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APPENDIX 1

SOLUTION FOR THE APPROXIMATE TEMPERATURE DISTRIBUTION WITHIN A MILL DURING GRINDING

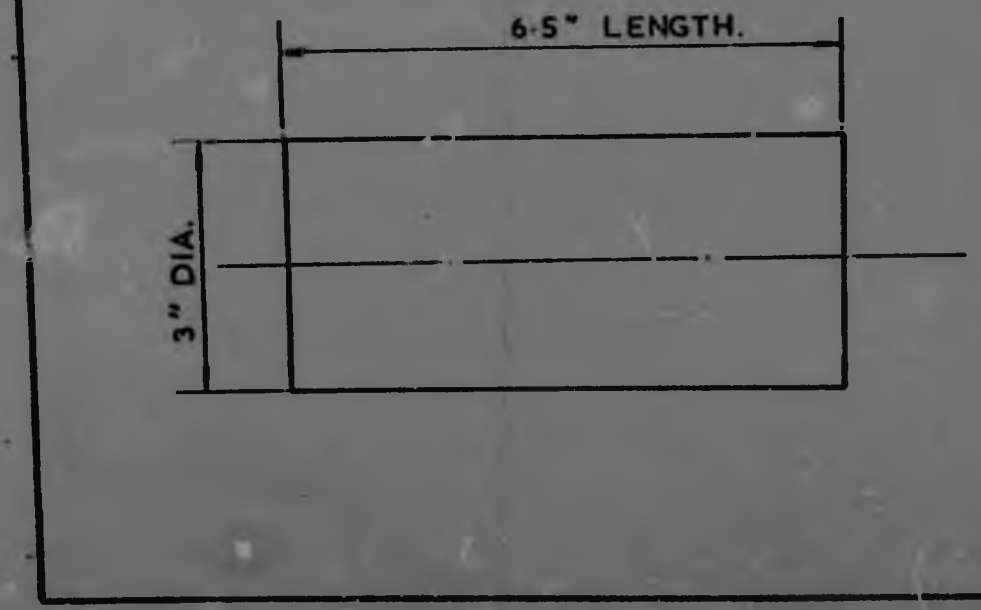
It is possible to estimate the approximate temperature distribution within a vibratory ball mill during grinding using a simple model, and measurement of the outside wall temperature of the mill during grinding. Measurements of the mill wall temperature were made with a Pye thermoprobe after the mill had been in operation for 10 hours. The mean temperature of 10 readings on the wall of the mill with the instrument was 55°C, and the ambient air temperature was 22°C; (several other readings were taken during the course of operation of various mill charges and the mill wall temperatures were in the range 49 - 61°C). It must therefore be assumed that a maximum temperature of about 60°C is achieved on the outside of the mill during grinding. Assume that the average ambient air temperature was 20°C.

Therefore 60°C = 140°F and 20°C = 68°F.

It was assumed that the heat from the surface of the mill was transferred to still ambient air at 20°C. The mill was assumed to be a horizontal cylinder with the dimensions shown in Figure 1.

FIG. NO. I.

DIMENSIONS OF MILL USED FOR VIBRATORY GRINDING.



From the theory of [illegible] convection for vertical plates:[1]

$$Y = CX^m$$

Where Y is the Nusselt number

X is the product of the Grashof and Prandtl numbers

C is a constant

m is a constant which depends on the nature of the fluid flow.

The coefficient of heat transfer by natural convection is given by:

$L = 0.19\ \Delta t^{1/3}$ in the turbulent range

$L = 0.29\ \left\{\frac{(\Delta t)}{(L)}\right\}^{\frac{1}{4}}$ in the laminar range

Where Δt is the temperature difference between the heated surface and still air.

L is the length of the heated surface (in the present example the diameter of the end pieces of the mill)

$$X = \left[\frac{L^3\ \rho^2 \beta g\ .\ t}{\mu^2}\right].\left[\frac{C_p\ \mu}{k}\right] = L^3\ \Delta t\ Z$$

$$\left[\frac{\rho^2\ \beta\ C}{\mu\ k}p\right] = L^3\ \Delta t\ Z$$

by rearrangement(where Z is a dimensionless group)

Where ρ is the density of air

μ is the kinematic viscosity

g is the gravitational constant

β is the reciprocal of the air temperature in degrees absolute

k is the thermal conductivity of air

C_p is the heat capacity of air

Graphs of Z against film temperature (t_f) are available from the literature.[2]

In the present example, if the surfaces of the mill are at 140°F, there must be convective heat transfer to the still air.

(a) Consider the heat transfer from the vertical end pieces $t_f = \frac{140 + 68}{2} = 104 = 564^{\circ}$ absolute

From $t_f = 564^{\circ}$ absolute $Z = 1.4 \times 10^6$ and the height of the plate is 3".

Therefore $X = L^3 \Delta t Z = \left[\frac{3}{12}\right]^3 \times 72 \times 1.4 \times 10^6$

$= 1.58 \times 10^6$

This indicates the laminar range

Therefore $h_c = 0.29 \left[\frac{72 \times 12}{3}\right]^{\frac{1}{4}}$

$= 0.29 \times 4.12$

$= 1.20$ Btu hr^{-1} $ft^{-2}(^{\circ}F)^{-1}$

Therefore heat lost from the end pieces = Q_1

Where $Q_1 = 2 \times 1.20 \times \pi \times (\frac{3}{12})^2 \times \frac{72}{4} = 8.5$ Btu hr^{-1}

$= 2150$ cals/hour

(b) Consider the heat transfer from the horizontal circular section of the mill.

$t_f = 104^{\circ}F$ thus the following data is obtained from standard tables[1]

$\rho_{air} = 0.00219$ slug ft^{-3}

$\mu_{air} = 0.00146$ slug ft^{-3} hr^{-1}

$C_p = 7.8$ Btu $slug^{-1}$ $(^{\circ}F)^{-1}$

$\beta = 1/(460 + 68) = 0.001895$ $(^{\circ}F)^{-1}$

$g = 32.2\ (3600)^2$ ft hr^{-2} which is the gravitational constant

N_{GR} = the Grashof number = $\left[\frac{D^3 \rho^2 \beta g \Delta t}{\mu^2}\right] = 2.11 \times 10^7$

where D is the length of the mill = 0.54 feet

N_{PR} = the Prandtl number = $\left[\frac{\mu C_p}{k}\right] = 0.695$

Therefore $N_{GR} \cdot N_{PR} = 0.695 \times 2.11 \times 10^7 = 1.47 \times 10^7$

Therefore $\log (N_{PR} \cdot N_{GR}) = 7.167$

Thus referring to standard tables $\log N_{Nm} = 1.450$

where N_{Nm} is the Nusselt number

Therefore $N_{Nm} = 28.0$ But $N_{Nm} = \frac{hD}{k}$

Therefore $h = \frac{28.0 \times 0.0157}{0.54}$

Therefore $h = 0.82$ Btu hr^{-1} ft^{-2} $(^{\circ}F)^{-1}$

Thus the heat lost over the circular portion of the mill is:

$$Q_2 = 0.82 \times \pi \times \frac{3}{12} \times 0.54 \times 72 \text{ Btu hr}^{-1}$$

$$= 24.1 \text{ Btu hr}^{-1}$$

Thus the total heat lost from the mill is $Q_1 + Q_2 = Q_3 = 24.1 + 8.5 = 32.6$ Btu hr^{-1} = 8210 calories per hour.

It has thus been established that the total heat flow through the walls of the mill during grinding is 8210 cals hr^{-1}. Thus it should be possible to obtain an approximate temperature distribution inside the mill provided certain simplifying assumptions are made which render the equations soluble. For this purpose consider only a circular section of the mill with a heat generating source representing the balls as a cylinder around the centre of the mill. Assume that the cobalt powder is in the form of an annulus with the acetone liquid occupying the intervening spaces. Assume that heat transfer from the balls to acetone, acetone to the cobalt powder, and acetone to the mill walls occurs only by convection. Thus the physical situation will appear as in Figure 2.

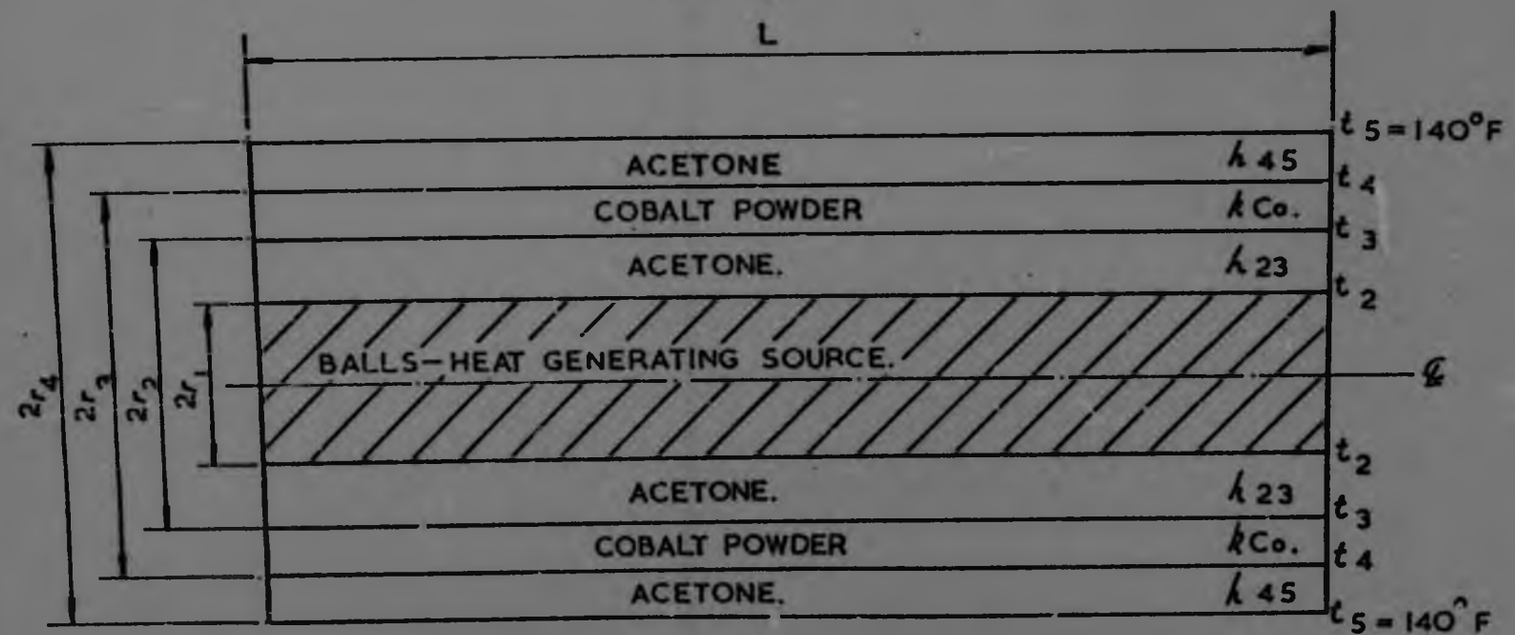
Let the various sections have the dimensions shown in Figure 2, and let the temperatures be as indicated. Assume t_5 (the internal temperature of the mill wall) is the same as that of the outside wall as measured, i.e. $140^{o}F$.

Therefore the flow of heat for the circular section is:[3]

$$Q_2 = 2\pi r_2 h_{23}(t_2 - t_3) L$$
$$= k_{Co} \cdot 2\pi L (t_3 - t_4)/\ln (r_3/r_2)$$
$$= 2 \pi r_4 h_{45} (t_4 - t_5)$$

Where k_{Co} is the thermal conductivity of cobalt.

FIG. NO. 2.



ASSUMED PHYSICAL SITUATION WITHIN VIBRATORY MILL.

The grinding balls would occupy 2000/(14.5 x 0.7) cc = 195 cc, where 2000 g is the weight of the grinding balls

14.5 g/cc is the density of the balls

0.7 is a factor to allow for the total ball volume assuming closest packing of the balls

Thus $195 = \pi r_1^2 h$

$r_1^2 = 3.8 \text{ cm}^2$

Therefore $r_1 = 1.95$ cm = 0.0642 feet

Assume that the cobalt is in the form of an annular cylinder, which is situated such that the centre of either annular region coincides with the mid point between the outside of the balls and the diameter of the mill, i.e. (3.80 - 1.95)/2 cm from either O.D. of the mill or from the outside of the heat generating source.

Assume that the cobalt powder had an effective density of 5 g/cc; therefore 500 g cobalt has a volume of 100 cc.

Assume that the cobalt annulus is 2 δ thick, thus volume of Cobalt } = 100 cc

$$= \pi \times 6.5 \times 2.54 \{(2.87 + \delta)^2 - (2.87 - \delta)^2\}$$

Thus $\delta = 0.175$ cm

Therefore referring to Figure 2

r_1 = 1.95 cm = 0.0642 feet

r_2 = 2.69 cm = 0.0882 feet

r_3 = 3.05 cm = 0.0991 feet

r_4 = 3.80 cm = 0.1240 feet

Therefore in order to evaluate the temperature distribution work from the outside towards the centre.

The convective heat transfer coefficient is approximately given by $h_c = h_{45} = 0.5 \left[\frac{\Delta t_{45}}{OD}\right]^{\frac{1}{4}}$

Where OD is the mill diameter in inches

Therefore $Q_2 = 24.1\ h_c\ A(t_4 - t_5)$

Where A is the surface area of the cylindrical portion of the mill

Therefore $(t_4 - t_5)^{5/4} = 151$

Therefore $t_4 - t_5 = 55^{\circ}F$

Therefore $t_4 = 140 + 55.0 = 195.0^{\circ}F$

$$h_{45} = h_{23} = 0.5 \left[\frac{55}{3}\right]^{\frac{1}{4}}$$

$$= 1.03 \text{ Btu hr}^{-1} \text{ ft}^{-2} (^{\circ}F)^{-1}$$

k_{Co} for cobalt is 41.6 Btu hr^{-1} ft^{-2} $(^{\circ}F)^{-1}$

Therefore $t_3 - t_4 = 0.022$

Therefore $t_3 = 195.022^{\circ}F$

Therefore $t_2 = 272.52\ ^{\circ}F$

Thus 3 temperatures within the mill have been established.

		(F - 32)°	°C
t_2	272.52°F	240.52	134
t_3, t_4	195°F	163.0	91
t_5	140°F	108.0	60

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APPENDIX 2

CALCULATION OF THE KINETIC ENERGY LOSS OF TWO IMPACTING SPHERES (1)

The collision of two non-rotating bodies at a point on the line connecting their centres of gravity is defined as central impact. This process is illustrated by the impingement of two smooth translating spheres as shown in Figure 1. Assume V_n is the common velocity at the end of approach

Therefore by conservation of kinetic energy

$$V_n = (m_1 V_{1xo} + m_2 V_{2xo})/(m_1 + m_2)$$

The normal impulses P_{1n} and P_{2n} for the approach and restitution periods are given by

$$P_{1n} = m_1 (V_{1xo} - V_n) = m_2 (V_n - V_{2xo})$$

$$P_{2n} = m_1 (V_n - V_{1xf}) = m_2 (V_{2xf} - V_n)$$

By definition of the coefficient of restitution (e):

$$e = \frac{P_{2n}}{P_{1n}} = (V_{2xf} - V_{1xf})/(V_{1xo} - V_{2xo})$$

Hence the final velocities may be calculated

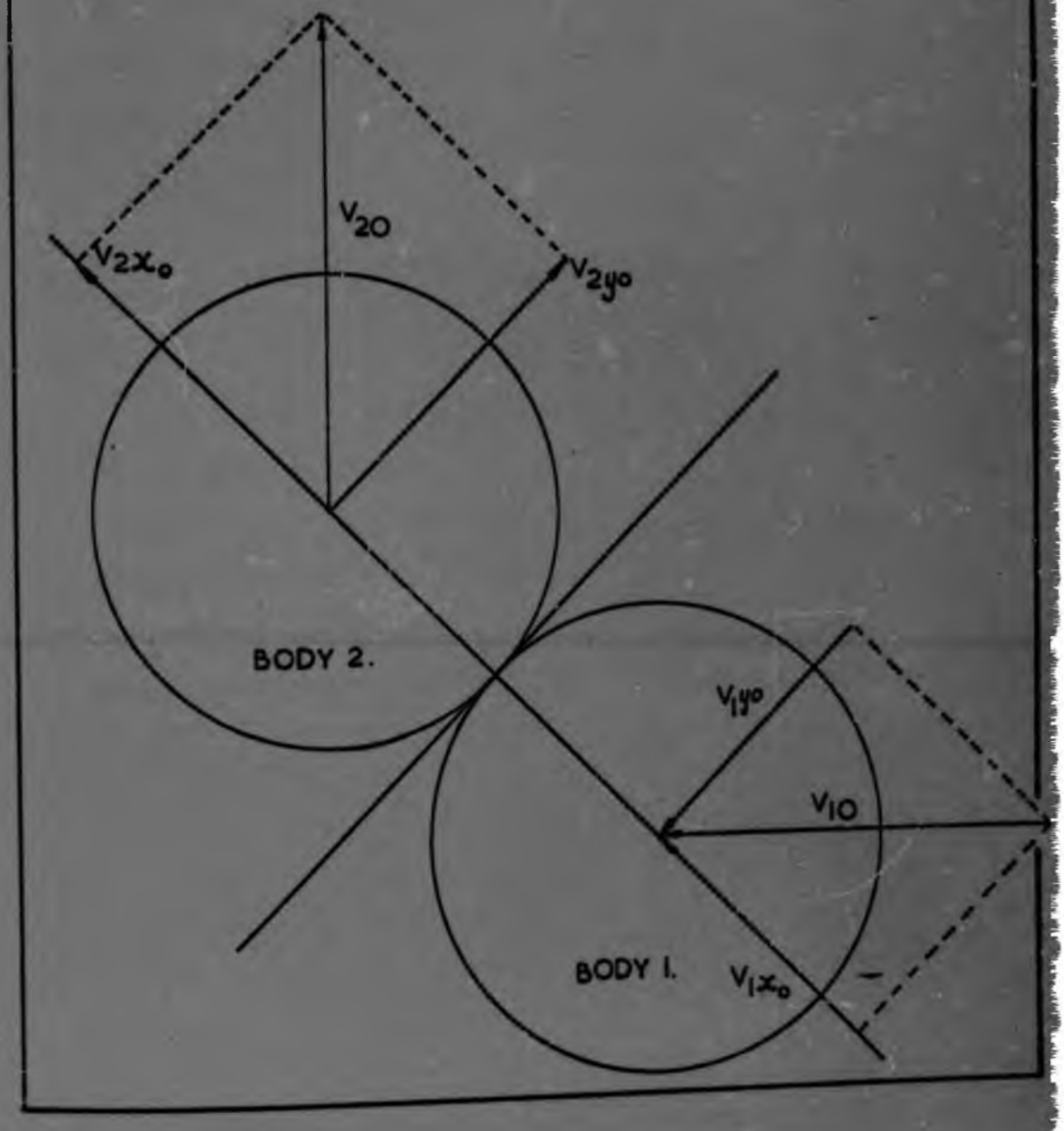
The change in kinetic energy is given by

$$\tfrac{1}{2}\Sigma m_i V_{ixf}^2 - \tfrac{1}{2}\Sigma m_i V_{ixo}^2 = \Delta T$$

$$\text{Therefore } \Delta T = \tfrac{1}{2} \frac{(m_1 . m_2)}{(m_1 + m_2)} (1 - e^2) (V_{1xo} - V_{2xo})^2$$

FIG. NO. 1.

IMPINGEMENT OF TWO TRANSLATING SPHERES.



The coefficient of restitution (e) was determined by dropping a round hard metal grinding ball onto a 10 % cobalt hard metal disc (which was 1 cm thick) from a height of 50 cm . The rebound height h* was measured with a metre rule mounted on a retort stand. The h* values obtained were 31.5, 32.3, 30.8, 32.6, 31.9, 30.7, 31.4, 32.5, 32.5, 32.9, and 32.4 cm yielding an average of 31.91 cm .

$$\text{Therefore } e^2 = \frac{h^*}{h} \text{ where } h = 50 \text{ cms}$$

$$= \frac{31.91}{50}$$

$$= 0.638$$

Assume that during grinding a 6 mm ball travelled up the mill wall such that its final position was 30° clockwise from the starting point[2]; Assume that the ball dropped from this position and collided with a stationary ball at the bottom of the mill. The velocity of impact would be 114.60 cm per sec. The hard metal ball weighed 30 g

Therefore the kinetic energy loss will then be

$$\tfrac{1}{2}\left(\frac{900}{60}\right) (0.362) \times 114.60 \times 981 \text{ cm-dynes (ergs)}$$

$$= 8.12 \times 10^4 \text{ ergs}$$

$$= \underline{8.12 \times 10^{-3} \text{ joules}}$$

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APPENDIX 3

CALCULATION OF THE MAXIMUM PRESSURE BETWEEN TWO IMPACTING HARD METAL GRINDING BALLS

From the Hertz Law of contact and Newton's second law of motion the following expression may be derived [1] for the maximum compressive pressure between two colliding bodies undergoing an elastic collision at the instant of zero relative velocity:

$$P_m = 0.2515\left[\left[\frac{V_o^2}{(\delta_1 + \delta_2)^4}\right]\left[\frac{m_1 \cdot m_2}{m_1 + m_2}\right]\left[\frac{R_1 + R_2}{R_1 R_2}\right]^3\right]^{1/5}$$

Where P_m, is the maximum pressure

V_o is the initial relative velocity

δ_1 is $\frac{1 - \sigma_1^2}{\pi E_1}$ for body 1

σ_1 is Poissons ratio for body 1

E_1 is Young's modulus for body 1

δ_2 is $\frac{1 - \sigma_2^2}{\pi E_2}$ for body 2

m_1 is the mass of body 1

m_2 is the mass of body 2

R_1 is the radius of body 1

R_2 is the radius of body 2

Assume the example in Appendix 2, where a ball falls vertically onto a stationary ball such that its velocity is 114.60 cm/sec immediately before impact;

σ for hard metal may be taken as 0.21 [2]

E for hard metal may be taken as 6.45×10^{12} dynes/cm^2 ($6,45 \times 10^{11}$ N/m^2) [2]

The grinding balls are 6 mm in diameter and weigh 30 g therefore

$$\rho_m = 0.2515 \left[\left[\frac{(114.60)^2}{(0.096)^4 \times 10^{-48}} \right] \left[\frac{30 \times 30}{60} \right] \left[\frac{0.6}{0.09} \right]^3 \right]^{1/5}$$

therefore $\rho_m = 2.305 \times 10^{11}$ dynes/cm^2 ($2,305 \times 10^{10}$ N/m^2)

Using Tabor's theory [3] the maximum compressive stress per unit area on a stationary cobalt particle of radius 1μ produced by an impacting ball is given approximately by

$$P_c = \frac{2\pi \ P_o \ R\alpha}{\pi \ (10^{-4})^2}$$

where P_o is the dynamic flow pressure of cobalt (which is assumed to be constant during the collision)

R is the radius of the hard metal ball

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

where Vo is the relative velocity of the two bodies in collision

m is the mass of impacting grinding ball

If p_o is assumed to be 50000 p.s.i., then substitution shows that P_c is 1.63×10^{15} dynes/cm^2 ($1,63 \times 10^{14}$ N/m^2) compared to a compressive yield strength for cobalt of 2.95×10^9 dynes/cm^2 [4] ($2,95 \times 10^8$ N/m^2). The yield strength is the boundary between the elastic and plastic regions. It must be assumed therefore that cobalt is plastically deformed during grinding.

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APPENDIX 4

DERIVATION OF THE ENERGY OF FORMATION OF A MONO-VACANCY IN COBALT

According to the thermodynamic theory of Mc Lennan[1], the energy required to form a mono-vacancy in a metal is given by:

$$E_{IV}^{f} = 8\pi\mu\, r^{3}\delta \qquad (1)$$

where E_{IV}^{f} is the energy of formation of the mono-vacancy

r is the radius of the spherical cavity to be formed

μ is the shear modulus of the metal

$\delta = U_o/r$

where U_o is the displacement of the radius of the cavity

This equation was derived[1] assuming: the metal is a spherical elastic continuum; a small spherical cavity of volume $V = \frac{4}{3}\pi r^{3}$ is cut from the centre of the metal, removed and redissolved reversibly in the bulk of the metal. An equation of state for the solid is assumed and by application of Maxwell's equations[2] E_{IV}^{f} is derived.

An approximation is made for the displacement U_o again by using the Maxwell equations and the equation of state for the solid.

The equation of state for the solid used is:

$$V = V_o(1 + \psi - \frac{p}{K})$$

where ψ is defined from $\frac{d\psi}{dT} = 3\beta$

where β is the linear thermal expansion coefficient

T is the temperature

This leads to

$$\delta = \frac{3K}{16\pi\mu\sqrt{3}} \Delta V \qquad (2)$$

Where K is the bulk modulus of the metal

ΔV is the dilation of the solid resulting from the displacement.

The formation volume V_{IV}^f of a monovacancy (a fraction f of the volume Ω of the solid per atom) has been measured for a number of metals. f values lying between 0.47 and 0.55 have been found. (For cobalt it has been assumed that f = 0.50, although as is shown later this renders a solution insoluble).

ΔV can be evaluated in the following way: The formation volume V_{IV}^f is the sum of Ω and ΔV rel.

Where ΔV rel. is the negative macroscopically observed relaxation

Therefore $V_{IV}^f = \Omega + \Delta V$ rel

The actual relaxation ΔV of the lattice is the sum of ΔV rel. and the difference between the volumes of the relaxed vacancy V_v and Ω.

Therefore $\Delta V = \Omega - V_v + \Delta V$ rel

$= V_{IV}^{f} - V_v$

Now the arbitrary assumption is made that the volume of an atom is $4\pi r_a^{3}/3$ where r_a is the Goldschmidt radius of the atom. Thus the volume of the relaxed vacancy is

$$4\pi/3(r_a - U_o)^3$$

and $V_v = \frac{4\pi}{3}(r_a^3 - 3r_a^2 U_o + 3r_a U_o^2)$

Experimentally V_{IV}^{f} is the fraction f of the volume per atom; in an f.c.c. lattice the volume per atom is $4\sqrt{2}r_a^3$

Therefore $\Delta V = 4\sqrt{2}\, r_a^3 f - \frac{4\pi}{3}(r_a^3 - 3U_o r_a^2 + 3r_a U_o^2)$

or $\Delta V = 4\pi r_a^3\left[\left(\frac{\sqrt{2}f}{\pi} - \frac{1}{3}\right) + \delta - \delta^2\right]$

Therefore using equation (2)

$$X\delta^2 - (X - 1)\delta + X\left[\frac{\sqrt{2}f}{\pi} - \frac{1}{3}\right] = 0 \qquad (3)$$

Young's modulus is related to the bulk modulus as follows[3]

$$E = 3K(1 - 2\sigma)$$

Where E is Young's modulus equal to 2.10×10^{12} dynes/cm^2 at 298°K for cobalt[4]

K is the bulk modulus

σ is Poisson's ratio which has a value of 0.32 for cobalt according to Koster[5]

Therefore $K = 1.96 \times 10^{12}$ dynes/cm^2

Young's modulus is related to the shear modulus (μ) by the equation[3]

$$E = 2\mu (1 + \sigma)$$

Therefore $\mu = 0.798 \times 10^{12}$ dynes/cm^2

Therefore $X = 1.84$

Assuming $X = 1.84$ and $f = 0.5$ equation 3 becomes

$$1.845\delta^2 - 0.845\delta + 0.198 = 0 \qquad (4)$$

Equation (4) has no solution with f equal to 0.5 f must be ≥ 0.74 in which case $\delta \geq 0.228$. The insolubility of equation (4) must arise from uncertainties due to anisotropy in the values of Young's modulus and Poisson's ratio.

However a value of δ may be derived in another way. From the continuum theory of point defects developed by Eshelby,[5] it can be shown that

$$\delta = \frac{\sqrt{2}(1 - f)}{\frac{3\pi (1 - \sigma)}{(1 + \sigma)}} \qquad (5)$$

Assuming f = 0.5, equation (5) yields a value of $\delta = 0.146$ or 14.6%. The radius of a cobalt atom is 1.157 $^{\circ}$A;[7] in metals there are ions[8] and it is realistic to take $\sqrt{a}$ as the radius of Co^{2+} which is 0.82°A.[9] Therefore substituting in (1) assuming Eshelby's method for δ and $\sqrt{a} = 0.82^{\circ}$A yields:

$$E_{IV}^{f} = \frac{8\pi \times 0.798 \times 10^{12} \times (0.83)^2 \times (10^{-8})^3 \times 0.146 \times 6.02 \times 10^{23}}{4.185 \times 10^7 \times 10^3}$$

= 23.3 k cals/g atom (97,86 k joules/g atom)

REFERENCES

(1) R.B. Mc Lennan - Trans. Met Soc of AIME 245 379 (1969).

(2) See S. Glasstone - Textbook of Physical Chemistry Macmillan London (1960) p 188 - 190.

(3) Cobalt Monograph - C.I.C. Brussels (1960) p 106.

(4) W. Koster - Z. Metallkunde 39 1 (1948).

(5) W. Koster - Applied Sci. Research 4A 329 (1954).

(6) J.D. Eshelby - Solid State Physics 3 79 (1954).

(7) T. Moeller - Inorganic Chemistry Wiley New York (1959) p 134.

(8) S. Glasstone - Reference 2 p 385.

(9) Reference 7 p 140.

APPENDIX 5

CALCULATION OF OXIDE FILM THICKNESSES PRESENT ON THE COBALT METAL POWDER PARTICLES PRIOR TO MILLING

Assume there are η spherical cobalt particles in 1 g.

The measured specific surface area is S_g m^2/g.

The powder contains y % of oxygen which is present as cobaltosic oxide.

r is the radius of the particle including the oxide layer.

γ is the thickness of the oxide layer.

Therefore $\eta\ 4\ \pi r^2 = S_g$ _____ (1)

Weight of oxide layer = $\frac{4}{3}\pi\eta\ \{r^3 - (r-\gamma)^3\} \times 6.07$ g

(where 6.07 g/cc is the density of Co_3O_4).

Therefore $\frac{4}{3}\pi\eta\ \{r^3 - (r-\gamma)^3\} \times 6.07 \times \frac{64}{242} = \frac{y}{100}$ _____ (2)

Therefore $\frac{4}{3}\pi\eta\ (r-\gamma)^3 \times 8.8 + \frac{4}{3}\pi\eta\ \{r^3 - (R-\gamma)^3\} \times 6.07 = 1$ _____ (3)

(Where 8.8 g/cc is the density of metallic cobalt).

By substitution of (2) in (3) $(r-\gamma)^3$ may be obtained as a function of η. The value of r in terms of η may be substituted in equation 1. Thus knowing S_g and y, values of η, r, and γ may be obtained.

Using the equations in Appendix 5 the following oxide layer thicknesses on each spherical particle were calculated to be present from the measured oxygen contents:

POWDER	THICKNESS (^{o}A)
Hoboken powder	84
Hoboken preannealed powder	43
CF - 6	37
CF - 6 preannealed powder	32
CF - 10	54
Pure hexagonal cobalt powder	39

Assuming that all the oxygen was associated with the hexagonal fraction the oxide thicknesses on each spherical hexagonal particle would be as follows:

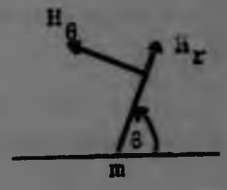
POWDER	THICKNESS (^{o}A)
Hoboken powder	141
Hoboken preannealed powder	51
CF - 6	140
CF - 6 preannealed powder	70
CF - 10	150

APPENDIX 6

CALCULATION OF THE MAGNETOSTATIC ENERGY OF AN ASSEMBLY OF PARTICLES

Consider an agglomerate formed of cobalt metal particles of radius a and magnetisation M packed in a agglomerate with face centred cubic packing as shown in Figure 1 with the directions of the magnetic moments as shown.

The field due to a dipole of moment m is given in terms of its radial and tangential components by:



$$H_r = \frac{\mu_0}{4\pi} \cdot \frac{2m \cos\theta}{r^3} \qquad H_\theta = \frac{\mu_0}{4\pi} \cdot \frac{m \sin\theta}{r^3}$$

We can resolve these into a parallel direction so that

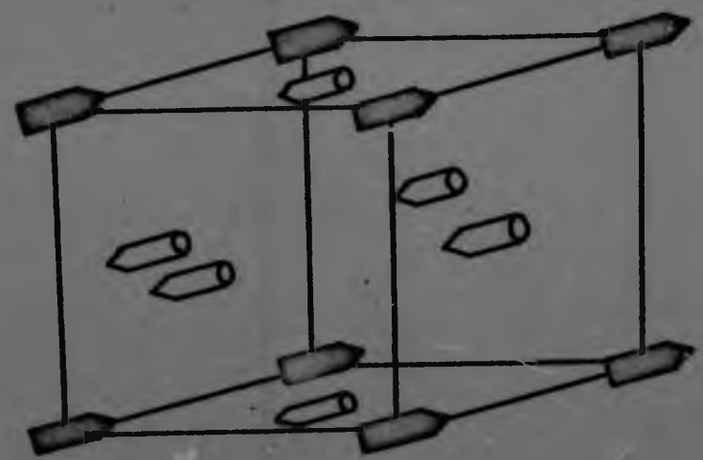
$$H_p = \frac{m}{4\pi r^3} (2\cos^2\theta - \sin^2\theta)$$

NEAREST NEIGHBOUR INTERACTIONS

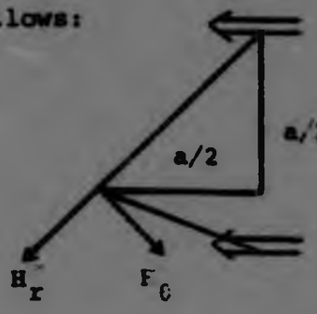
4 sites at $\theta = 90^\circ$ $r = \frac{a}{\sqrt{2}}$ These are points at the cube corners. Therefore $H_1 = \left[\frac{4m}{4\pi A^3} \; 2.\sqrt{2}\right]$.

FIG. NO. 1.

ASSUMED MODEL OF COBALT PARTICLES ARRANGED IN A FACE CENTRED CUBIC ARRAY WITH MAGNETIC MOMENTS AS SHOWN.



For points at the face centre position pair off as follows:



(Symmetry dictates that only axial component is non zero)

For one dipole $H_r = \frac{2m}{4\pi} \frac{a/2}{a/\sqrt{2}} \cdot \frac{2\sqrt{2}}{a^3}$

This resolved along axis is $H_r' = \frac{2m}{4\pi} \frac{2}{a^3} \cdot \frac{1}{\sqrt{2}} = \frac{m}{4\pi} \cdot \frac{2\sqrt{2}}{a^3}$

$$H_\theta' = \frac{-m\ 2\sqrt{2}}{4\pi\sqrt{2}\ a^3\ \sqrt{2}} = -\frac{\sqrt{2}m}{4\pi a^3}$$

There are 4 such units yielding a field along the axis of $H_2 = 4\ (H_r' + H_\theta') = \frac{4m}{4\pi a^3}\ (2\sqrt{2} - \sqrt{2}) = \frac{4\sqrt{2}}{a^3} \cdot \frac{m}{4\pi}$

There is an additional interaction such as:

$\theta = 135^\circ$

$H_r' = \frac{2m}{4\pi} \cdot \frac{2\sqrt{2}}{a^3} \cdot \frac{1}{2}$

$H_\theta' = \frac{2m}{4\pi} \cdot \frac{2\sqrt{2}}{a^3} \cdot \frac{1}{2}$

Therefore $H' = \frac{\sqrt{2}m}{\sqrt{2}a^3}$

Therefore $H_3 = H'$

Therefore for the first set of nearest neighbours field is axial and of magnitude $H_1 = H_1 + H_2 + H_3 =$

$$\frac{m}{4\pi} \cdot \frac{16\sqrt{2}}{a^3}$$

SECOND NEAREST NEIGHBOURS

There are 4 yielding $H_1 = \frac{-4m}{4\pi a^3}$

1 at $\theta = 0$ Therefore $H_2 = \frac{2m}{4\pi a^3}$

1 at $\theta = 90^\circ$ Therefore $H_3 = \frac{2m}{4\pi a^3}$

Thus due to second nearest neighbours

$H_2 = H_1 + H_2 + H_3 = 0$

THIRD NEAREST NEIGHBOURS

There are 24. $|\cos\theta| = \frac{1}{2}/\sqrt{3/2} = \frac{1}{\sqrt{6}}$ and $r = \sqrt{3/2}\,a$

There will be 16 contributions of the type

$\frac{m}{4\pi r^3}\cdot(3\cos^2\theta - 1)$

Therefore $H_1' = -\frac{16\sqrt{2}}{3\sqrt{3}a^3}\cdot\frac{m}{4\pi}$

There will also be 8 with $\cos\theta = \frac{1}{\sqrt{3/2}} = \sqrt{2/3}$

Therefore $H_2' = \frac{16\sqrt{2}}{3\sqrt{3}a^3}\cdot\frac{m}{4\pi}$

Therefore $H_3 = H_1 + H_2 = 0$

FOURTH NEAREST NEIGHBOURS

There are 12

$r = \sqrt{2}\,a$

4 with $\theta = 90^\circ$

Therefore $H_1 = \frac{-\sqrt{2}}{a^3}\cdot\frac{m}{4\pi}$

8 with $\theta = 45^\circ$

Therefore $H_2 = \frac{\sqrt{2}m}{a^3 4\pi}$

Therefore $H_4 = 0$

FIFTH NEAREST NEIGHBOURS

There are 24 with $r = \frac{\sqrt{10}}{2} a$

8 with $\theta = 90^o$

Therefore $H_1 = \frac{-64}{\sqrt{10}.100a^3} \cdot \frac{(m)}{(4\pi)}$

16 with $\cos \theta = \frac{1}{\sqrt{10}}$

Therefore $H_2 = - \frac{89.6}{\sqrt{10}.100a^3} \frac{(m)}{(4\pi)}$

Therefore $H_5 = - \frac{153.6}{100\sqrt{10}\ a^3} \frac{m}{4\pi}$

SIXTH NEAREST NEIGHBOURS

$r = \sqrt{3}\ a \qquad \cos \theta = \frac{1}{\sqrt{3}}$

There are 8

Therefore $H = \frac{8m}{4\pi a^3} (3 \cos^2 \theta - 1) = 0$

Therefore $H_6 = 0$

Thus up to including the 6th nearest neighbour interactions, the internal field will be

$$H_{(6)} = \sum_1^6 H_1 = \frac{17.75m}{4\pi a^3}$$

Thus if particles of radius a (metres) and magnetisation M (ampere turns per metre) are considered the binding energy will be

$$U = \frac{-17.75}{a^3} \cdot \mu_o \frac{M^2 v^2}{4\pi} \text{ joules}$$

since $m = Mv$ (v = volume)

$U = -mB$

$B = \mu_o (H + M)$

Therefore $U = -31.6.10^{-7}\ a^3\ M^2$ joules

SPECIMEN CALCULATION

Consider a particle with 2μ diameter

Volume of particle = $\frac{4\pi}{3}.(1 \times 10^{-4})^3$ cc

Mass of particle = $\frac{4\pi}{3}(1 \times 10^{-4})^3 \times 8.8$ g

At 20°C pure cobalt has a magnetisation of 161 gauss/g or 161 oersted/g [1]

Therefore Magnetisation = $\frac{4\pi}{3}(1 \times 10^{-4})^3 \times 8.8 \times 161$ oersted

$= \frac{4\pi}{3}(1 \times 10^{-4})^3 \times 8.8 \times 161 \times 79.58$ [2] $\frac{\text{amp-turns}}{\text{metre}}$

Therefore U = -31.6×10^{-7} $(4 \times 10^{-6})^3 \times$

$\{\frac{4\pi}{3}(1 \times 10^{-4})^3 \times 8.8 \times 161 \times 79.58\}^2$

$= \underline{6.5 \times 10^{-36} \text{ joules}}$

REFERENCES

(1) Cobalt Monograph Centre du Information du Cobalt Brussels 1960, p 95.

(2) 1 Oersted ≡ 79.58 amp turns per metre.

APPENDIX 7

THE MAGNETIC BINDING ENERGY OF A COBALTOSIC OXIDE AGGLOMERATE

Although Co_3O_4 has no permanent moment it has been estimated that the induced magnetic moment is about $3\mu_B$ per molecule,[1] which corresponds to a magnetisation of about 0.06 e.m.u. per g.[1]

Assuming a model similar to that for cobalt, but composed of Co_3O_4 the binding energy may be calculated for a particle of 2μ diameter.

Volume of particle $= \frac{4\pi}{3} (1 \times 10^{-4})^3$ c.c.

Weight of particle $= \frac{4\pi}{3} (1 \times 10^{-4})^3 \times 6.07$ g

Magnetisation $= \frac{4\pi}{3} (1 \times 10^{-4})^3 \times 6.07 \times 0.06$

$= \frac{4\pi}{3} (1 \times 10^{-4})^3 \times 6.07 \times \frac{0.06}{10^{-3}}$

Amp turns per metre

Binding energy $= -31.6 \times 10^{-7} (1 \times 10^{-6})^3 \left[\frac{4\pi}{3} (1 \times 10^{-4})^3 \times 6.07 \times \frac{0.06}{10^{-3}} \right]^2$

$= \underline{7.28 \times 10^{-54} \text{ joules}}$

(1) W.L. Roth J. Physics Chem. Solids 25 1 (1964).

APPENDIX 8

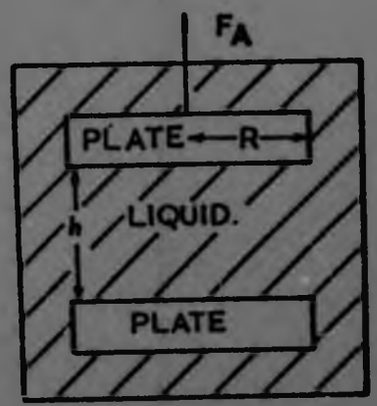
STEFAN'S FORMULA

If two surfaces are imme sed in a fluid appreciable viscou: forces may be involved in pulling the surfaces a:art. As the surfaces are separated the liquid must flow in to the space between them, and a large force may be required to separate the two surfaces in a short time.

Very large forces will be required to separate parallel surfaces which are close together. Consider two flat circular discs completely immersed in a Newtonian fluid of viscosity η, as shown in Figure 1. Stefan showed that the force F_A required to pull the surfaces apart from an initial separation h_1 to a final separation h_2, in a time t is given by:

$$F_A = \frac{3\pi\eta R^4}{4t} \cdot \left[\frac{1}{h_1^2} - \frac{1}{h_2^2}\right]$$

FIG. NO. 1.



TWO PLATES IMMERSED IN A FLUID OF VISCOSITY η

APPENDIX 9

METHOD USED FOR THE DETERMINATION OF THE COBALT CONTENT OF ACETONE USED AS GRINDING FLUID

25 ml aliquots of the samples were evaporated to dryness: 3 ml 50 % H_2SO_4 and 1 ml concentrated HNO_3 were added and heating continued until fuming. The contents of the beaker were transferred to a 100 ml Volumetric flask and made up to the required volume with distilled water. An aliquot was taken and neutralised to phenol phthalein with 25 % NaOH. 2 ml Spekker acid, 10 ml nitroso R salt solution and 10 ml sodium acetate solution were added to the solution. The contents of the beaker were boiled vigorously for 1½ minutes, and diluted to 100 ml. The cobalt was measured spectrophotometrically at 520 mμ using a standardised cobalt sulphate solution for calibration.

TABLE X : TABLE OF t VALUES FOUND AND THE LEVEL OF THEIR SIGNIFICANCE

	MT	S_s (2)	$(Hc)_1$	TC	O_2	FC	Co
MT		18.2 HS 18.2 HS 17.4 HS	7.81 HS 8.60 HS 8.71 HS	0.29 NS 0.59 NS	5.61 HS 6.25 HS	2.07 PS	0.89 NS
S_s			8.24 HS 8.70 HS 8.10 HS	1.10 NS 0.45 NS	6.45 HS 7.80 HS	2.50 PS	1.67 NS
$(Hc)_1$				0.89 NS 2.32 S	3.59 S 3.79 PS	2.24 PS	0.15 NS
TC					1.12 NS 1.50 NS	0.22 NS	7.80 HS
O_2						1.54 NS	0.96 NS
FC							0.50 NS
Co							

	θ	4πσ	$(Hc)_2$	VPN	Σθ	S_{swc}	$d_{wc}λ$	S_sCo	MT	S_s	$(Hc)_1$	TC	O_2	FC	Co	C
θ		0.08 NS 0.22 NS 1.74 NS	2.75 S 0.00 NS 2.32 PS	19.8 HS 1.04 NS 14.2 HS	4.21 HS 0.29 NS 4.45 HS	3.11 S 0.22 NS 3.00 S	4.95 HS 0.30 NS 5.70 HS	0.83 NS 0.29 NS 0.60 NS	2.42 PS 0.89 NS 2.75 S	2.86 S 1.26 NS 3.30 S	5.25 HS 0.15 NS 7.35 HS	2.00 NS 1.98 NS	1.88 NS 0.83 NS	0.00 NS	0.83 NS	0 1 2
4πσ			1.67 NS 0.29 NS 5.29 HS	0.73 NS 0.44 NS 2.91 S	2.00 NS 1.68 NS 2.91 S	1.40 NS 2.66 S 5.39 HS	1.60 NS 3.20 S 4.90 HS	0.21 NS 0.84 NS 4.28 HS	2.00 NS 2.72 S 8.81 HS	2.59 PS 3.00 S 8.10 HS	2.14 PS 1.54 NS 5.75 HS	4.59 HS 0.61 NS	1.19 NS 2.42 PS	1.19 NS	8.40 HS	0 1 2
$(Hc)_2$				4.81 HS 1.75 NS 4.70 HS	9.20 HS 2.20 PS 7.21 HS	9.20 HS 0.61 NS 8.85 HS	9.82 HS 0.89 NS 9.80 HS	6.25 HS 5.12 HS 5.25 HS	18.50 HS 0.30 NS 9.30 HS	22.4 HS 0.50 NS 13.1 HS	8.60 HS 1.99 NS 4.36 HS	0.70 NS 1.34 NS	6.65 HS 0.40 NS	2.24 PS	0.83 NS	0 1 2
VPN					5.90 HS 3.20 S 5.95 HS	4.50 HS 3.01 S 4.70 HS	6.64 HS 3.89 S 8.90 HS	0.40 NS 2.72 S 4.70 HS	4.15 HS 2.55 S 4.59 HS	4.95 HS 3.11 S 5.40 HS	6.40 HS 5.95 HS 8.20 HS	1.19 NS 1.59 NS	3.20 S 2.00 NS	0.90 NS	0.15 NS	0 1 2
Σθ						9.50 HS 8.10 HS 6.25 HS	13.10 HS 9.80 HS 8.90 HS	3.49 S 4.24 HS 4.59 HS	8.90 HS 2.92 S 8.60 HS	8.70 HS 3.31 S 7.68 HS	9.24 HS 4.35 S 6.28 HS	0.21 NS 0.44 NS	3.80 S 1.50 NS	2.07 PS	0.00 NS	0 1 2
S_{swc}							15.1 HS 14.6 HS 11.4 HS	5.45 HS 3.21 S 7.35 HS	13.4 HS 3.88 S 6.65 HS	9.50 HS 4.99 HS 8.10 HS	7.89 HS 4.70 HS 5.11 HS	1.19 NS 0.66 NS	4.70 HS 2.65 S	2.42 PS	0.15 NS	0 1 2
$d_{wc}λ$								3.88 S 3.69 S 6.65 HS	10.40 HS 4.15 HS 8.62 HS	9.80 HS 4.72 HS 9.80 HS	10.90 HS 4.45 HS 7.35 HS	1.20 NS 0.22 NS	4.49 HS 2.96 S	2.55 PS	0.15 NS	0 1 2
S_sCo									7.10 HS 2.58 PS 7.05 HS	5.70 HS 3.05 S 7.20 HS	2.74 PS 4.80 HS 2.84 S	0.45 NS 0.84 NS	2.84 PS 0.84 NS	2.00 NS	0.15 NS	0 1 2

NOTES:

(1) THE SYMBOLS AND CODING ARE USED AS IN TABLE IX

(2) UNDER EACH PROPERTY THE LEFT HAND VALUE INDICATES THE MAGNITUDE OF t, THE RIGHT HAND THE SIGNIFICANCE.

(3) THE CODING OF SIGNIFICANCE IS AS FOLLOWS:
NS = NOT SIGNIFICANT
PS = POSSIBLY SIGNIFICANT
S = SIGNIFICANT
HS = HIGHLY SIGNIFICANT

— THE LEVELS ARE DISCUSSED IN THE TEXT.

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

A thesis presented to the Faculty of Engineering,
University of the Witwatersrand,
in fulfilment of the requirements for the degree of
Doctor of Philosophy
by
G.J. Rees B.Sc. (Hons.) (Rand).

TABLE 2.1

SUMMARY OF INITIAL COBALT POWDER PROPERTIES AND AT STATES OF MINIMUM SPECIFIC SURFACE AREA.

COBALT POWDER NUMBER	INITIAL PROPERTIES.				AGGLOMERATED POWDER PROPERTIES.				GRINDING TIME TO REACH MINIMUM S_S (HRS.)
	(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) ALLOTROPIC RATIO.	OBSERVATION ON SCANNING ELECTRON MICROSCOPE.	
CF—6 POWDER.	1·25	0·35	0·74	POWDER PARTICLES HAD RELATIVELY SMOOTH SURFACES & WERE GENERALLY ROUNDED IN SHAPE LITTLE EVIDENCE OF SURFACE ROUGHNESS A FEW AGGLOMERATES PRESENT.	150	0·90	2·60	EVIDENCE OF COLD WELDING, SOME EVIDENCE OF FINE PARTICLES EMBEDDED IN THE AGGLOMERATES.	20
HOBOKEN COBALT POWDER (GRINDING OF THIS POWDER 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)	2·10 (2·05)	THE TYPE OF AGGLOMERATES FORMED WAS NOT EXAMINED.	10 (10)
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 1 μ IN SIZE PARTICLES GENERALLY ROUNDED DISPERSION DIFFICULT BECAUSE OF FINE PARTICLE SIZE.	261	0·97	NO CUBIC COBALT OR COBALT OXIDE DETECTED.	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 ESPECIALLY AFTER 20 HRS. GRINDING	90
ANNEALED HOBOKEN COBALT POWDER.	1·07	0·77	0·62	POWDER WAS MORE AGGREGATED THAN THE UNANNEALED MATERIAL FILAMENTARY NATURE OF ELEMENTARY PARTICLES CLEARLY VISIBLE.	NO EVIDENCE OF ANY AGGLOMERATION DURING 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 AGGLOMERATION DURING GRINDING				—
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	3·90	AFTER 50HRS. GRINDING PARTICLES HAD SMOOTH SURFACES FINE PARTICLES WERE EVIDENT AFTER 70 HRS. OF GRINDING	30

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.

2

THE « γ ε 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)