount in mg. in 300 ml. grinding fluid

\+ The allotropic ratio - hexagonal to cubic

C = 100 % cubic

H = 100 % hexagonal

X Mixture of hexagonal cobalt and Co_3O_4 - improperly reduced

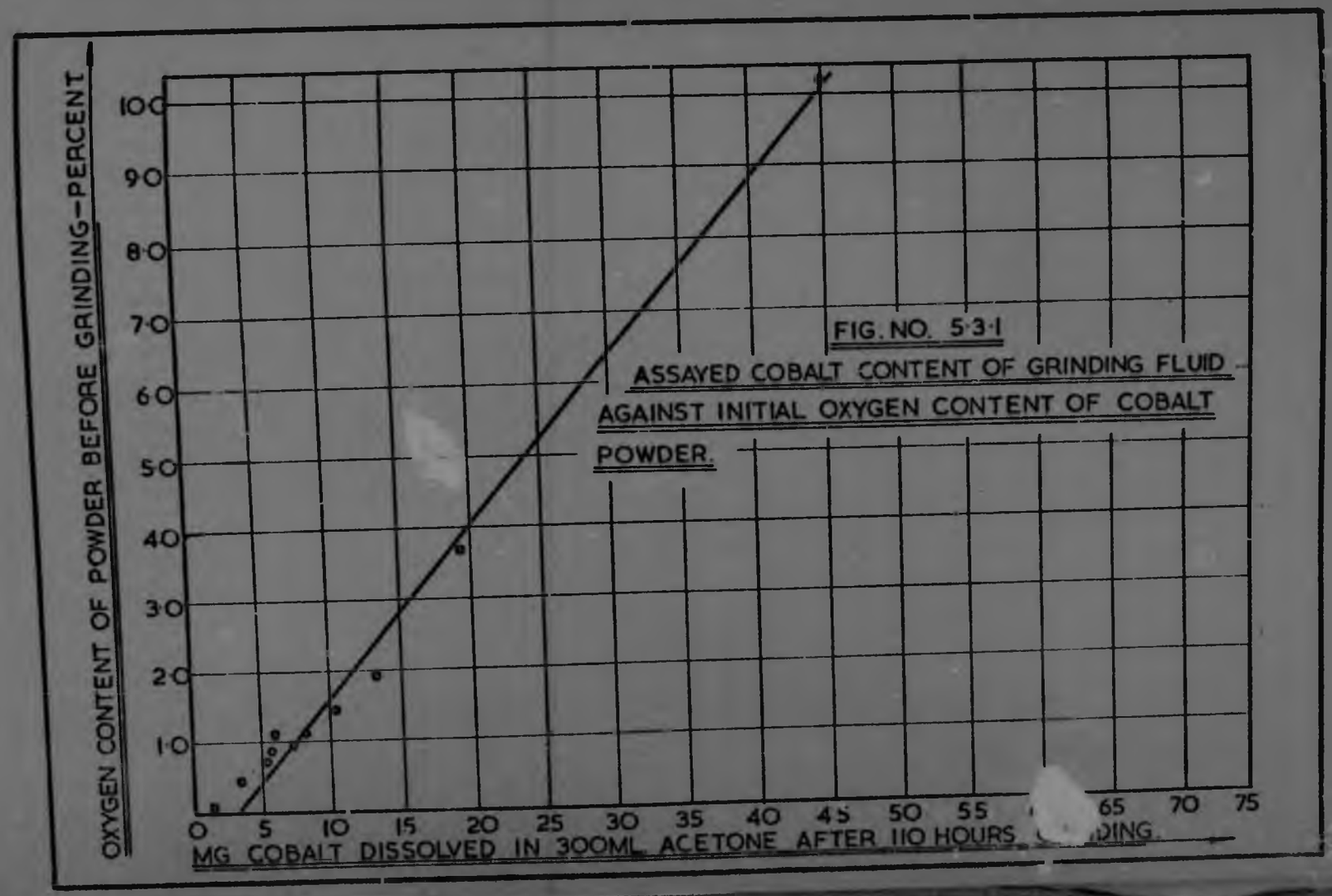
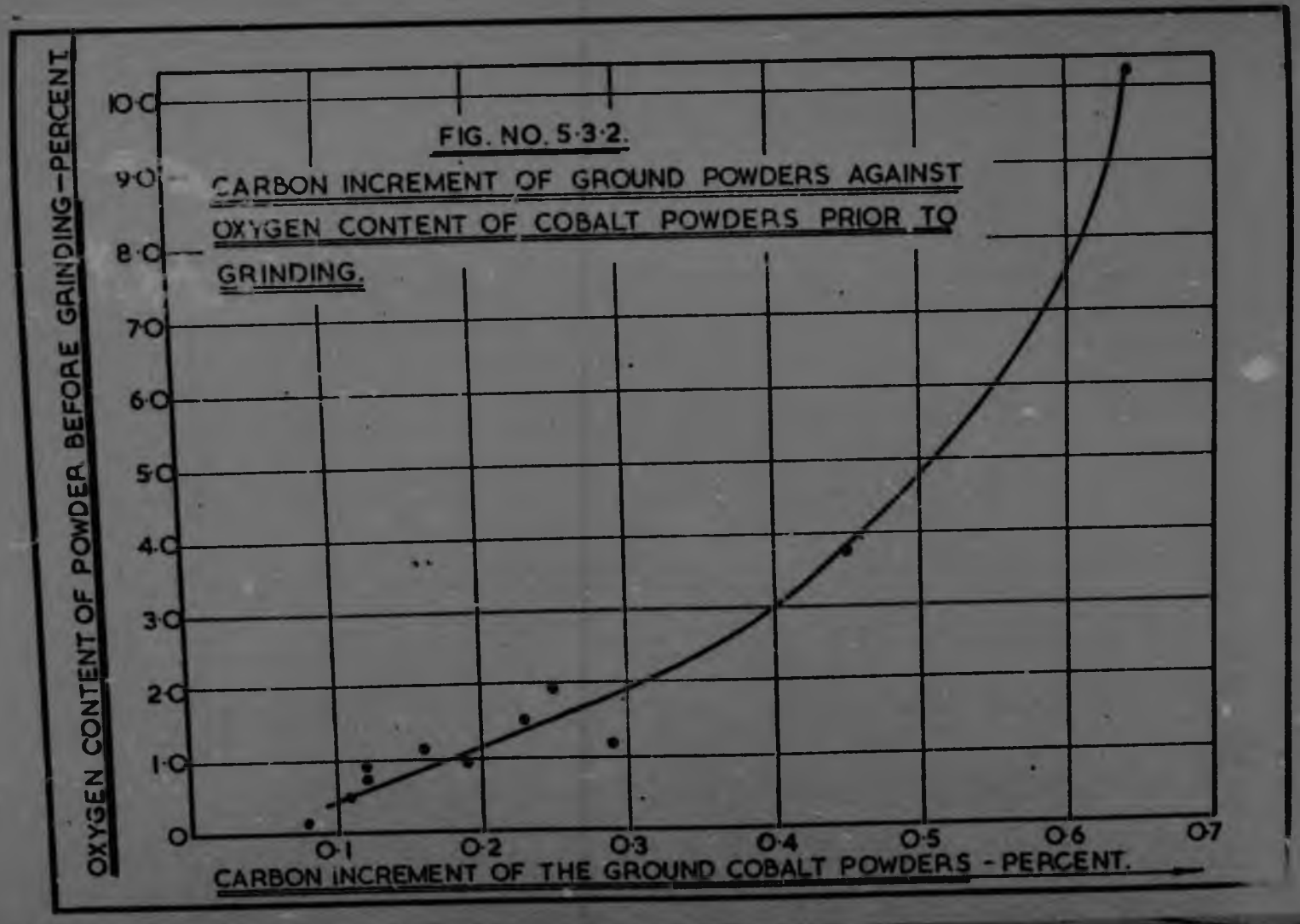
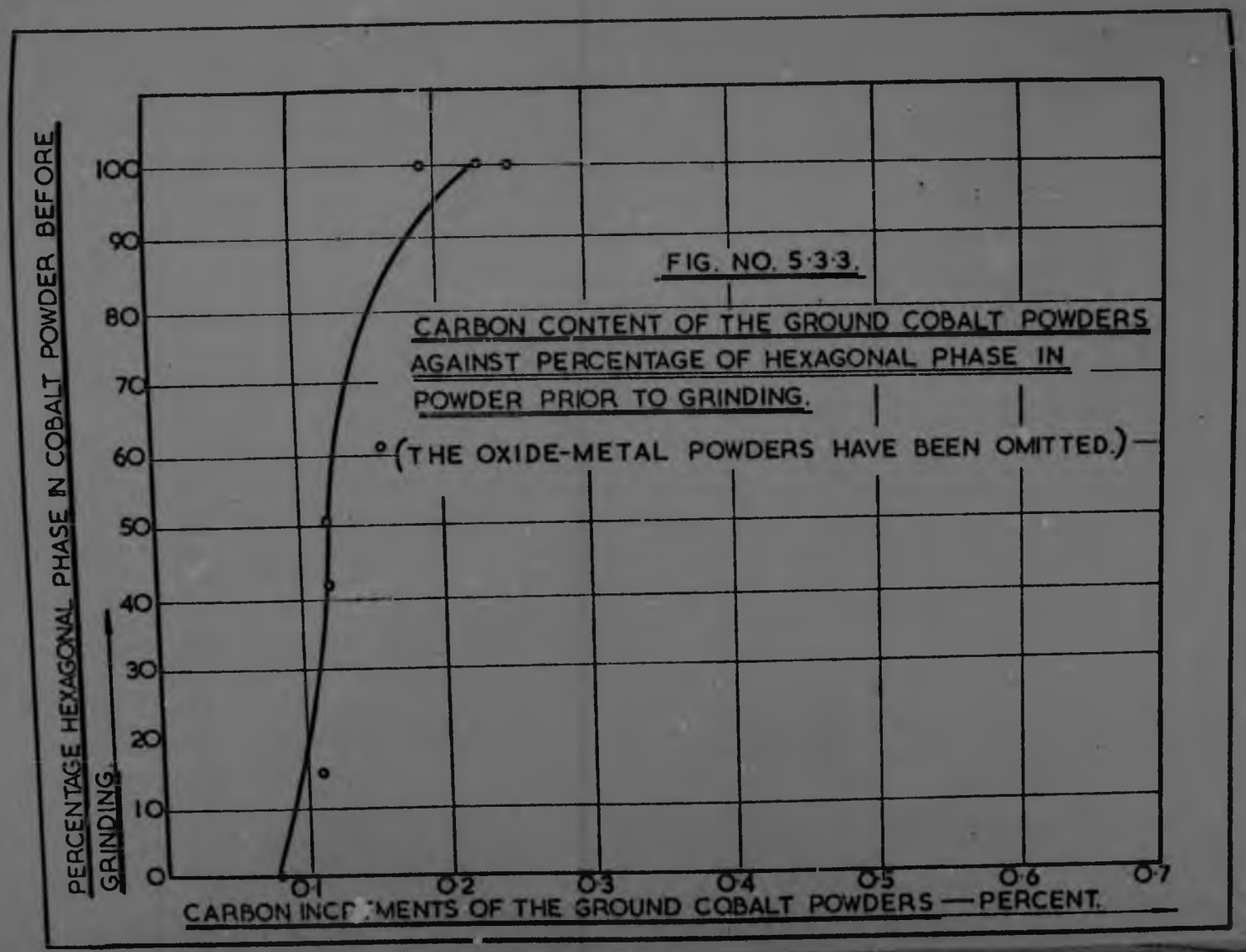


FIG. NO. 5·3·1

ASSAYED COBALT CONTENT OF GRINDING FLUID AGAINST INITIAL OXYGEN CONTENT OF COBALT POWDER.


FIG. NO. 5·3·2.
CARBON INCREMENT OF GROUND POWDERS AGAINST OXYGEN CONTENT OF COBALT POWDERS PRIOR TO GRINDING.
OXYGEN CONTENT OF POWDER BEFORE GRINDING - PERCENT.
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CARBON INCREMENT OF THE GROUND COBALT POWDERS - PERCENT.


PERCENTAGE HEXAGONAL PHASE IN COBALT POWDER BEFORE GRINDING.
100
90
80
70
60
50
40
30
20
10
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
CARBON INCR MENTS OF THE GROUND COBALT POWDERS — PERCENT.
FIG. NO. 5·3·3.
CARBON CONTENT OF THE GROUND COBALT POWDERS AGAINST PERCENTAGE OF HEXAGONAL PHASE IN POWDER PRIOR TO GRINDING.
(THE OXIDE-METAL POWDERS HAVE BEEN OMITTED.)

The correlation of the data shown in Figures 5.3.1. and 5.3.2. tend to confirm the suggestions made earlier that the extent of the reaction with the acetone during grinding is governed by the initial oxygen content of the cobalt powder and some of this oxygen must be in the form of cobaltosic oxide to permit the reactions indicated to occur.

On the other hand the reaction

$Co(S) \longrightarrow Co^{++}\ (aq) + 2e$ has an associated free energy of $\Delta G = -12800$ cals per g atom (-53,57 k joules per ; atom). (314) Thus the thermodynamic prediction is that cobalt could dissolve in the water yielding Co^{2+} ions.

The following evidence is presented to indicate that cobalt oxide is responsible for the observed reaction and not cobalt metal:

(1) Co_3O_4 has a spinel type structure which is hygroscopic.

(2) Water in contact with $\{(Co^{3+})_2O\}$ could provide a source of Co^{2+}, because of the inherent instability of non-complexed Co^{3+} in water.

(3) The smaller size of the oxide particles compared with the metal particles suggests that the solubility (although small) would be higher for oxide than for metal.

(4) The correlation between the carbon content of the ground metal, the cobalt content of the acetone used for grinding and the oxygen content of the cobalt powders prior to grinding.

However the finer metal powders with the higher oxygen contents have a higher surface free energy than the coarser powders. If the observed effect could be attributed to metal dissolution, the finer metal powders would be anticipated to yield a larger dissolved cobalt content in the acetone after grinding.

In order to prove more conclusively the origin of the cobalt dissolved in the acetone the following experiment was carried out. A 1 Kg batch of cobalt powder was prepared by reduction of oxide in hydrogen at 400°C for 1 hour; the oxygen content was 2.10 % and the specific surface area 2.90 m^2/g. 500 g of this powder was reheated in hydrogen at 400°C for 3 hours; the specific surface area was 2.05 m^2/g and the oxygen content 1.02 %. Both batches of cobalt were ground in acetone for 110 hours. The acetone used for the cobalt powder with the higher oxygen yielded 15.0 mg dissolved cobalt in the 300 ml acetone, whereas the batch with the lower oxygen content yielded 7.6 mg cobalt dissolved in 300 ml acetone.

The specific surface areas of the metal powders before grinding were of the same order whereas the oxygen levels differed by a factor of about 2. The dissolved cobalt contents after grinding differed by a factor of approximately 2. This suggests that oxygen chemisorbed on the cobalt is the cause of the chemical reaction during grinding.

In Section 4 it was suggested that some of the organic material produced by reaction after long grinding times became adsorbed on the metal powder particles and prevented re-adhesion. It was pointed out that adsorption of organic material on cobalt would be probable because of the electronic structure of the metal. The calculation described earlier in this section suggested that sufficient organic material was present for a monolayer to be formed on the metal particle surfaces. The structural features of both phorone and mesityl oxide which are relevant to their surface adsorption properties are the polar groups, the presence of the olefinic linkages and the lengths of the alkyl chains.

The adsorption process would be expected to occur by the same mechanism for both hexagonal and cubic cobalt powders since it is recognised that a metal's surface adsorption character for a specific compound depends on its electronic structure and not on its crystal structure.

Surface adsorption characteristics of the transition metals are related primarily to the percentage of "d-band character" of the metal [216] and not to its crystal size parameters which was originally supposed. [216]

It was suggested that adsorption of olefinic compounds occurs on the surfaces of the metal powder particles during grinding. The type of adsorption was not specified; it would be very difficult to prove conclusively, using a readily available experimental technique whether physical or chemisorption had occured. However the process of chemisorption is considered to be irreversible at the temperature at which adsorption occured initially, since a chemical compound is formed on adsorption. [217] In certain cases it is thought that the chemical compound produced by chemisorption may be desorbed by heating to a temperature much higher than that at which adsorption occured initially. [217]

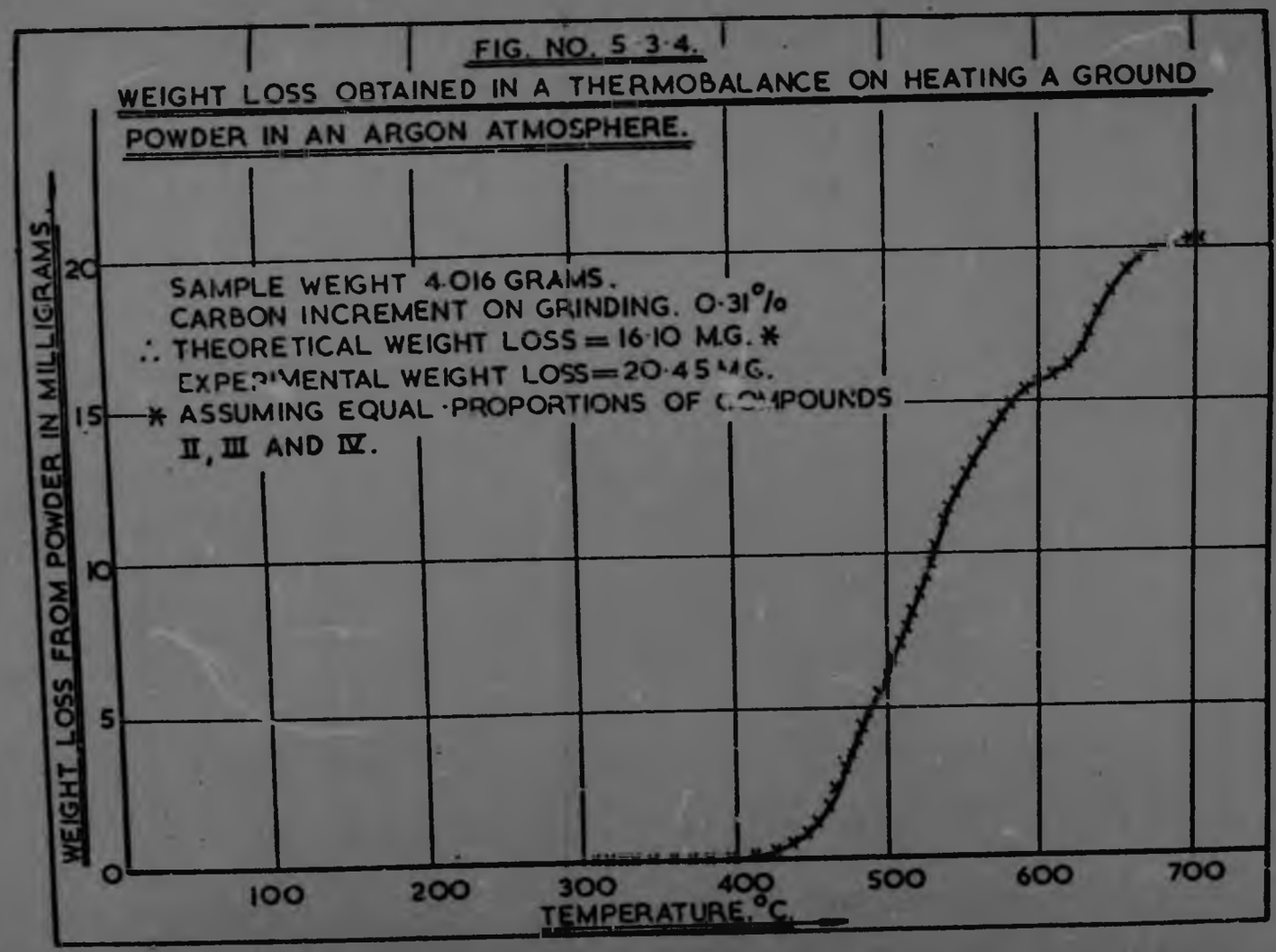
Using this feature of the chemisorption process, it should be possible to heat a ground cobalt powder in an inert atmosphere in a thermobalance and record the temperature range in which desorption occurs. If desorption occurs at a temperature much higher than that at which adsorption occurs it must be assumed that chemisorption occured initially.

In order to investigate the desorption, a 4 g sample of ground cobalt derived from one of the powder batches prepared for one of the experiments where the used grinding fluid was fractionally distilled was heated in an Argon atmosphere in a Stanton Thermobalance. Figure 5.3.4. shows the weight loss - temperature curve obtained on heating the sample. No weight loss occured at the temperature at which adsorption could have occured. A weight loss did occur however in the temperature range 400 - 700°C. The total weight loss recorded was about 25 % greater than would be expected if the olefinic compounds alone had been desorbed. In certain cases it has been observed that a chemical compound consisting of components from both adsorbate and adsorbent can be desorbed at a temperature higher than that at which chemisorption occured initially.(217) This somewhat indirect evidence suggests that the chemical compounds produced during grinding are chemically adsorbed on the surfaces of the metal powder particles. Heating of ground cobalt powders in an inert atmosphere was repeated several times; in all cases a weight loss in the 400 - 700°C temperature range occured.

The possibility of chemisoption of compounds with olefinic linkages occuring on finely divided cobalt metal at the temperatures attained during grinding must be considered:

FIG. NO. 5·3·4.

WEIGHT LOSS OBTAINED IN A THERMOBALANCE ON HEATING A GROUND POWDER IN AN ARGON ATMOSPHERE.



Phorone is an unsaturated α-β ketone; such compounds show marked additive properties at the positions of the double bonds.[203] Chemisorption is thought to be involved in these reactions, some of which can occur at temperatures as low as 200°C.[211] Heterogeneous hydrogenation at 180°C with fine cobalt has been reported.[211] Chemisorption from solution is known to occur at room temperature in certain systems[218],[219],[220] containing organic compounds and finely divided metals. In view of this evidence it must be assumed that both phorone and mesityl oxide produced during grinding could be chemically adsorbed on the metal powder particles during grinding.

The data shown in Figures 5.3.1. - 5.3.3. indicate that cobalt powders that are predominantly h.c.p. in structure prior to grinding have a greater extent of reaction with acetone during grinding than do cobalt powders which are predominantly cubic in structure initially. However these data were obtained after an extended grinding period, and yield no information regarding the rate at which the organic compounds were produced during grinding. As the rates of formation of phorone and mesityl oxide could influence the adhesional characteristics of the metal powders during grinding, it is important to investigate the manner in which the organic compounds are produced during grinding using cobalt powders with different initial allotropic ratios and oxygen contents.

A measure of organic compounds adsorbed can be obtained by assaying the ground metal powders for total carbon after various grinding times.

Several cobalt powders were prepared using the reduction procedures given in Chapter 2 of Volume 1. The properties of the initial powders are summarised in Table 5.3.2. The powders were ground in acetone and samples were removed after various milling intervals. The samples of the ground metal were assayed for total carbon. Figure 5.3.5. summarises the carbon increments obtained with grinding time. Noteworthy from these data is that Powder 1 (initially cubic in structure) increased in carbon during the first 50 hours of grinding much more rapidly than did powder 5 in the same period. (Powder 5 was initially hexagonal in structure). These data suggest that predominantly hexagonal powders increase slowly in carbon during the initial stages of grinding; a very rapid increase in carbon occurs during the later stages of grinding. On the other hand predominantly cubic powders increase in carbon rapidly during the first stages of grinding after which the carbon increment remains practically constant. It was recorded earlier that oxide films on cubic cobalt show increased straining compared with films on hexagonal cobalt.

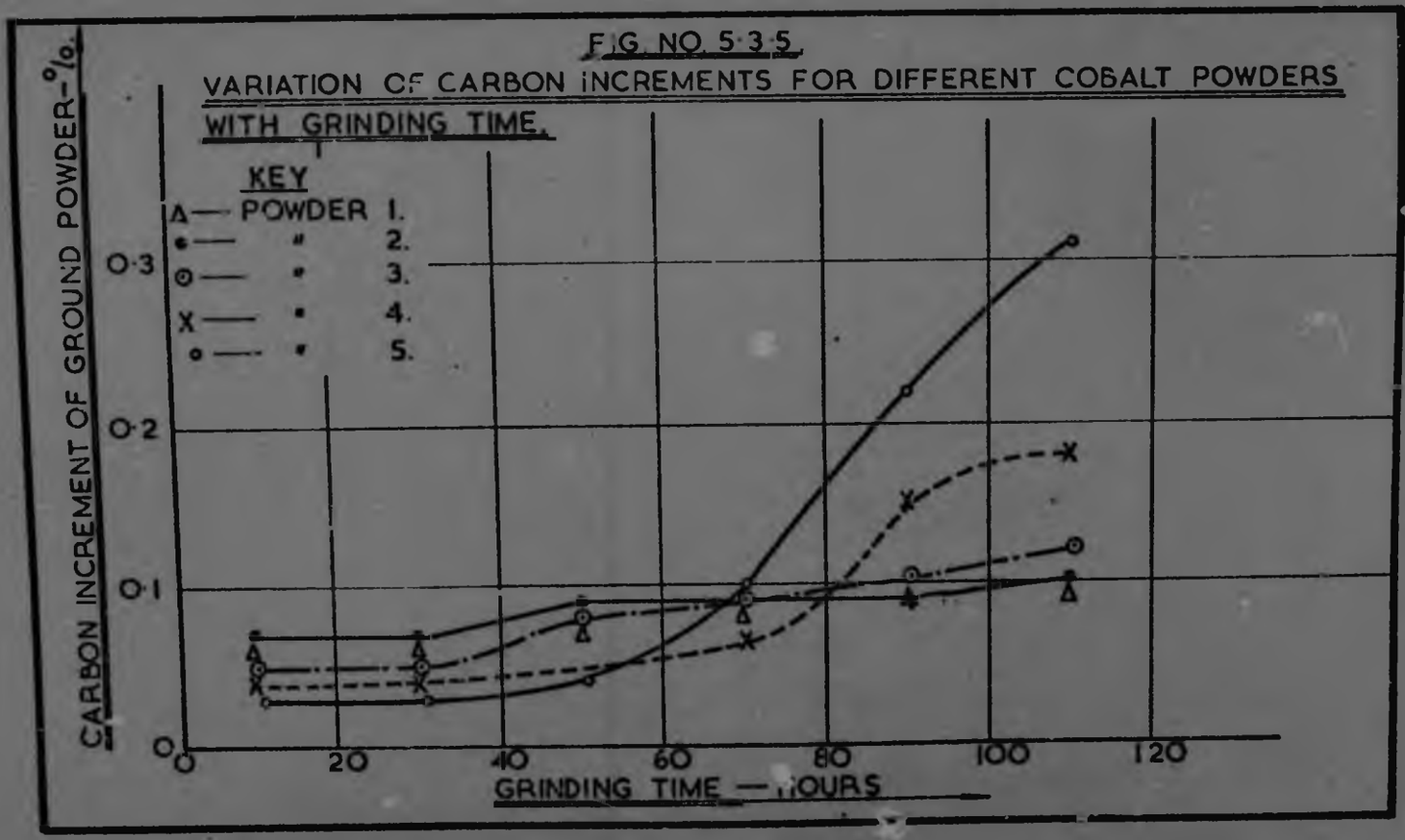
TABLE 5.3.2.

PROPERTIES OF COBALT POWDERS USED FOR DETERMINING CARBON INCREMENTS

Powder Number	Initial Carbon Content %	Allotropic Ratio H/C	Initial Surface Area m^2/g	Initial Oxygen Content %
1	0.03	C	0.39	0.02
2	0.03	0.69	1.15	0.65
3	0.04	1.15	1.62	1.27
4	0.04	1.49	1.89	1.88
5	0.05	H	2.65	3.01

FIG. NO. 5·3·5

VARIATION OF CARBON INCREMENTS FOR DIFFERENT COBALT POWDERS WITH GRINDING TIME.



It appears therefore that the carbon increments of the powders measured during grinding of the powders may be related to the mechanical stability of the chemisorbed oxide films present on the metal powder particles prior to grinding. In other words, cubic cobalt powders with strained oxide films show a rapid increase in carbon content of the ground samples during the initial stages of grinding after which the carbon remains esentially constant, whereas hexagonal cobalt powders with more stable oxide films show slow carbon increments during the initial stages of grinding with a rapid increase in the carbon content being recorded during the latter part of the grinding cycle.

5.3.3. THE IMPORTANCE OF THE CHEMICAL REACTION

The experimental evidence suggests that a chemisorbed layer is formed on the metal particles during grinding. This strongly bound layer could prevent adhesion of metal particles.

However the chemical reaction in grinding could have another important consequence. The process of adsorption is accompanied by the evolution of heat (217), and a decrease in the free energy of the adsorbent results.

It is generally recognised that the heats of chemisorption are comparable with the energies of the chemical bonds being broker and formed during chemisorption, and the heats of chemisorption are of the order of 40 k cals/g mole (167,4 k joules/g mole)[217]. It is not possible to calculate an order of magnitude value of the heat of chemisorption when phorone and mesityl oxide are adsorbed on cobalt for the extent of coverage of the metal by adsorbate and the orientation of the chemisorbed molecules cannot be established. As a consequence the decrease in surface free energy of the metal resulting from adsorption cannot be calculated. However in the case of deformed cobalt the decrease in free energy on adsorption will arise not only from the formation of an adsorbed chemical compound but will also be related to the presence of dislocations on the metal particle surfaces[221],[222]. There is ample evidence that surface dislocations enhance chemisorption. This property of dislocations is caused by a chemical unsaturation in the neighbourhood of a dislocation core[223].

In the ground cobalt powders there is an excess surface free energy compared with cobalt in a bulk state, and also the cold worked condition is thermodynamically metastable compared with the unstrained state.

Chemisorption will therefore tend to reduce the total free energy of the ground metal and in addition prevent adhesion of metal particles. Because of the higher electron density at the positions of the olefinic linkages and the $3d^7 4s^2$ cobalt structure it would be anticipated that any adsorption of the organic molecules would occur with the olefinic linkages most firmly adhered to the metal. If this occured the alkyl groups would be directed towards the liquid. In the case of mesityl oxide there would be three carbon atoms on either side of the double bond, and for phorone there would be three carbon atoms on either side of each of the double bonds. The carbonyl groups would be expected to be compatible with the metal rather than with the liquid because of the higher electron density in the region of the O atoms. These surface adsorption characteristics suggest that the organic molecules would not be adsorbed at right angles to the direction of the carbon chain, but at a small angle such that the carbon chain was practically parallel to the surface of the metal. In this way the entire surface of the metal powder particles could be covered with a multilayer of adsorbed material. If this suggested adsorption process did occur, metal-metal adhesion would certainly be reduced. It is probable therefore that as fine particles are comminuted from agglomerates after the state of maximum agglomeration has been reached, adsorption of organic material from the liquid occurs which prevents re-adhesion.

5.4. GRINDING OF COBALT METAL POWDERS IN ALTERNATIVE GRINDING FLUIDS

A 2.5 Kilo batch of cobalt powder was prepared by hydrogen reduction of cobaltosic oxide at 700°C for one hour. The powder had a specific surface area of 1.32 m^2/g; the hexagonal to cubic allotropic ratio was 0.48, and the oxygen content was 0.75 %.

500 g batches of this powder were ground in an 800 ml capacity ball mill using 2 Kg 6 mm hard metal balls as the milling medium. Different grinding fluids were used in each charge. The grinding fluids employed were acetone, ethanol, ordinary tap water and distilled water.

The powders were milled for 10, 20, 30, 50, 70, 90 and 110 hours and small powder samples of 8 g were removed after each milling interval. The specific surface area and allotropic ratio of each ground powder were determined.

Figure 5.4.1. (i - iv) summarises the results obtained and shows the variations in powder properties with grinding time.

The use of acetone results in a powder agglomeration during the initial stages of grinding, in a manner similar to all those powders studied previously.

FIG. NO. 5·4·ti

SPECIFIC SURFACE AREA AND ALLOTROPIC RATIO AGAINST GRINDING TIME FOR COBALT POWDER GROUND IN ACETONE.

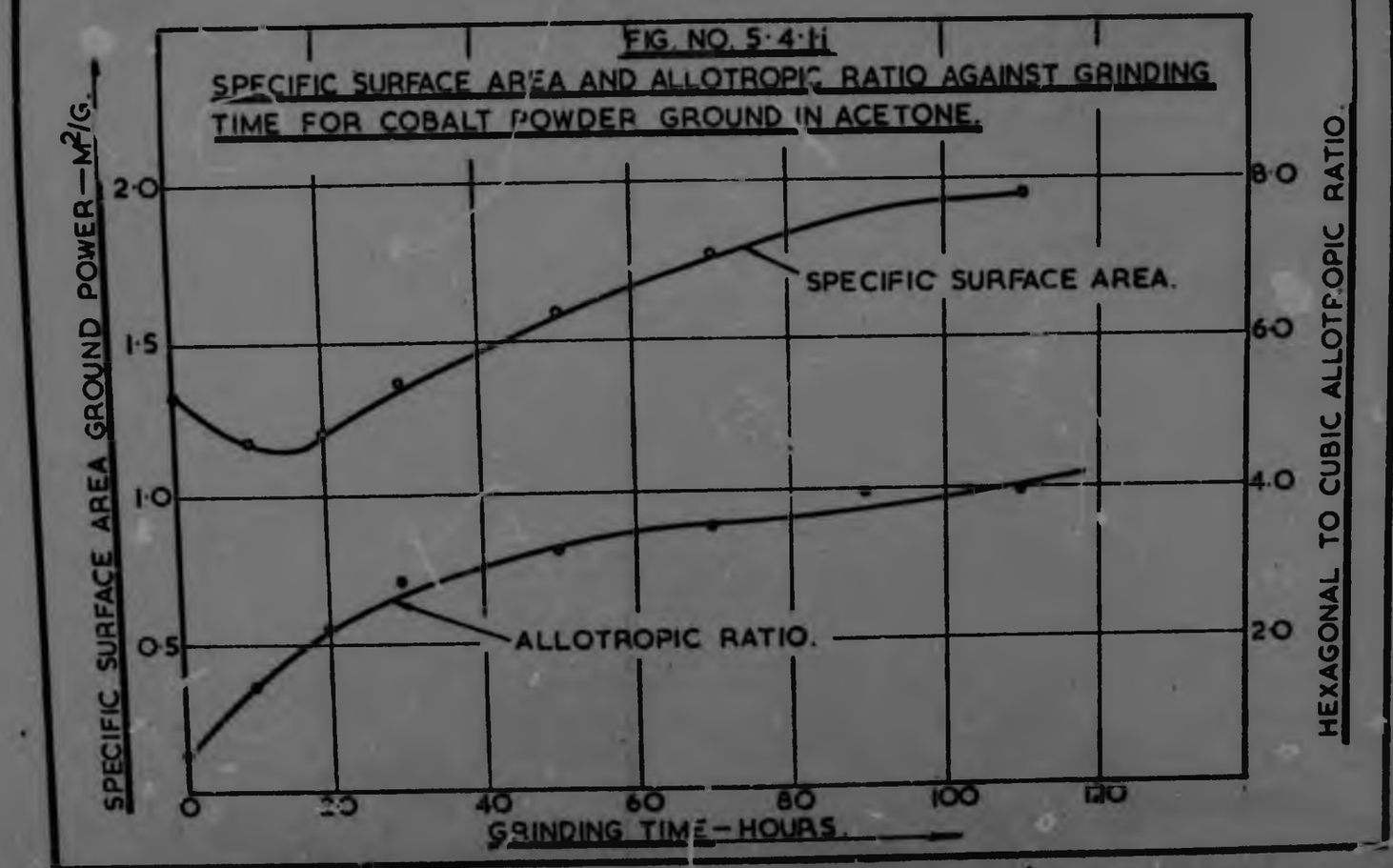
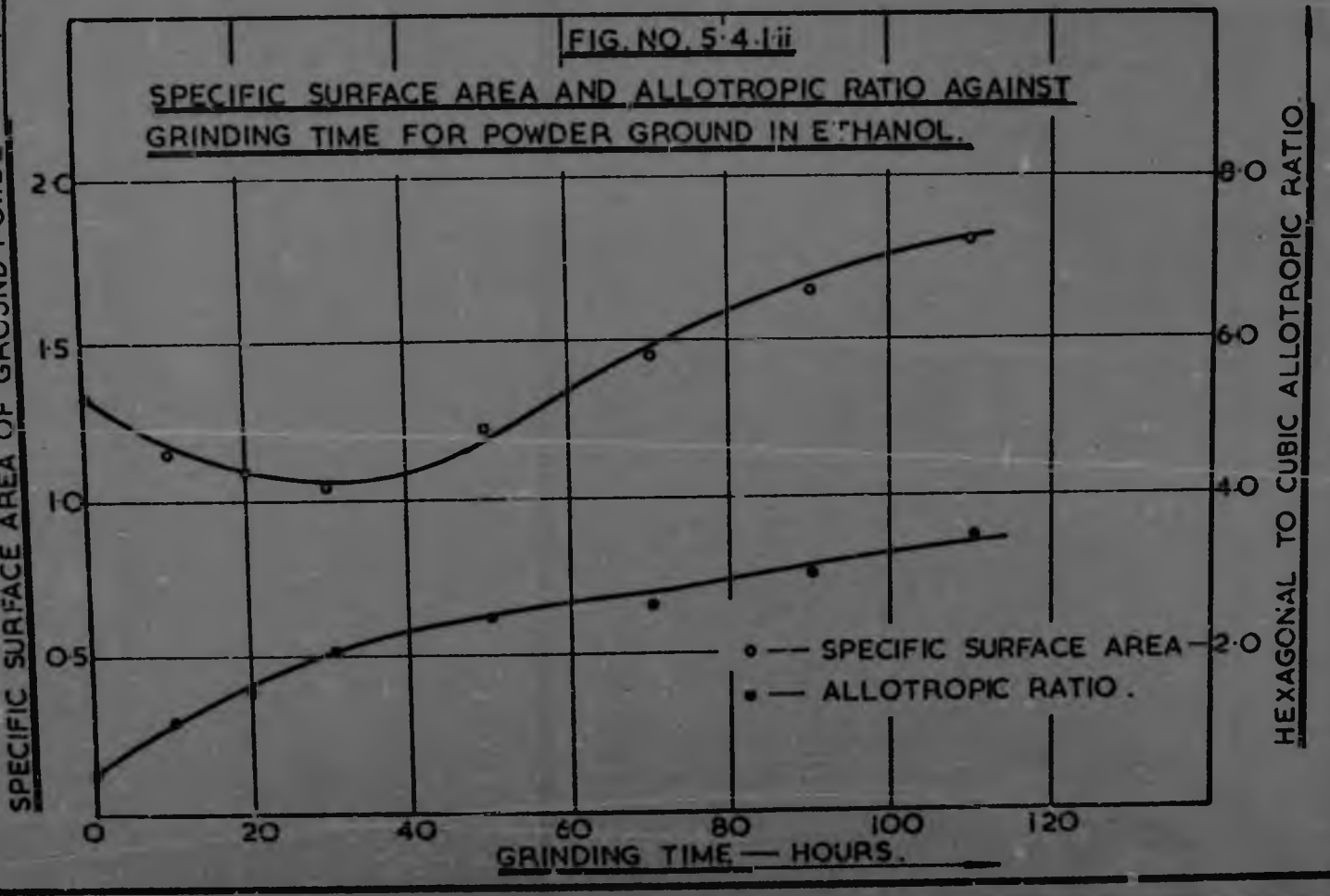


FIG. NO. 5·4·1ii

SPECIFIC SURFACE AREA AND ALLOTROPIC RATIO AGAINST GRINDING TIME FOR POWDER GROUND IN ETHANOL.



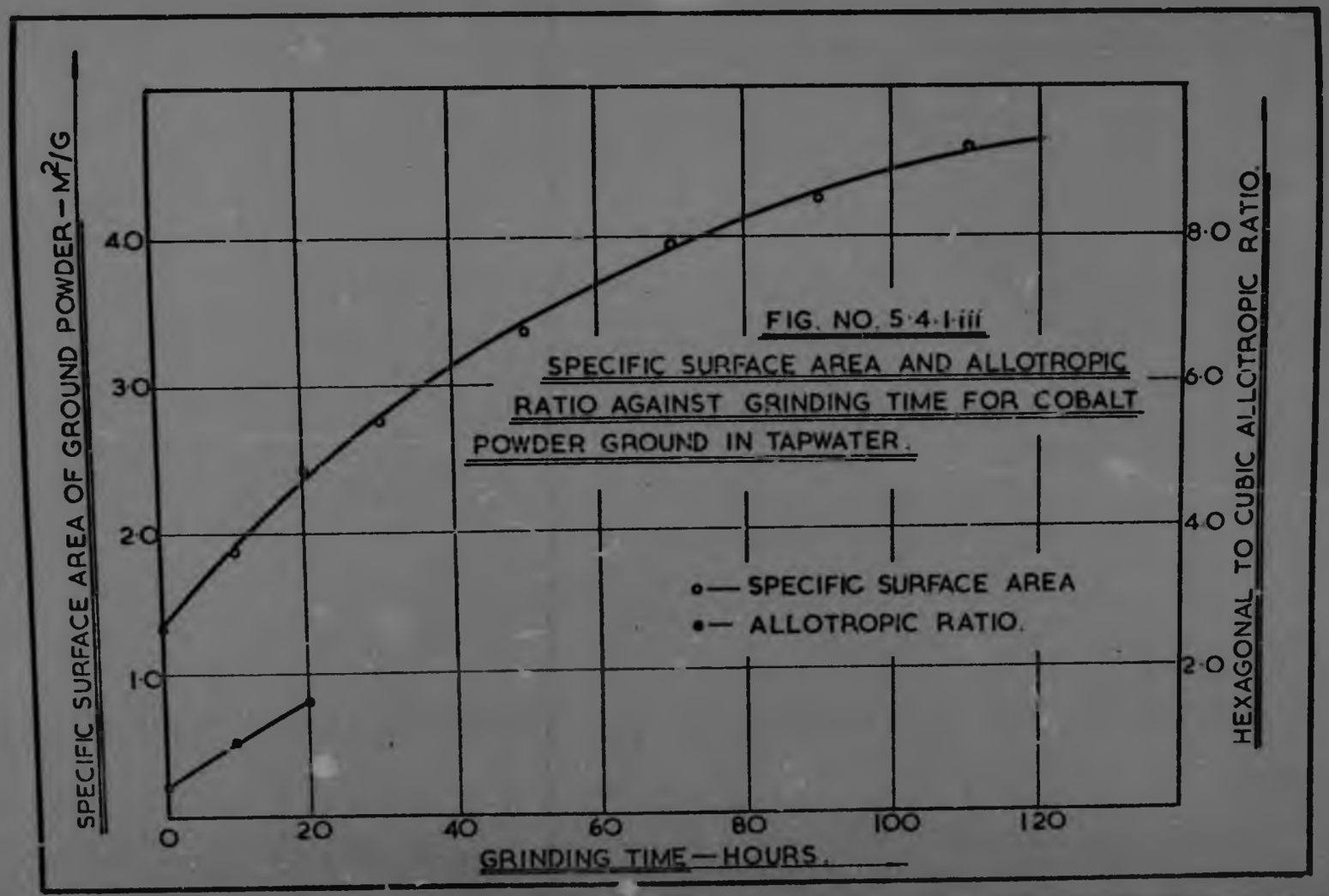


FIG. NO. 5·4·1·iii

SPECIFIC SURFACE AREA AND ALLOTROPIC RATIO AGAINST GRINDING TIME FOR COBALT POWDER GROUND IN TAPWATER.

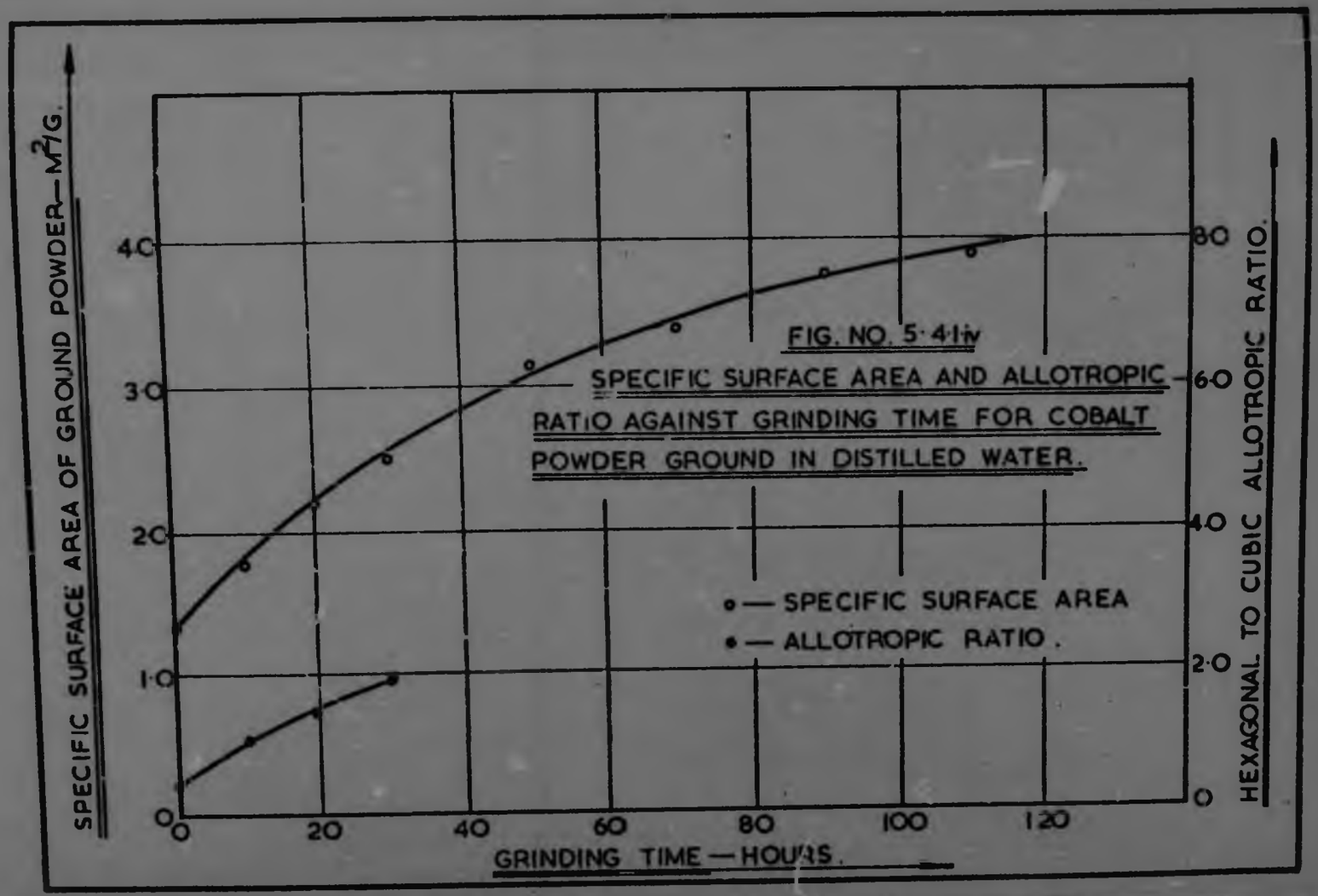


FIG. NO. 5·41iv

SPECIFIC SURFACE AREA AND ALLOTROPIC RATIO AGAINST GRINDING TIME FOR COBALT POWDER GROUND IN DISTILLED WATER.

Tap water results in no agglomeration of the metal powder particles, and a continuous increase in specific surface area with grinding time. After 10 hours of grinding, X ray diffraction analysis showed that a considerable quantity of CoO was present, and as grinding proceeded the strongest X ray line of Co_3O_4 appeared. After 20 hours grinding it was not possible to determine the allotropic ratios in the ground metal due to the presence of the large quantity of oxide. There was a considerable gas pressure release on opening the mill. It is suggested that the gas formed was hydrogen.

For the room temperature reaction:

$3\,Co\,(S) + 4H_2O(l) \longrightarrow Co_3O_4\,(S) + 4H_2(g)$ the free energy change is: (224)

ΔG^{O} = -182,000 - 0 - (0 - 4 x 56720) cals

= 44.88 k cals

= 187,8 k joules

Thus this reaction is thermodynamically unfavourable. Thermodynamic data indicate that the following reactions are also unfavourable: (224)

$Co\,(S) + H_2O(l) \longrightarrow CoO(S) + H_2(g)$

$3CoO(S) + H_2O(l) \longrightarrow Co_3O_4(S) + H_2(g)$

However the reaction:

$Co(S) \rightarrow Co^{++}(aq)$ is favourable since the free energy change is -12800 cals (equal to -53 570 joules) at 298°K.

Thermodynamics therefore indicate that direct conversion of the metal to oxide is unlikely, but the oxide could be formed through the divalent cation. In the case of tap water the reaction could have been accelerated by the presence of dissolved oxygen or an anion (such as chloride). On the other hand, although thermodynamics predict that direct conversion of metal to oxide is not likely, special factors such as the large surface area and the cold worked nature of the powder could have assisted the reaction. In any event a considerable quantity of CoO was formed during grinding and no metal-metal adhesion was possible, which could contribute to agglomeration.

Using distilled water as the milling fluid, no powder agglomeration was evident. The X ray diffraction patterns indicated that the proportion of CoO formed was much reduced compared with the case when tap water was used. Here again the oxidised material produced on grinding must have prevented metal-metal adhesion.

On opening the mill in which the cobalt powder had been ground in ethanol, the release of a very small quantity of gas was noted which may have been due to the reaction:

$$Co + 2C_2H_5OH \longrightarrow Co(C_2H_5O)_2 + H_2$$

This reaction of ethanol is characteristic with electropositive metals. Ethanol does not undergo any other reactions with cobalt or the oxides of cobalt. The occluded carbon in the ground cobalt powder after grinding was much less than noted for acetone. After 110 hours of grinding the cobalt powder contained 0.10 % carbon after milling in ethanol.

The use of ethanol as milling fluid resulted in a larger decrease in specific surface area during the initial stages of grinding than was noted in acetone. The cause of this may be the greater viscosity of ethanol compared with that of acetone. The relevant viscosities at 25°C are 0.320 centipoise for acetone and 1.32 c.p. for 95 % ethanol.(225) The chemical reactions resulting in the formation of hydrogen must have occured to a very small extent and did not interfere with the agglomeration.

The electrical polarisability effect would promote greater agglomeration in acetone compared with ethanol. The dielectric constant of ethanol at 25°C is 25.8 compared with a value of 21.4 for acetone.(226)

5.5. THE DISLOCATION DENSITY AND DISLOCATION DISTRIBUTION IN COBALT POWDERS

5.5.1. INTRODUCTION

It was noted earlier that it was not possible to obtain transmission photomicrographs of the cobalt powders at 100 Kv. As information regarding the presence of dislocations is necessary to explain the grinding behaviour of different cobalt powders it is important to investigate the data that may be derived from X ray diffraction patterns of the ground powders.

5.5.2. AVAILABLE X RAY DIFFRACTION TECHNIQUES

For pure hexagonal cobalt powders, which show no traces of the f.c.c. phase on X ray diffraction, the stacking fault probability may be derived by three independent methods that have been reported in the literature:

(1) Mitra and Halder's method (discussed in Chapter 2 of Volume 1)[238].

(2) The line breadth method of Rao et al. (also discussed in Chapter 2 of Volume 1)[227].

(3) The Fourier analysis method used by Rao et al.[227] This technique employs Pike's method[228] for determination of the centre of gravity and Stokes' method[229] for evaluation of the Fourier coefficients.

In addition this technique enables the domain size and r.m.s. strain to be evaluated. Rao et al[227] originally applied the technique for the determination of the faulting, strain and domain size of the $(10\bar{1}1)$ planes of the h.c.p. phase. An L_o value of 50^oA was used where $L_o = na_3$ where n is the harmonic number and a_3 is the Sin θ interval within which the peak is expressed as a Fourier series.

Mitra and Halder's method[238] (used in Section 4.7. of Volume 1) also yields information about the domain size and r.m.s. strain.

For f.c.c. metals Wagner[230] has shown that the deformation and twin stacking fault probabilities may be calculated using the observed peak shift as a measure of the deformation stacking fault probability. This technique may be applied when the density of both types of deformation error is low.[230]

For powders which consist of a mixture of f.c.c. and h.c.p. cobalt complete analysis of the faulting and dislocation density in both phases is not possible, because of the overlapping of certain of the profiles of both phases (in particular the (111) of the f.c.c. and the (0002) of the h.c.p. and both these are of high intensity).

Theoretically, the dislocation density of a deformed metal can be evaluated if the particle size D and r.m.s. strain $\langle \varepsilon^2 \rangle^{\frac{1}{2}}$ are known.[231]

The dislocation density ρ_D calculated from the domain size is given by:[231]

$$\rho_D = \frac{3n}{D^2}$$

Where ρ_D is the dislocation density

D is the domain size

n is the number of dislocations per block of side length D. (In severely deformed metals n is assumed to be unity).

In addition the dislocation density may be calculated from the strain broardening $\langle \varepsilon^2 \rangle^{\frac{1}{2}}$ by the formula:[231]

$$\rho_S = \frac{k\langle \varepsilon^2 \rangle}{Fb^2}$$

Where ρ_S is the dislocation density

ε is the strain broardening

b is the Burgers vector of the dislocation

F is a strain energy factor which allows for the occurence $k = 6\pi EA/\mu \ln(\frac{r}{r_o})$teractions

k is given by $k = 6\pi EA/\mu \ln(\frac{r}{r_o})$

Where E is Young's modulus of the metal

A is a factor with a numerical value of 2 for a Cauchy distribution and $\pi/2$ for a Gaussian distribution.

μ is the shear modulus of the metal

$\ln\left(\frac{R}{r_o}\right)$ is taken to be 4 in Williamson's and Smallman's analysis.[231]

Calculation of Young's modulus and the shear modulus using the compliance coefficients[232] (using Mc Skimin's data[233] for the compliance coefficients) and assuming a Cauchy distribution (which is thought to be valid for a number of deformed metals[231]) indicates that k has the following values in h.c.p. cobalt:

For the direction parallel to the hexagonal axis

$k = 38.8$

For the $\langle 11\bar{2}0 \rangle$ direction $k = 11.9$

For $\langle 20\bar{2}3 \rangle$ and $\langle 40\bar{4}3 \rangle$ directions $k = 15.4$

Assuming Kosters[234] experimentally measured values of Young's modulus $k = 24.9$.

Values of ρ_s can only be calculated if a value of F is known or assumed. The simplest assumption that can be made is that F is unity which corresponds with the model with n equal to unity.[231]

However Williamson and Smallman's equation for ρ_s given above must be incorrect since the following formula derived by Stibitz[235] was used for the stored energy:

$$V = 3E(A\epsilon^2)/2$$

Where V is the stored energy

Subsequently Faulkner[238] proved that Stibitz' formula for the stored energy was erroneous, and showed that the stored elastic energy in an isotropic medium is given by:

$$V = \frac{15E\langle\varepsilon^2\rangle}{2(3 - 4v + 8v^2)}$$

Where v is Poisson's ratio

Reworking Williamson and Smallmans' formula for ρ_S shows that it should be given by

$$\rho_S = \frac{5k\langle\varepsilon^2\rangle}{Fb^2(3 - 4v + 8v^2)}$$

Williamson and Smallman[231] have shown that in deformed metals where there are pile ups of dislocations ρ_S will differ from ρ_D, and the true dislocation density is given by:

$$\rho = (\rho_S . \rho_D)^{\frac{1}{2}}$$

Where ρ is the true dislocation density

The number of dislocations (n') in a pile up is given as follows:[231]

$$n' = \left[\rho_S / \rho_D\right]^{\frac{1}{2}}$$

5.3. RESULTS

ρ_D and ρ_S were calculated for the h.c.p. phase of all the powders described in Chapter 4 of Volume 1. The line breadth method of Mitra and Halder[238] was used for evaluating D, ε and $(3\alpha + \beta)$.

Hence ρ and n' were calculated.

The Fourier method of Rao et al (227) was applied to the $(10\bar{1}1)$ reflections of the fine hexagonal powder samples-(which was prepared by hydrogen reduction of cobaltosic oxide at 400°C)

Wagner's method (230) was used for estimating the deformation and twin stacking fault probability of the cubic cobalt powder described in 5.1. of this volume.

ρ_D was calculated with n equal to unity; the corrected expression for ρ_S was used; V was calculated using Faulkner's expression with the energy expressed in joules/g. Koster's (237) value of Poisson's ratio was used; Koster's value of Young's modulus was used for calculating k; the Burgers vector of the dislocations was assumed to be 3°A in all cases; the apparent surface energy (E in joules/g) was calculated from the measured specific surface areas of the powders, assuming that the surface energy of cobalt is 2000 ergs/cm^2.

The results obtained are summarised in tabular form as follows:

Table 5.5.1. CF-6 Cobalt powder

Table 5.5.2. CF-10 Cobalt powder

Table 5.5.3. Hoboken Cobalt powder

Table 5.5.4. Annealed CF-6 powder

Table 5.5.5. Annealed Hoboken Cobalt powder

Table 5.5.6. Ultrafine hexagonal cobalt powder

Table 5.5.7. Cubic cobalt powder described in Section 5.1.

5.5.4. COMMENTS ON RESULTS

From the examination of the data in the Tables, the following points are noteworthy:

(1) For all the samples studied ρ_D differs from ρ_S which suggests that the dislocations are piled up into groups with an average of 20 to 30 dislocations per group. As noted in 3.2. this behaviour is expected because of the single operative slip system in h.c.p. cobalt. In the cobalt powders prior to grinding there is also some evidence of the dislocations being in groups.

(2) Annealing of the CF-6 and Hoboken powders leads to a decrease in the dislocation density compared with the values recorded in the unannealed powders. However the annealing treatment leads to increased n' values in the ground powders, which suggests that the annealed powders would be more prone to brittle fracture during grinding than the unannealed powders.

(3) The results show that the dislocation density increases throughout the course of grinding.

TABLE 5.5.1.

POWDER: CF-6 Cobalt powder							
Grinding Time Hours	$\rho_D cm^{-2}$	$\rho_S cm^{-2}$	ρcm^{-2}	n'	V joules/g	E joules/g	$3\alpha + \beta$
No grinding	$1,57 \times 10^9$	3.16×10^{10}	7.10×10^9	4	0,04	0,65	0.0041
5	1.65×10^9	9.81×10^{10}	1.28×10^{10}	8	0,14	1,62	0.0163
10	2.13×10^9	6.15×10^{11}	3.62×10^{10}	17	0,86	1,34	0.0172
20	2.42×10^9	7.82×10^{11}	8.15×10^{10}	18	1,09	1,28	0.0165
30	3.46×10^9	1.92×10^{12}	1.06×10^{11}	23	1,67	1,82	0.0154
50	5.19×10^9	2.15×10^{12}	1.51×10^{11}	21	2,99	2,29	0.0141
70	6.82×10^9	3.28×10^{12}	1.91×10^{11}	22	4,56	2,51	0.0130
90	7.63×10^9	4.76×10^{12}	2.26×10^{11}	25	6,65	2,71	0.0099
110	9.81×10^9	5.20×10^{12}	2.45×10^{11}	23	7,20	2,94	0.0086
130	1.43×10^{10}	5.72×10^{12}	2.86×10^{11}	20	8,00	3,16	0.0079

TABLE 5.5.2.

POWDER: CF-10 Cobalt powder							
Grinding Time Hours	ρ_D cm^{-2}	ρ_S cm^{-2}	ρ cm^{-2}	n'	V joules/g	E joules/g	$3\alpha + \beta$
No grinding	1.94×10^9	3.28×10^{11}	2.52×10^{10}	13	0,46	0,41	0.0098
5	2.18×10^9	4.98×10^{11}	3.30×10^{10}	15	0,69	1,52	0.0192
10	3.32×10^9	5.42×10^{11}	4.24×10^{10}	13	0,76	1,74	0.0251
20	4.18×10^9	6.76×10^{11}	5.33×10^{10}	13	0,94	1,68	0.0274
30	4.74×10^9	7.62×10^{11}	6.05×10^{10}	14	1,06	1,65	0.0246
50	5.32×10^9	8.95×10^{11}	6.91×10^{10}	15	1,24	1,86	0.0232
70	6.58×10^9	1.19×10^{12}	8.84×10^{10}	15	1,65	2,10	0.0172
90	7.02×10^9	2.14×10^{12}	1.24×10^{11}	15	2,84	2,38	0.0169
110	8.65×10^9	3.60×10^{12}	1.76×10^{11}	15	5,00	2,42	0.0154
130	1.02×10^{10}	4.10×10^{12}	2.05×10^{11}	15	5,71	2,68	0.0142

TABLE 5.5.3.

POWDER: Hoboken Cobalt Powder							
Grinding Time Hours	ρ_D cm^{-2}	ρ_S cm^{-2}	ρ cm^{-2}	n'	V joules/g	E joules/g	$3\alpha + \beta$
No grinding	8.95×10^{8}	4.11×10^{10}	6.10×10^{9}	7	0,05	1,09	0.0018
5	1.15×10^{9}	2.69×10^{11}	1.76×10^{10}	15	0,37	1,38	0.0041
10	1.26×10^{9}	6.89×10^{11}	2.94×10^{10}	24	0,96	1,55	0.0054
20	4.69×10^{9}	2.21×10^{12}	1.02×10^{11}	22	3,06	1,88	0.0066
30	6.30×10^{9}	4.30×10^{12}	1.65×10^{11}	26	5,95	2,18	0.0058
50	7.80×10^{9}	6.70×10^{12}	2.28×10^{11}	30	9,30	2,50	0.0051
70	9.60×10^{9}	8.50×10^{12}	2.86×10^{11}	30	11,80	2,71	0.0049
90	2.42×10^{10}	8.80×10^{12}	4.64×10^{11}	19	12,35	2,84	0.0047
110	4.16×10^{10}	7.80×10^{12}	5.70×10^{11}	14	10,80	3,10	0.0040
130	5.30×10^{10}	7.20×10^{12}	6.16×10^{11}	11	10,00	3,34	0.0038

TABLE 5.5.4.

POWDER: Annealed CF-6 powder							
Grinding Time Hours	$\rho_D cm^{-2}$	$\rho_S cm^{-2}$	ρcm^{-2}	n'	V joules/g	E joules/g	$3\alpha + \beta$
No Grinding	1.77×10^{8}	3.62×10^{10}	2.53×10^{9}	14	0,05	0,55	0.0002
5	3.54×10^{8}	1.85×10^{11}	8.10×10^{9}	23	0,26	1,26	0.0007
10	5.45×10^{8}	3.45×10^{11}	1.37×10^{10}	25	0,48	1,70	0.0014
20	4.78×10^{8}	1.03×10^{12}	2.23×10^{10}	46	1,43	1,83	0.0016
30	6.43×10^{8}	1.96×10^{12}	3.56×10^{10}	55	2,72	2,06	0.0023
50	7.71×10^{8}	1.32×10^{12}	3.19×10^{10}	41	1,83	2,25	0.0017
70	8.39×10^{8}	1.67×10^{12}	3.74×10^{10}	44	2,32	2,46	0.0011
90	1.00×10^{9}	1.22×10^{12}	$3,49 \times 10^{10}$	35	1,69	2,64	0.0012
110	1.72×10^{9}	9.40×10^{11}	4.01×10^{10}	23	1,30	2,85	0.0019
130	3.19×10^{9}	1.17×10^{12}	6.10×10^{10}	19	1,62	3,04	0.0015

TABLE 5.5.5.

POWDER: Annealed Hoboken Powder							
Grinding Time Hours	$\rho_D cm^{-2}$	$\rho_S cm^{-2}$	ρcm^{-2}	n′	V joules /g	E joules /g	$3\alpha + \beta$
No grind -ing	2.19×10^{8}	6.15×10^{9}	1.16×10^{9}	5	0,008	0,95	0.0001
5	4.49×10^{8}	3.45×10^{11}	1.24×10^{10}	28	0,48	1,41	0.0003
10	6.07×10^{8}	5.17×10^{11}	1.77×10^{10}	34	0,72	1,92	0.0009
20	8.85×10^{8}	1.12×10^{12}	3.15×10^{10}	35	1,56	2,06	0.0026
30	1.19×10^{9}	1.96×10^{12}	4.82×10^{10}	41	2,73	2,14	0.0019
50	1.74×10^{9}	$2,58 \times 10^{12}$	$6,70 \times 10^{10}$	26	3,72	2,29	0.0017
70	2.94×10^{9}	2.86×10^{12}	9.16×10^{10}	32	4,00	2,43	0.0015
90	4.45×10^{9}	2.36×10^{12}	1.02×10^{11}	23	3,30	2,55	0.0023
110	5.15×10^{9}	1.84×10^{12}	9.75×10^{10}	19	2,55	2,70	0.0014
130	6.40×10^{9}	1.32×10^{12}	9.20×10^{10}	14	1,74	2,81	0.0015

TABLE 5.5.6

POWDER: Extra Fine Hexagonal Cobalt Powder							
Grinding Time Hours	$\rho_D cm^{-2}$	$\rho_S cm^{-2}$	$\rho\ cm^{-2}$	n'	V joules /g	E joules /g	$\alpha+\alpha'/3$
No grinding	1.65×10^{8}	3.60×10^{9}	1.19×10^{9}	7	0,014	7,45	0.0087
10	1.94×10^{11}	1.30×10^{14}	4.75×10^{12}	27	2,07	4,80	0.0089
20	3.24×10^{11}	1.95×10^{14}	7.80×10^{12}	24	2,70	4,61	0.0110
30	8.19×10^{11}	4.80×10^{14}	1.89×10^{13}	24	6,50	3,79	0.0126
50	1.48×10^{12}	8.70×10^{14}	3.56×10^{13}	24	12,10	2,74	0.0174
70	1.73×10^{12}	1.50×10^{15}	5.10×10^{13}	30	20,80	2,44	0.0188
90	2.94×10^{12}	3.10×10^{15}	9.54×10^{13}	32	43,00	1,89	0.0179
110	3.14×10^{12}	2.56×10^{15}	8.94×10^{13}	26	35,60	2,01	0.0165
130	2.29×10^{12}	2.10×10^{15}	6.94×10^{13}	30	29,10	2,37	0.0142

TABLE 5.5.7.

POWDER: Cubic cobalt powder described in Section 5.1							
Grinding Time Hours	$\rho_D cm^{-2}$	$\rho_S cm^{-2}$	ρcm^{-2}	n′	V joules /g	E joules /g	$3\alpha + \beta$
5	1.77×10^{10}	2.89×10^{12}	2.26×10^{11}	13	4,01	0,35	0.0086
10	1.12×10^{10}	1.88×10^{13}	4.57×10^{11}	41	26,00	0,36	0.0141
15	3.79×10^{10}	1.81×10^{13}	8.24×10^{11}	22	25,20	0,34	0.0153
20	6.20×10^{10}	1.24×10^{13}	8.76×10^{11}	14	17,20	0,31	0.0176
30	5.35×10^{10}	1.04×10^{13}	7.49×10^{11}	14	14,40	0,26	0.0152
50	1.00×10^{11}	1.80×10^{13}	1.34×10^{12}	13	25,00	0,33	0.0146
70	1.21×10^{11}	1.58×10^{13}	1.37×10^{12}	12	22,00	0,43	0.0116
90	1.72×10^{11}	1.24×10^{13}	1.46×10^{12}	8	17,20	0,84	0.0105
110	2.27×10^{11}	8.90×10^{12}	1.42×10^{12}	6	12,40	1,32	0.0088
No grinding No Hexagonal phase detectable by X ray diffraction* (250)							

* Wagner's method showed the following on the as prepared powder in the cubic phase:
The probability of occurence of deformation faulting (α) = 0.0180
The probability of occurence of twin faulting (β) = 0.0006

(4) Considering the arbitrary assumptions that are made in the derivations of ρ_D and ρ_S comparisons of differences in dislocation densities of different powders would probably not be valid. However the results do suggest that the hexagonal and cubic powders prepared by hydrogen reduction of cobaltosic oxide have higher dislocation densities than the commercial cobalt powders.

(5) Wagner's technique (230) provides some useful results on the stacking fault defects present in the cubic cobalt powder prior to grinding. Deformation stacking faults as well as a very small proportion of twin (or growth) faults are present. It was suggested in Chapter 2 of Volume 1 that the deformation arises from a volume change during reduction. However it appears that twinning does not constitute a major part of the faulting arising from the volume change deformation; the deformation type stacking fault predominates.

(6) In Chapter 4 of Volume 1 it was assumed that D was a dimension of the coherently diffracting domains, and that the powder particles consisted of an array of single crystallites with dimension D. Without electron transmission it is not possible to confirm this suggestion. Although there have been a number of X ray diffraction investigations (227), (238) of deformed cobalt, there have been no suggestions as to the physical significance of D.

In deformed aluminium it has been suggested that (239) D corresponds to the slip band spacing. In Chapter 4 of Volume 1, as a result of the decrease in D with grinding time it was suggested that the agglomerates formed consisted of aggregates of particles of dimension D bonded together. As a result of the discussion given in Section 3.6 of this Volume it is realised that this conclusion was erroneous. However it is not possible to suggest the significance of the D parameter. The significance of D can only be established by electron transmission studies on the powders.

(7) The stored energy results for the h.c.p. phase of the ground powders are not directly comparable with the stored energy values reported for a number of deformed metals (231). This arises because a number of results reported in the literature were derived using Stibitz formula, which Faulkner showed to be incorrect. Use of Faulkner's formula for stored energy leads to values that are approximately 1.96 times those obtained using the Stibitz formula. The results in the Tables do however show that the stored energy in surface regions of the powders are of comparable magnitude to the surface energies. However V is the total stored energy arising from the presence of dislocations, and no information can be obtained as to the relative contributions to V of the "sessile" and "glissile" dislocations.

The two types of dislocations will behave differently with further grinding. Thus the two types of dislocations will contribute to the total free energy of a powder, but the sessile dislocations are locked, and any decrease in free energy that occurs during grinding will take place by different processes for the sessile and glissile dislocations.

(8) No information regarding vacancies is obtained from the data, and the techniques used do not take account of porosity which may be present in the agglomerates.

(9) All the results suggest that an annealing of the stacking faults takes place during the later stages of grinding. As was noted in Section 4.7. of Volume 1, this phenomenon cannot be satisfactorily explained. It might however be associated with high temperatures generated at the instant of impact of colliding balls and the small particles, but this is only a speculative assumption which cannot be proved.

(10) In general little information of value can be derived from X ray diffraction analyses of the powders, which can explain differences in grinding behaviour.

5.6. DIFFERENCES IN DISPERSION OF COBALT IN HARD METAL POWDER BATCHES PREPARED WITH CUBIC AND HEXAGONAL COBALT POWDERS

In Chapter 5 of Volume 1, electron micrographs of ground hard metal powder mixtures were shown; the hard metal powder mixtures were prepared using commercial cobalt powders with different initial allotropic ratios. It was concluded that differences in the degree of dispersion of the cobalt in the hard metal mixtures, using different commercial powders could not be readily detected.

In order to investigate this problem further, batches of hard metal were prepared using a tungsten carbide powder with a pure hexagonal cobalt powder, and the same tungsten carbide powder was ground with a cobalt powder which was cubic in structure. Electron micrographs of the ground powders were prepared using the techniques described previously.

Two hard metal powder batches were prepared from the same carbide powder; in one of the batches hexagonal cobalt powder prepared by hydrogen reduction of cobaltosic oxide at 400°C was used. In the second batch of hard metal cobalt powder prepared by hydrogen reduction at 800°C was used.

This cubic powder contained no detectable traces of the hexagonal modification. Both batches contained 10 % by weight of cobalt. The powders were ground in acetone for 2, 4 and 24 hours. An 800 ml mill was used.

Figure 5.6.1. (x 4000) shows a region of agglomerated carbide grains with an agglomerate of cobalt which has only a small number of carbide grains embedded in it. The mixture shown in Figure 5.6.1. was prepared with the initially cubic cobalt powder; the mixture had been ground for two hours. Figure 5.6.2. (x 9600) shows aggregated carbide grains, which are practically devoid of cobalt in the same hard metal mixture.

Figures 5.6.3., 5.6.4., and 5.6.5. (all x 9600) show the hard metal mixture prepared with hexagonal cobalt powder after two hours of grinding. Large carbide grains are seen to be dispersed in the cobalt agglomerates.

Figures 5.6.6. and 5.6.7. (both x 9600) show the mixture prepared with the initially cubic cobalt powder after 4 hours of grinding. Small individual carbide particles can be seen to have been "beaten" into the cubic cobalt agglomerates, but there is little evidence of cobalt around the asperities of the carbide grains.



FIGURE 5.6.1.

Hard metal mixture prepared with cubic powder ground for 2 hours (x 4000)



FIGURE 5.6.2.

Aggregated carbide grains practically devoid of cobalt (x 9600)

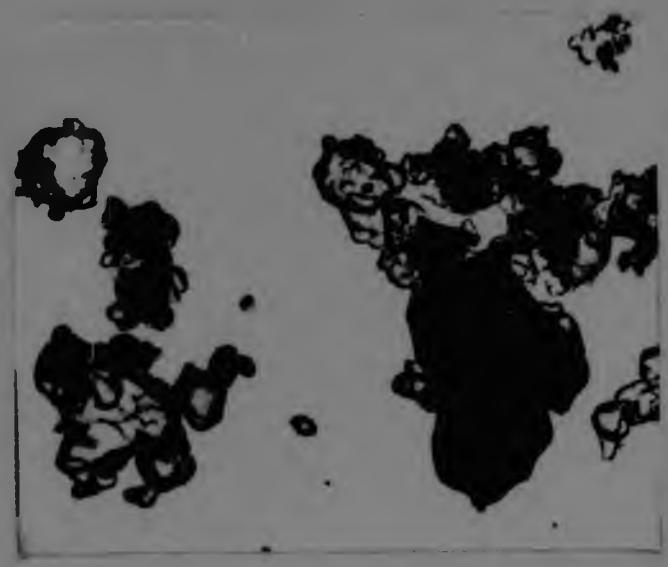


FIGURE 5.6.3.

(x 9600)

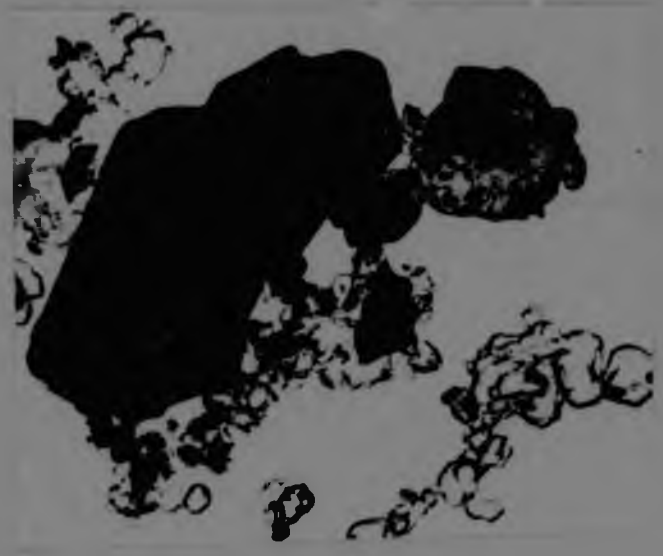


FIGURE 5.6.4

Hard metal mixture prepared with hexagonal cobalt after 2 hours of grinding

(x 9600)



FIGURE 5.6.5.

Hard metal mixture prepared with hexagonal cobalt after 2 hours grinding (x 9600)



FIGURE 5.6.6.

Hard metal mixture prepared with initially cubic cobalt after 4 hours of grinding (x 9600)



FIGURE 5.6.7.

Hard metal mixture prepared with initially cubic cobalt after 4 hours of grinding (x 9600)

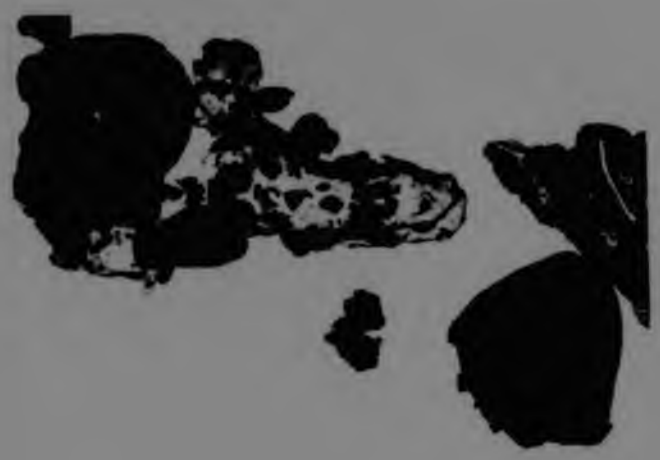


FIGURE 5.6.6.

Hard metal mixture prepared with initially cubic cobalt after 4 hours of grinding (x 9600)

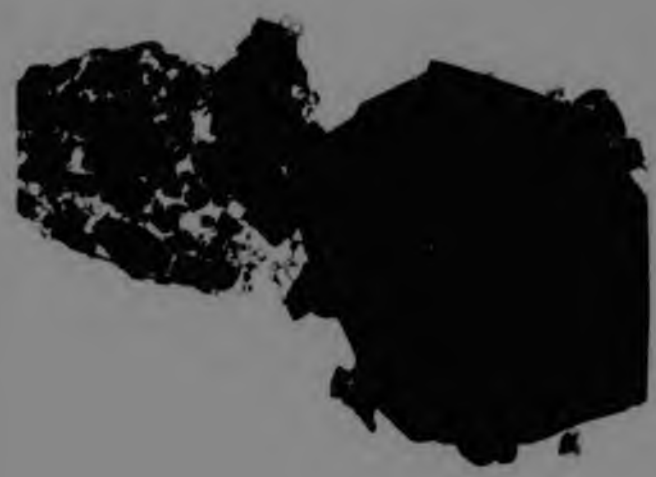


FIGURE 5.6.7.

Hard metal mixture prepared with initially cubic cobalt after 4 hours of grinding (x 9600)

Figure 5.6.8 (x 9600) shows a similar structure after 4 hours of grinding of the powder mixture prepared with the cobalt powder which was initially cubic in structure. Figure 5.6.9. (x 9600) shows another region in the same mixture which is practically devoid of cobalt.

Figures 5.6.10. and 5.6.11. (both x 9600) show the mixture prepared with the cobalt powder which was initially hexagonal in structure after 4 hours of grinding. The cobalt adhering to the asperity of the carbide grain in Figure 5.6.11. is noteworthy.

Figure 5.6.12. (x 56000) shows fine carbide particles embedded in cobalt agglomerates after 4 hours grinding; initially cubic cobalt powder was used. A similar structure is evident in Figure 5.6.13. (x 22000); there is little evidence for cobalt dispersed around the edges of the larger carbide grains in this figure.

As the grinding time is increased, discernible differences between hard metal powders prepared with cobalt powders with different initial allotropic ratios become less evident; this is clear from Figures 5.6.14., 5.6.15., and 5.6.16. Figure 5.6.14. (x 25000) shows the mixture prepared with initially hexagonal cobalt after 24 hours grinding.



FIGURE 5.6.8.

(x 9600)



FIGURE 5.6.9.

(x 9600)

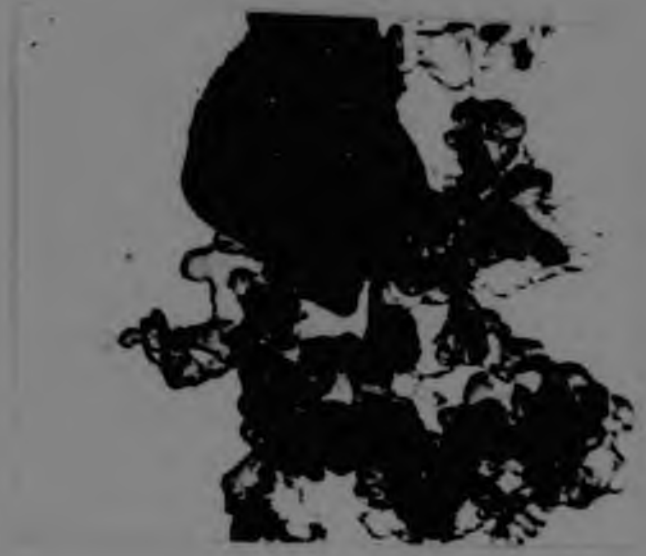


FIGURE 5.6.10.

(x 9600)



FIGURE 5.6.11.

(x 9600)



FIGURE 5.6.12.

Fine carbide grains embedded in a cobalt agglomerate (x 56000)

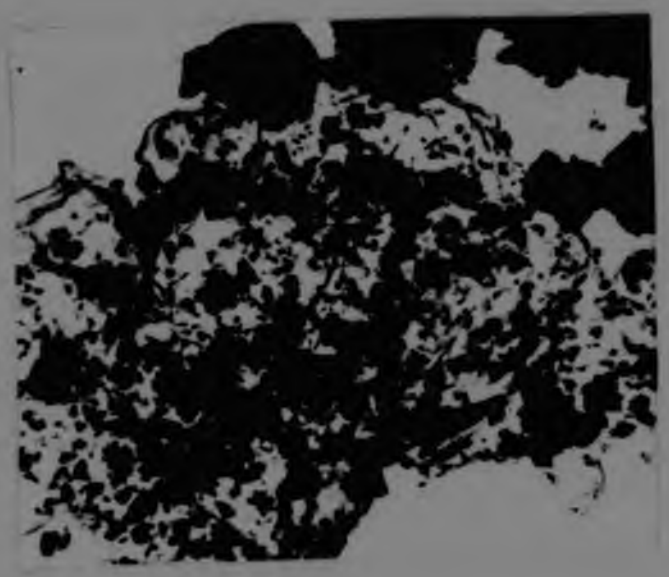


FIGURE 5.6.13.

Carbide grains embedded in a cobalt agglomerate (x 22000)



FIGURE 5.6.14.

Hard metal powder after 24 hours of grinding (initially hexagonal cobalt)

(x 25000)

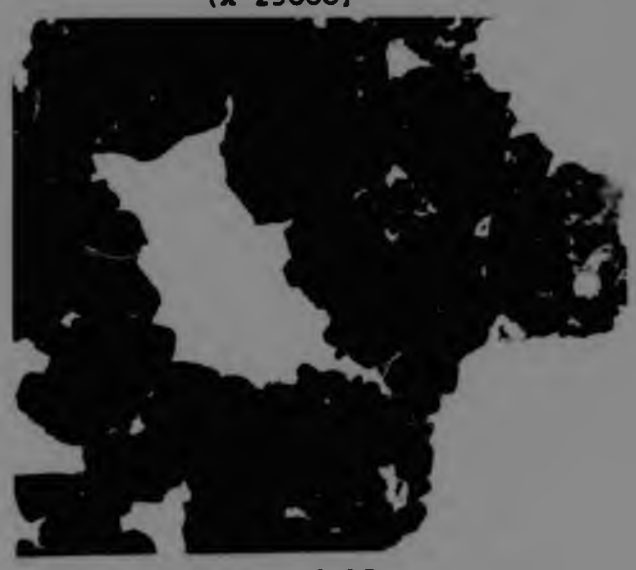


FIGURE 5.6.15.

Hard metal powder after 24 hours of grinding (initially cubic cobalt)

(x 25000)



FIGURE 5.6.16.

Hard metal powder after 24 hours grinding

(initially cubic cobalt) (x 25000)

Figure 5.6.15. and Figure 5.6.16. (both x 25000) show the mixture after 24 hours of grinding where initially cubic cobalt powder was used. It is difficult to detect differences in the degree of dispersion of cobalt in these three samples.

This set of micrographs clearly shows differences in the dispersion of the cobalt after short grinding times when hexagonal and cubic cobalt powders are used for the preparation of hard metal mixtures. Using the initially cubic cobalt powder fine carbide grains are embedded in the ductile agglomerates during the early stages of grinding. With hexagonal powder the individual particles of cobalt agglomerate; impact of carbide particles appears to result in fracture of the weakly bonded metal agglomerates and adhesion of the cobalt to the larger carbide grains.

In Chapter 5 of Volume 1 it was suggested that during grinding the carbide grains were embedded in the cobalt aggregates; another process which was suggested to occur was a rolling of the cobalt aggregates into thin foils. This mechanism is probably correct for predominantly cubic cobalt powders; with hexagonal cobalt powder fracture of the agglomerates and adhesion to the larger carbide grains probably occurs during the initial stages of milling.

6. DISCUSSION

6.1. INTRODUCTION

The experimental programme has confirmed a number of the suggestions made in Section 4; in particular evidence of a chemical reaction during the grinding of cobalt metal powders in acetone has been obtained. The experimental work described in Section 5.4. indicated that the use of different milling fluids had a significant effect on the grinding characteristics of cobalt powder.

In Volume 1 it was noted that predominantly hexagonal cobalt powders reached the state of minimum specific surface area after shorter grinding times than did predominantly cubic cobalt powders. Hexagonal cobalt powders proved to be very suitable for achieving satisfactory hard metal compact densities after short grinding times. To thoroughly explain these findings it is necessary to briefly summarise a number of features associated with the cobalt powders. These features were reviewed in Section 3:

(1) The proportions of the allotropes of cobalt present: As discussed in Sections 3.2. and 4. the h.c.p. phase should be more easily comminuted than the f.c.c. phase during grinding.

More extensive slip prior to fracture is expected from the f.c.c. form than from the h.c.p. form.

(2) The presence of dislocations: Dislocations present in the powders prior to grinding are expected to influence the fracture characteristics. Dislocations were also thought to be responsible for the phenomenon of "cold-welding". Surface dislocations would reduce the true area of contact between adhering particles. The dislocations present on the surfaces of the metal particles after reduction could influence the dispersion of chemically bonded oxide that is formed on exposure of the powder to the atmosphere; the role of surface dislocations on oxidation of surfaces has been previously discussed.[221] As dislocations are chemically reactive surface sites[223] dislocations could influence the free energy change that occurs on adsorption of the chemical compounds that are produced during grinding in acetone. The dislocations present at any stage during grinding may be of more than one type; both sessile and glissile dislocations could be present.

(3) The presence of oxide films: Chemically bonded oxide films are present on certain areas of the metal powders prior to grinding.

These films will alter the surface free energies of the powders compared with the pure metal. The oxide films are responsible for the chemical reaction in acetone and thus the strains present in the oxide films prior to grinding will influence the rate at which the organic compounds are produced during grinding. Oxide films on h.c.p. cobalt are expected to exhibit lower dislocation densities than oxide films on f.c.c. cobalt. These oxide films are expected to exhibit only slightly reduced adhesional characteristics compared with those of the metal. The oxide films are probably non-stoichiometric and are expected to exhibit a certain degree of plasticity during grinding.

(4) The specific surface areas of the powders prior to grinding: As a consequence of the incomplete bonding of the surface atoms of the metal as compared with those in the interior of the particles, the powders have an associated surface free energy which is anisotropic in both allotropes of cobalt in microscopic regions, but which is approximately proportional to the specific surface area of the powders.

From a consideration of the above factors it is possible to propose a theory for the agglomeration behaviour during grinding of cobalt powders with different initial characteristics.

6.2. THEORY OF AGGLOMERATION OF COBALT POWDERS

An individual powder particle in a powder mass probably has unique characteristics; no two particles will be exactly alike with respect to the properties: phase ratio, surface free energy, oxide content, dislocation density and particle size.

Thus in order to explain the grinding characteristics of a given powder mass it is necessary to consider the average properties of the given powder.

The following section represents an attempt to explain the grinding characteristics of different metal powders. In order to explain different grinding characteristics consider the terms which contribute to the total free energy G of unit weight of a metal powder during the various stages of grinding:

$$G = G_I + G_S + G_B$$

where G is the total free energy of the powder per unit weight

G_I is the internal free energy

G_S is the surface free energy

G_B is the free energy associated with mosaic boundaries in the powder mass

$$G_I = G_o + D_o$$

Where G_o is the free energy of bulk cobalt (which will differ for cubic and hexagonal cobalt)

D_o is the free energy due to the presence of dislocations in the bulk

$$G_S = G_M + G_{ox}$$

where G_M is the surface free energy of the metal

G_{ox} is the free energy of the oxide

$$G_M = G_{MS} + G_{DS}$$

Where G_{MS} is the surface free energy associated with the specific surface area of the metal

G_{DS} is the surface free energy associated with the dislocations on the metal particle surfaces

$$G_{ox} = G^o_{\text{oxide}} + G_{Do} + G_{oS} + G_{DoS}$$

Where G^o_{oxide} is the free energy of bulk cobalt oxide

G_{Do} is the free energy associated with the presence of dislocations in the oxide film

G_{oS} is the surface free energy of cobalt oxide

G_{DoS} is the surface free energy arising from the presence of dislocations in the surface of the oxide film

Thus the free energy of a powder prior to grinding is given by:

$$G = G_B + G_o + D_o + G_{MS} + G_{DS} + G^o_{\text{oxide}} + G_{Do} + G_{oS} + G_{DoS} \quad (1)$$

This equation shows that the free energy of a powder is greater than that of bulk cobalt. There is thus a driving force for the system to lower its total free energy if this is possible.

Prior to grinding the powders must be assumed to be in an unstable thermodynamic state compared with bulk material due to the excess of surface free energy. Impacting of the powder by the balls during grinding permits some of the excess free energy to be reduced as a result of agglomeration; however at the same time the impacting balls raise the dislocation density of both metal and oxide. The total free energy is thus raised and there is thus a further driving force for the system to reduce its total energy. The free energy may be reduced by any of the following processes:

(1) "Cold welding".

(2) Physical adhesion of metal-metal and metal oxide surfaces.

(3) Adsorption of olefinic compounds.

(4) Formation of an additional amount of h.c.p. cobalt which is slightly more stable than the f.c.c. form[22] by an amount of the free energy change involved in the transformation which is about 100 cals/g atom.[240]

(5) Elimination of vacancies at particle surfaces.

(6) Elimination of the energy associated with pile ups of dislocations at twin sites, stacking faults and particle boundaries.

In order to test this hypothesis it would be necessary to follow the total free energy of a number of powders during the course of grinding by examining individually all the terms in equation (1) on various ground powders. In this way the grinding time necessary to achieve the minimum specific surface area could be predicted.

Physical measurements of all the energy terms would have to be made on a certain number of individual particles, such that the statistically averaged value of each energy term was representative of the entire powder mass. In certain powders accurate measurements of all the terms in equation (1) would be difficult; in particular in certain of the powders the dislocation densities in the oxide films could not be easily measured.

In this argument classical thermodynamics has been used; strictly classical thermodynamics only applies to systems at equilibrium. However the total free energy of a powder should yield some information regarding the grinding behaviour of a powder, although the use of free energy is not correct theoretically as the system is not in equilibrium.

With the present results equation (1) cannot be discussed in a quantitative sense, although some qualitative suggestions regarding the various terms in equation (1) can be made for various cobalt powders with different initial characteristics. The processes (1) to (6) which can lead to a reduction in the total free energy cannot occur to the same extent in all cobalt powders. For example as dictated by the crystal structures of the two allotropes of cobalt, "cold-welding" and physical adhesion cannot occur to the same degree in h.c.p. cobalt as they can in f.c.c. cobalt. Predominantly h.c.p. powders therefore tend to reduce their free energy by agglomeration and limited physical adhesion and "cold welding" and in order to reduce the total free energy further, reduction of energy associated with pile ups of dislocations occurs (resulting in fracture) and at the same time adsorption of olefinic compounds occurs. Thus the specific surface area of the ground material starts to increase after a shorter grinding time than is the case for predominantly cubic cobalt powders. Ultrafine hexagonal cobalt powders represent a special case due to the much finer particle size compared with the commercial cobalt powders, and the much larger amount of oxide present; thus a relatively long grinding period is necessary to reach the state of minimum specific surface area.

Another serious limitation on the testing of equation (1) is the estimation of the free energy change resulting from adsorption. Although it may be possible to measure the heat of adsorption, the entropy change on adsorption cannot be readily calculated and thus the free energy change cannot be evaluated. Furthermore the heat of adsorption will vary with extent of coverage; [217] thus the free energy change due to this process is a constantly varying quantity during the course of grinding. Some evidence of physical adsorption is also expected prior to chemisorption. The Gibbs adsorption isotherm can be used for estimating the free energy change occuring on physical adsorption but Herring [241] has pointed out that the Gibbs adsorption equation is not valid if the state of strain adjoining the surface changes during the adsorption process.

Thus it may be concluded that it may be theoretically possible to assess the grinding behaviour of different cobalt powders in terms of the changes in total free energy that occur; however due to the practical difficulties it is not possible to prepare quantitative energy balances for different powders during the various stages of grinding.

6.3. APPLICATION OF THE THEORY OF DIFFERENT GRINDING BEHAVIOUR TO THE COBALT POWDERS DESCRIBED IN CHAPTER 4 OF VOLUME 1

As noted in the previous section practical measurements of physical properties of the powders do not enable the behaviour of a given cobalt powder on grinding to be explained quantitatively. In addition as was shown in Section 5.5. measurements of the dislocation density cannot be made with great reliability. In general, however, it must be assumed that a greater proportion of h.c.p. cobalt in the powder prior to grinding will lead to an increased rate of comminution during grinding than would be the case for a powder that contained a large proportion of the f.c.c. phase. Furthermore the powders that contain a high proportion of h.c.p. phase initially do tend to have more oxygen than powders that are predominantly cubic in structure. This may be seen by reference to Table 2.1. Thus in cobalt powders of approximately the same particle size there will be a tendency for the predominantly h.c.p. powders to reduce their total free energy by fracture and chemisorption. On the other hand predominantly cubic powders tend to reduce their free energy by "cold-welding" and conversion of the f.c.c. form to the h.d.p. form. Thus the time rate of approach to the state of minimum specific surface area is slower in the case of the predominantly cubic powders than for the predominantly h.c.p. powders.

This confirms the results found experimentally.

The grinding behaviour of the annealed CF-6 and Hoboken cobalt powders are difficult to explain in detail. Annealing was found to increase the proportion of the h.c.p. phase, reduce the oxygen content, and to reduce the specific surface area of the powders. The dislocation density of the h.c.p. phase of the powders was reduced. During grinding no agglomeration of these powders occured. It must be presumed therefore that the free energy reduction due to the dislocations and specific surface area decrease which occured during annealing reduced the total free energy such that no further free energy change on grinding could occur by agglomeration. It is also noteworthy that the annealing increased the number of dislocations in the pile ups in the ground powders. The free energy change occuring during grinding resulted in an increase in specific surface area of the powder. It is difficult to suggest ways in which this free energy reduction occured.

6.4. OTHER FACTORS ASSOCIATED WITH GRINDING OF COBALT POWDERS

In Section 3.4. it was suggested that the Rehbinder effect could not contribute to the fracture of the ductile metals.

The ultimate fracture of the oxide films could have arisen from the Rehbinder effect, but it is suggested that the Rehbinder effect was not very pronounced because acetone is a liquid of low viscosity; the liquid would have been able to penetrate readily any cracks that were present or were formed in the oxide. This fact together with the time for which the oxide films could persist during grinding suggests that the Rehbinder effect contributed little to the fracture of the oxide films.

As the Rehbinder effect is probably not operative with ductile metals, chemisorption of organic compounds produced during grinding probably did not contribute to the comminution of the metals.

Thus during the grinding of cobalt powders in acetone it is suggested that the Rehbinder effect made an insignificant contribution to the comminution process of both the oxide and the metal.

Some suggestions were made earlier that "cold-welding" of metal powder particles could arise from dislocation slip processes, and diffusion probably does not play any role in the agglomeration process. It was suggested that the type of bonding formed during "cold welding" must be the same as is found in a polycrystalline metal with sets of dislocations at the grain boundaries;

during grinding slip processes occur between favourably orientated particle regions to form a metallic bond in which there are no long range stresses.

Twinning probably occurs during grinding of cobalt powders, but the extent of twinning cannot be evaluated. Twinning is expected in both allotropes of cobalt.

6.5. APPLICATION OF FINDINGS TO THE PREPARATION OF HARD METAL POWDER MIXTURES

The work described in Chapter 5 of Volume 1 showed that hexagonal cobalt powders were preferable to cubic powders in hard metal milling in order to achieve satisfactory sintered densities within a minimum grinding time. In Section 4 the probable reasons for the superiority of the hexagonal modification were given. The experimental work described in Section 5.6. tended to confirm the suggestions made in Section 4, namely that impact of the carbide grains against the cobalt agglomerates occured, and the large carbide grains could adhere to the weakly bonded hexagonal cobalt agglomerates; in the case of the predominantly cubic cobalt powder only the fine carbide grains could be embedded in the cobalt agglomerates.

From the experimental work described in 5.4. it is possible to make some suggestions as to the characteristics of the grinding fluid for hard metal milling,-the use of which should lead to satisfactory densification after the shortest possible grinding time.

A major requirement of the grinding fluid is that it should not result in any chemical reaction with the tungsten carbide which will alter substantially the carbon balance of the powder mixture and ultimately cause the appearance of undesirable phases in the sintered hard metal compacts. Because of the nature of the bonding formed in the cobalt agglomerates, hexagonal cobalt would still be preferable to cubic cobalt, but certain fluids could promote adhesion of the hexagonal metal particles. In so far as the cobalt is concerned the milling fluid should show a very small extent of chemical reaction with either cobalt or cobalt oxide during the initial stages of grinding otherwise metal-metal adhesion may be substantially reduced. The property of the fluids which could lead to increased adhesion is the viscosity. Increased agglomeration of cobalt with ethanol compared with acetone was noted in the experimental work.

Ethanol would therefore be expected to be more satisfactory than acetone in hard metal grinding. Thus it is suggested that an ideal liquid for hard metal milling should have a viscosity higher than that of either acetone or ethanol and result in no chemical reaction with either cobalt or tungsten carbide during the initial stages of grinding.

Some time ago, Worn, *(242)* in not well documented evidence stated that an oxidising atmosphere during grinding promoted the agglomeration of iron powders, and suggested that the addition of cobalt oxide might promote dispersion of the cobalt during hard metal milling. No experimental results were given, however. This work has shown that the presence of cobalt oxide in hard metal milling is important in order that the grinding time may be reduced, but the oxygen must not be present in the form of individual particles of cobalt oxide but rather as thin films of metal oxide on the cobalt particles prior to grinding. It was through oxide-oxide bonding, it was suggested, that adhesion of ultrafine hexagonal cobalt powders occured.

7. CONCLUSIONS

The grinding in acetone of cobalt powders with different initial allotropic ratios has been qualitatively described. Suggestions have been made for the mechanisms of the processes which are likely to occur during grinding. Not all the suggestions made could be tested experimentally, principally because the internal structure of the particles could not be examined directly. Thus suggestions regarding the importance of dislocations introduced during grinding could not be experimentally confirmed. Some preliminary experiments suggested that thinning of the powders to electron transparency could alter the character of the powders.

The behaviour during grinding is determined not only by the mechanical properties of the two allotropes of cobalt; interaction effects caused by the milling fluid and the presence of oxide films on the surfaces of the metal powder particles also occur.

Some suggestions for the possible mechanism of the "cold welding" process have been made. This effect is shown to a large extent by cobalt powders which contain a high proportion of the cubic allotrope initially.

Probable reasons for the suitability of predominantly hexagonal cobalt powders in hard metal milling have been suggested. Some properties of an ideal milling fluid for hard metal manufacture have been defined for these alloys where cobalt is used as the auxiliary metal.

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