

powder Metallurgy

(B) Metal powder production by electrolytic Method:

— Electrolytic process is aqueous process and is based on the movement of anions and cations and consequently dissolving at anode and depositing at Cathode, respectively.

The mechanism of transport / movement of these ions is as:

- (I) Diffusion (depends on the size of ions and temp of the electrolyte)
- (II) Convection (depends on the temp and stirring of electrolyte)
- (III) Migration (depends on the current density)

In another words we can say that in aqueous electrolytic process, there is movement or transport of ions by diffusion or convection and deposition of ions (by bath temp & stirring) and deposition of ions due to current density / Cathodic current density

~~principle of aqueous electrolysis for~~ (p-2)

~~Thermodynamics of aqueous electrolysis~~

Introduction of Aqueous Electrolysis process:

The common metals ^{powders} such as Cu, Fe, Ni & Cobalt etc are produced by aqueous electrolysis process. Mostly Cu is produced by electrolysis process because for many applications a very pure copper is required. As we know electrolysis process is quite expensive because of costly unit charge of electricity for commercial purpose. In spite of that, we prefer production of Cu, Fe, Ni & Co ~~for~~ by these process, since demand of high grade powder is needed and electrolysis process can only give such high grade pure metal powders.

No Need to

Advantages of this process

(P-3)

- High purity powders can be obtained (99.95%)
- The metal powders have excellent pressing and sintering properties
- Cheap raw materials can be used i.e. acid pickling bath, leaching solution etc.

Disadvantages :-

- There is high consumption of electricity in this process. Unit charge of electricity, for commercial purpose, is too high.
- The low production rate gives rise to high production cost.
- Dendritic shaped (tree like shape) powder is obtained, which has a large surface area making the powder very surface-active. So, after electrodeposition intensive washing of the powder and thorough drying are needed. etc.

there will be too much oxidation and corrosion in the product. (p-4)

The powders needed to be packed well and sealed in air tight for transportation in order to avoid much surface oxidation.

principle of aqueous electrolysis process :-

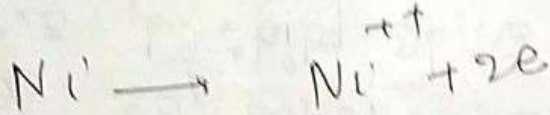
Thermodynamics of aqueous electrolysis

Elements	Zn ⁺⁺	Fe ⁺⁺	Ni ⁺⁺	Su ⁺⁺	Pb ⁺⁺	H ⁺	Sb ⁺⁺	Cu ⁺⁺	Hg ⁺⁺
Electrode Potential (Volt) (E°)	-0.76	-0.44	-0.26	-0.14	-0.126	0	+0.11	+0.34	+0.79

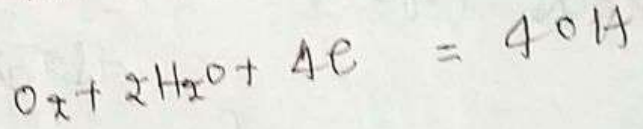
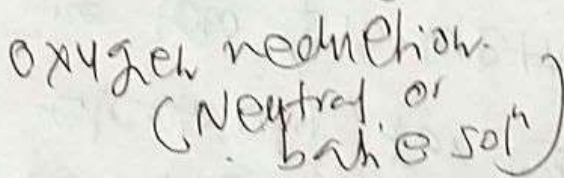
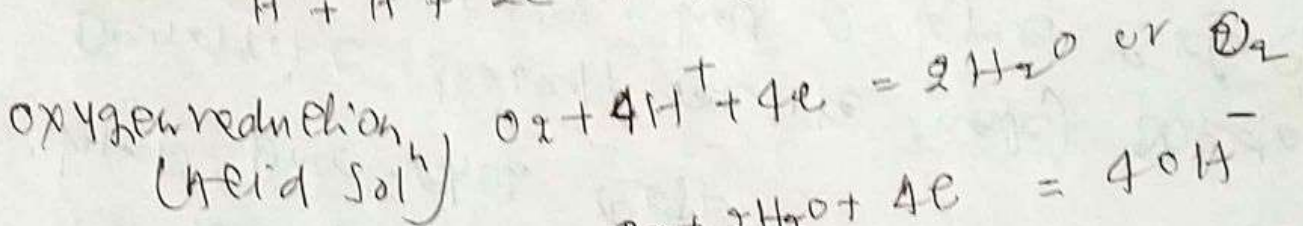
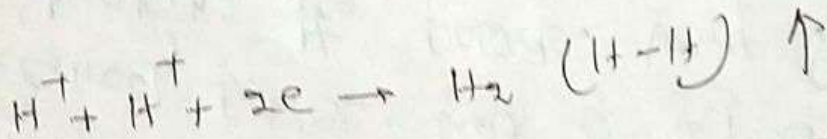
- All elements on the positive side of hydrogen are easy to deposit on the cathode.
- The deposition of metals on the negative side of hydrogen in the electrochemical series may be performed by decreasing H⁺ concentration i.e. increasing pH of the bath or increasing metal ion concentration.

Mechanism / Reaction of Ni-plating

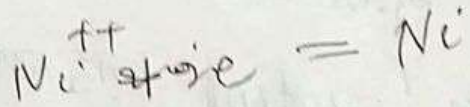
At anode:



Cathode:



Metal ion reduction



- In electroplating, our aim is adhering, dense, hard and coherent deposit.

→ But for obtaining powdery loose deposit or a spongy deposit on cathode, there must be hydrogen evolution in high amount at cathode, at the same time of deposition of metal powders. This hydrogen evolution will not allow to powder particles to bind together & it remains as loose. Over to

this reason total energy is not used for powder deposition. Some amount is spent in hydrogen evolution at cathode. Thus it lowers the cathodic current efficiency.

The following are factors affecting the characteristics of electrodeposition: →

(I) Current Density (CD): Here Current Density refers to the cathode, which is of interest to the electrodeposition of metals.

Coarser and denser deposit
at Cathode.

(P-7)

- For all practical purposes to get a dense deposit an empirical formula may be used :-

$$I = 0.2 k c \rightarrow \text{for dense deposit}$$

Where $I =$ Cathodic current density
 $k =$ is a constant depending on the electrolyte & varies b/w = 0.5 to 0.9
 $c =$ Concentration of bath i.e. metal ions
Concentration.

$$I = k c \rightarrow \text{for fine structure \& loose deposit}$$

Thus fine & very loose deposit $I > 0.2 k c$
Coarse and dense deposit $I < 0.2 k c$

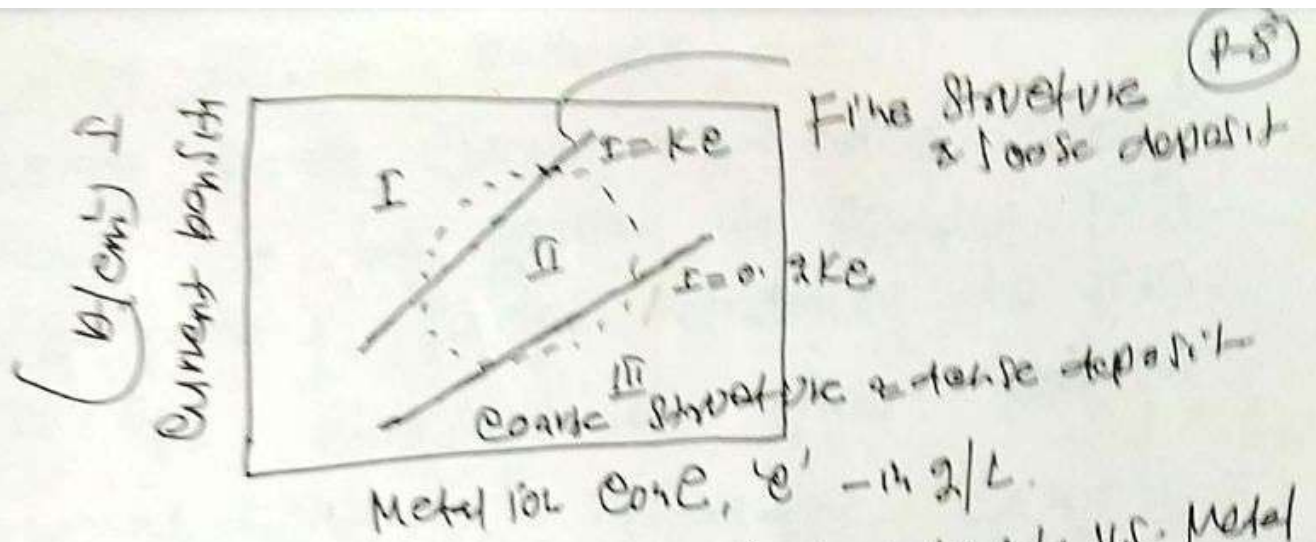


Fig (A) Plot of Cathodic current density vs. Metal ion concentration (c).

- The intermediate zone as shown in Fig (A) by dotted circle is suitable for powder production at any combination of current density & concentration within the circle.
- Working in intermediate region, we get a cathodic deposit which does not spall off easily from cathode.
- At zone I a fine structure and very loose deposit is obtained which get detached from the cathode quite often, thus deposits get into solution again and decrease the current efficiency.

- At Zone -II: → Cathodic deposit becomes dense, coarse and hard which needs to be ground to powder thus incorporating work hardening to the particles making the poor powder compressibility. Therefore, Zone -II is preferred i.e. within the dotted circle. (p-9)

(III) Bath temperature: → It increases the mobility of ion by diffusion and convection, thus more ions will migrate/move towards the cathode, thus making the condition equivalent to increasing metal ion concentration at cathode, thus giving the dense deposit.

(IV) Hydrogen ion concentration: → At the cathode, there is evolution of hydrogen gas at the same time, there is deposition of metal powder. Due to evolution of hydrogen gas is bubbling of hydrogen,

WJ Dikshu = 20-03-21
NDT



it does not allow the bonding
together of the metal particles. Thus
loose powderly with coherent & dense
deposit is obtained. According to the
~~the~~ deposit of metal on the positive
side of H^+ in the electrochemical series,
the H^+ ion concentration in the electrolyte
should be sufficient high for powderly
deposit. On the other hand, for the
metal on the negative side of H^+ in
the electrochemical series, the H^+ ion
concentration should be low i.e. increasing
pH of the bath, in order to avoid much
lowering of current efficiency due to
much hydrogen evolution and get
sufficient high powderly deposit in case of
-ve side of H^+ in electrochemical series.

(v) Different additives to the electrolyte :-

- Inorganic additive such as H_2O_2 , nitrate oxidizing etc are used to cause slight surface oxidation on particles which retards the growth rate and we obtain ~~the~~ finer deposit.
- Organic additive such as colloidal agent i.e starch, gum, gelatine, soap etc, get absorbed on particle surface, which retards the growth. we get finer & brittle deposit.

① Commercial process for the Electrodeposition of Copper:

(4-12)

pure Copper powders are mostly used for electrical and electronic applications.

Anode plates are cast from commercial grade copper containing negligible amount of arsenic and antimony.

Sulphate bath is used. The copper powder obtained is dendrite shape. These powder has good compactionability (due to good interlocking of particles) and compressibility (due to high purity of the powder which gives high plasticity to the particles).

Table: Condition for electrodeposition of Copper in aqueous bath

Condition	Dense deposit	Powdery deposit
CuSO ₄ in electrolyte	40 to 60 g/L	25 to 60 g/L
H ₂ SO ₄ in electrolyte	120 to 130 g/L	100 to 200 g/L
CD (Cathodic)	120 to 200 A/m ²	1000 to 2000 A/m ²
Bath temp	45 to 60 °C	45 to 60 °C

(P-13)
- During electrolysis after each 15 to 20 minutes electrolysis is stopped and the cathodes are taken out and stripped off. The powdery deposit that is obtained is washed thoroughly so that no trace of electrolyte is left on the deposit. After filtration in a rotating ~~type~~ drum type filter under vacuum the cake of powder is scraped off from the filter. After that it is dried in oven and packed and properly sealed in polythene bags.

problem arises during continuous electrolysis process.

- At the anode copper is getting dissolved but the same amount of copper is not depositing at the cathode, which means the lowering of cathode current efficiency because some amount of energy is lost for the cathodic evolution of hydrogen gas. So there is progressive building up of copper ion concentration in the bath, especially near the anodes. So, there is increase in metal ions concentration in the bath (ie it deposit will try to become coarse & dense).



Therefore, some corrective measures (P-14) are taken to maintain the metal ion concentration of the bath.

- (a) Periodically we can do take out some part of electrolyte from the bath and replenishing it with distilled water or a fresh amount of electrolyte having low concentration of metal ion, so that the overall concentration is maintained.



② Commercial process for the electrodeposition of Iron (p-15)

- Since Iron (Fe^{++}) is more electronegative than hydrogen in the electrochemical series, therefore, there is continuous ~~and~~ hydrogen evolution at cathode in an acidic sulphate bath.
- In order to ~~obtain~~ facilitate the loose powdery iron deposit, high current density and low metal ion concentration can not be used.
- If we use high current density at cathode and low metal ion concentration, there will be only hydrogen gas evolution at cathode, without any deposition of metal.
- Therefore, low current density and high metal ion concentration are used, in order to obtain dense deposit.

(3) Dilution = 30-35%
NDT

Table: Conditions for electrodepositon of Iron (0-16)
in aqueous bath

Conditions	Spongy Coherent deposit
FeSO ₄ in electrolyte	120 to 140 g/L
NaCl in electrolyte	40 to 50 g/L
H ₂ SO ₄ in electrolyte	0.2 to 0.28 g/L
Bath temp	45 to 50° C.
Cathodic current density	400 to 500 A/m ²

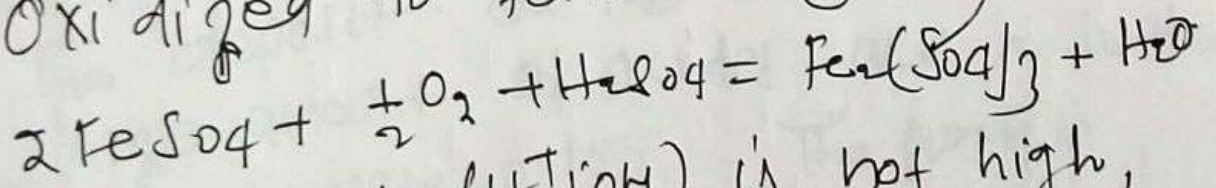
- Here NaCl is added in order to keep the electrical conductivity of the bath
- Here H⁺ ion concentration is less, thus less amount of hydrogen gas evolution at cathode, which results into dense deposit. Moreover, the dense deposit is made brittle to facilitate mild grinding for making powder. This is done by stopping the electrolysis at certain time intervals to allow formation of thin oxide layer on the surface of the deposit and again the electrolysis is resumed.

(3) Efficiency = 30-35%

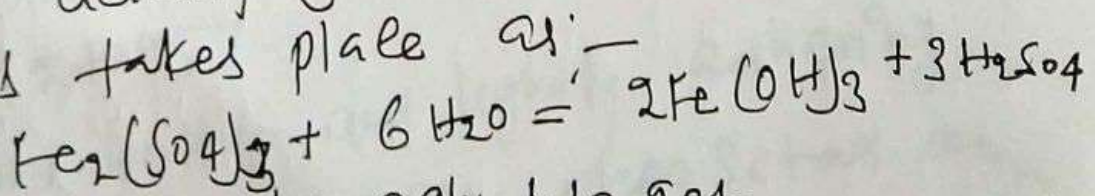
- This is repeated several times P-17
 so that we get a layered structure
 which is very brittle to grind into
 powder in a ball mill.

- Anodes are made of mild steel plates or
 cathodes are made of polished stainless
 steel. Here bath is made of pvc
 plastic materials.

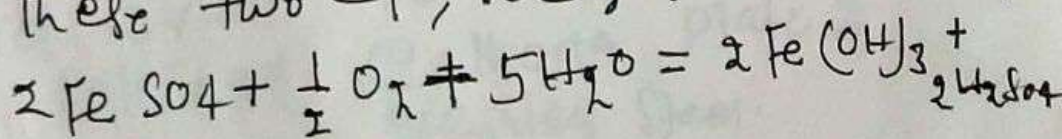
*IMP like copper, here building up of Fe^{++}
 ion concentration near the anode is
 not done, because of the
 oxidation reaction near the anode with
 the oxygen in air. Fe^{++} ions (ferrous ions)
 concentration increases it ~~goes~~ gets
 oxidized to ferric ion (Fe^{+++}) as:



Since the acidity (H^+ ion) is not high,
 hydrolysis takes place as:-



By adding these two eqn, we get



(3) $\text{Diphenyl} = 30-35\%$
 NDT

(P-18)
All these reactions of self
rectification of the composition of
electrolyte are reversible in nature.

— During the process of electro deposition,
the ferric hydroxide ($Fe(OH)_3$) precipitates
out from the solution near the anodes,
thus ~~avoid~~ removing the hazards of
excess Fe^{++} ions in nature.

— To avoid the contamination of electrolyte
as well as cathodic deposit with
 $Fe(OH)_3$ precipitates, anodes are covered
or wrapped in cotton bags where
precipitates get collected as anode
mud.

— The deposit on the cathodes contains
large amount of oxides and a little
carbon upto 0.15%. The purity is
92 to 95%.

— The brittle and lightly adhering
solid sheets are deposited on
the polished cathode plate of
stainless steel.

(3) $\eta_{\text{iron}} = 30-35\%$
NDT

- The electrodeposited sheets of Iron are easily detached from the cathode plate, broken into pieces and then subjected to grinding in ball mills to obtain Iron powder containing a significant amount of oxygen and hydrogen.
- The powder is annealed in suitable reducing atmosphere in a furnace at a temp of 700°C.
- We get Iron powder more than 99% purity along with good compressibility & compactibility properties.

(3) Density = 30-35%
NDT

26/07/15
SET-5

Characterization of powder

(P-1)

Introduction: The properties of PIM products depends on the consolidation behaviour of powder, which in turn depend on the characteristics of powder. These properties are mainly depend upon which method powder has been produced.

For example:

By atomization → We can get both spherical and irregular shaped particles

By Electro deposition → we can get dendritic shaped particles

By reduction of oxide → Irregular and porous particles are obtained.

By mechanical comminution of brittle materials

Angular particles or in other words particles having cleavage fractures together with sharp corners and edges are obtained.

The powder characteristics can be grouped as: - Chemical characteristics, physical characteristics and Technological characteristics. (p-2)

Now consider one by one.

(A) Chemical characteristics: It is used to analyze the oxygen content in powder, alloying elements are present in constituent powders. Abrasive powders which are present in these are analyzed and it is called chemical characteristics of the powder. It is tested by two methods: -

- (a) Hydrogen loss test, and
- (b) Acid insoluble test.

Now Consider (a) Hydrogen loss test.

It is used to Calculate the approximate amount of oxygen, adsorbed gas and moisture present in the powder.

Procedure

It is tested / analyzed by the powder sample by loss in weight of powder sample after heating in dry hydrogen gas.

— According to Metal powder Industry Federation (MPIF), USA,

5 gm of powder sample is taken in dry ceramic boat. Firstly ceramic boat is treated at a certain temp, in order to ensure that all volatile impurities during manufa are expelled out.

Ceramic boat (containing 5 gm of Iron powder sample) is heated in tube furnace at ~~1150~~ 1150°C for 60 minute in hydrogen atmosphere.

Note - in case of copper powder, it's heated at ~~800~~ 875°C for 30 minutes

The loss in the weight is recorded as the hydrogen loss.

For Iron or copper this value of the order of 0.2%.

Limitation of these test

(i) If H_2O_3 , SiO_2 , MgO (non-reducing) is present in powder sample. Then it can not be analyzed by hydrogen loss method.

(ii) If carbon or sulphur is present, ~~then it can not be analyzed~~ then it will increase the weight than actual. So, it can not be analyzed by Hydrogen loss method.

(iii) If alloy powder contains Zn, Cd etc as alloying elements, it can not be analyzed by hydrogen loss method, because these elements get vaporized on heating at the test temp & we get reported value more than the actual value.

(iv) The specified temp & time of heating for coarse powders, may not be ~~tested~~ sufficient. We get lower hydrogen loss value than actual value, because some unreacted core in the particles is present.

Thus, all above limitation can be resolved by another testing method i.e. acid insoluble test.

(b) Acid insoluble test:

Acid insoluble test is used for the metal powder in order to find out the content of SiO_2 , Al_2O_3 , Silicates, Carbides etc are present in powder, since it is ~~not~~ insoluble in acid.

- These constituent are very abrasive in nature. Hence it will damage the die surface during compaction of the powder. If they are present in powder without intention.
- According to MPD, 5 gm of powder sample is dissolved in dilute HNO_3 or HCl for Iron or copper powders.
- The solution is heated until reaction ceases.

- The concentrated solution is then diluted and heated to boiling and filtered after cooling it.

- The filter paper with the residue in it is burnt in a porcelain crucible when the filter paper only burns and vaporizes leaving behind the residue the weight of which is the acid insoluble value of the powder.

- The acceptable limit is around 0.2% wt.

- For estimation of alloying element in powder, any standard and conventional analytical procedure can be adopted.

- But presence of insoluble impurity can be only estimated by acid insoluble value test is mandatory.

— If the level of impurity in powder is above 0.2% by wt, then powder sample must be rejected. (P-8)

(B) Physical characteristics →

(I) particle shape and specific surface area →

⇒ particle shape has influence on the packing of powders, which in turn affects the compaction and sintering behaviour of the powder.

⇒ particle shape and surface roughness has a strong influence on the relative movement of the particles, thus affecting its flow properties.

→ For example: → dendritic shape of powder gives poor flow characteristics where as smooth spherical powder gives very good flow.

- Spherical powder with rough surface does not give a good flowability because of enhanced particle-to-particle friction.

- Again very fine powder, the poorer will be the flow because finer powder has very large specific surface area (cm^2/g), thus giving large amount of particle-to-particle contacts points, where friction force acts giving rise to higher internal friction. Thus sliding gets restricted and we get poor flow property of the finer powder.

- Specific surface area of a particular material is given as cm^2/g . It is very important property of a powder regarding its influence on

Consolidation behaviour of the powders. (p-10)

For example: γ 1 cm sides of solid cubes, has surface area = 6 cm^2

\ominus Similarly 0.1 cm sides of cubes has 60 cm^2

— Similarly 0.01 cm sides of cubes has 600 cm^2

— Similarly 1 μm sides cubes, the surface area = $60,000 \text{ cm}^2$

γ — Thus finer sized powders one can obtain a huge surface area, which has a tremendous influence on the consolidation process.

γ — But in actual practice, we do not get cubic particles. We get irregular shaped particles, which ~~is~~ The multiplying factor is of the order of 10.

Table:- Specific Surface area of Iron powder as dependent on particle size and powder production method.

Method of powder production	Average particle size (μm)	Specific Surface Area (cm^2/g)
Reduction of oxides	68	576
Reduction of oxides	51	945
Reduction of oxides	06	5160
Electrolytic deposition	79	265
Electrolytic deposition	63	452
Electrolytic deposition	53	1150
Carbonyl process	07	3460

In Industry, a rough estimation of the surface area is done by examining the particle shape under microscope and measuring the average particle size ^{shape} by standard method.

The Brunauer - Emmet - Teller (BET) method is used to measure the specific surface area as it is based on the amount of gas which is adsorbed on the particle surface area of a powder in a mono molecular layer. A helium-nitrogen stream of known composition is allowed to flow continuously over a powder sample cooled by liquid nitrogen; the sample adsorbs a quantity of nitrogen proportional to its surface area.

(P-12)
- When the coolant is removed and the sample warms the nitrogen adsorbed on its surface is desorbed. The quantity of nitrogen liberated is measured by a special technique.

(II) particle size and size distribution:

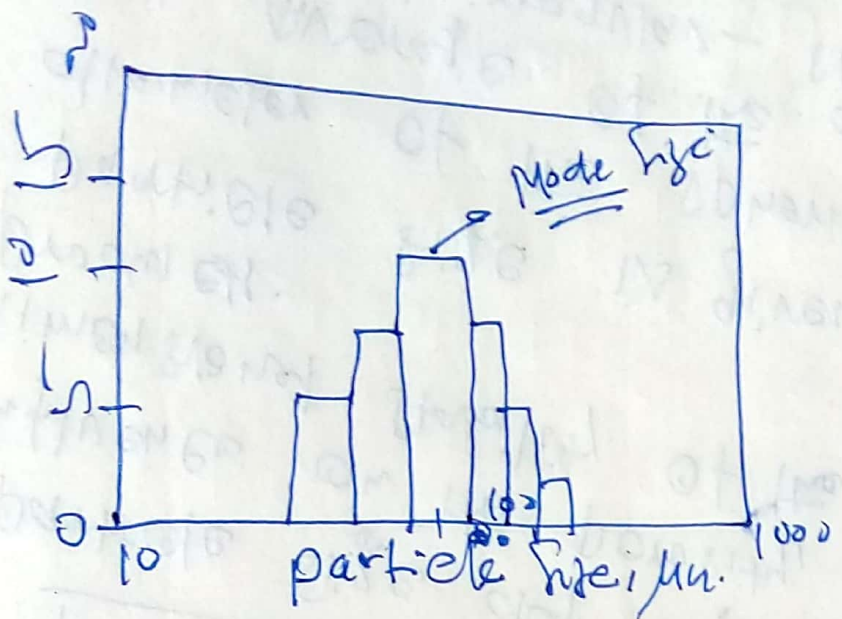
particle size and size distribution influence on the porosity, strength and dimensional stability of the powder products.

particle size is given by the diameter of the spherical particles and average of the diameter of granular / irregular-shaped particles.

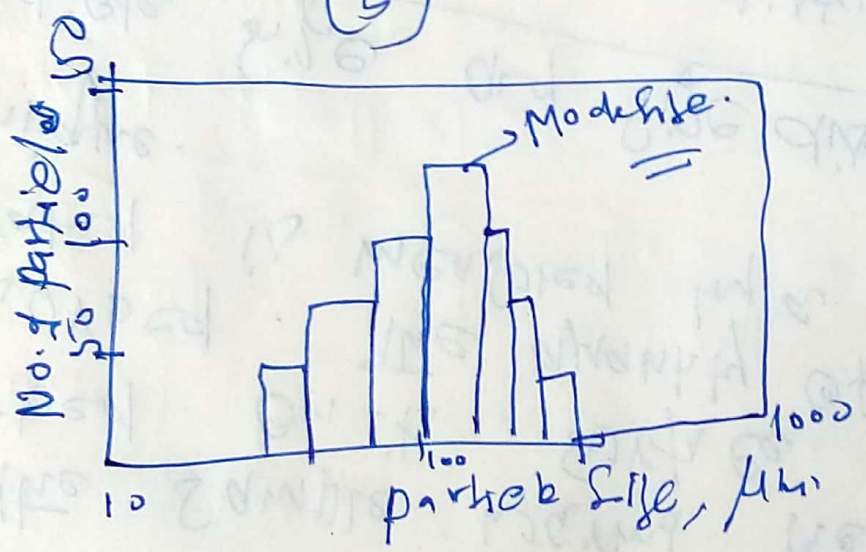
After producing the powder, we never get the same particle size all through. It has a distribution of different sizes.

weight %

(a)



(b)



- A proper distribution of particle sizes can give max^m packing density. Thus, we can say

- ~~That~~ That a distribution of particle-size is more wanted than single sized one.

- But in case of metallic filters, diffusers, percolators, etc. where uniform pore size and continuous pore channels are useful.

- particle size can be calculated as:
Sieve analysis methods.

(a)

Sedimentation method;

Debye-Scherrer formula: →

(b)

XRD analysis method.

(c)

$$d = \frac{0.9\lambda}{B \cos\theta}$$

Where $\beta = FWHM$

$$\lambda = CuK\alpha = 1.54 \text{ \AA}$$

$2\theta = \text{Max}^m \text{ Intensity}$, 50° where $\theta \approx \cos\theta$ value.

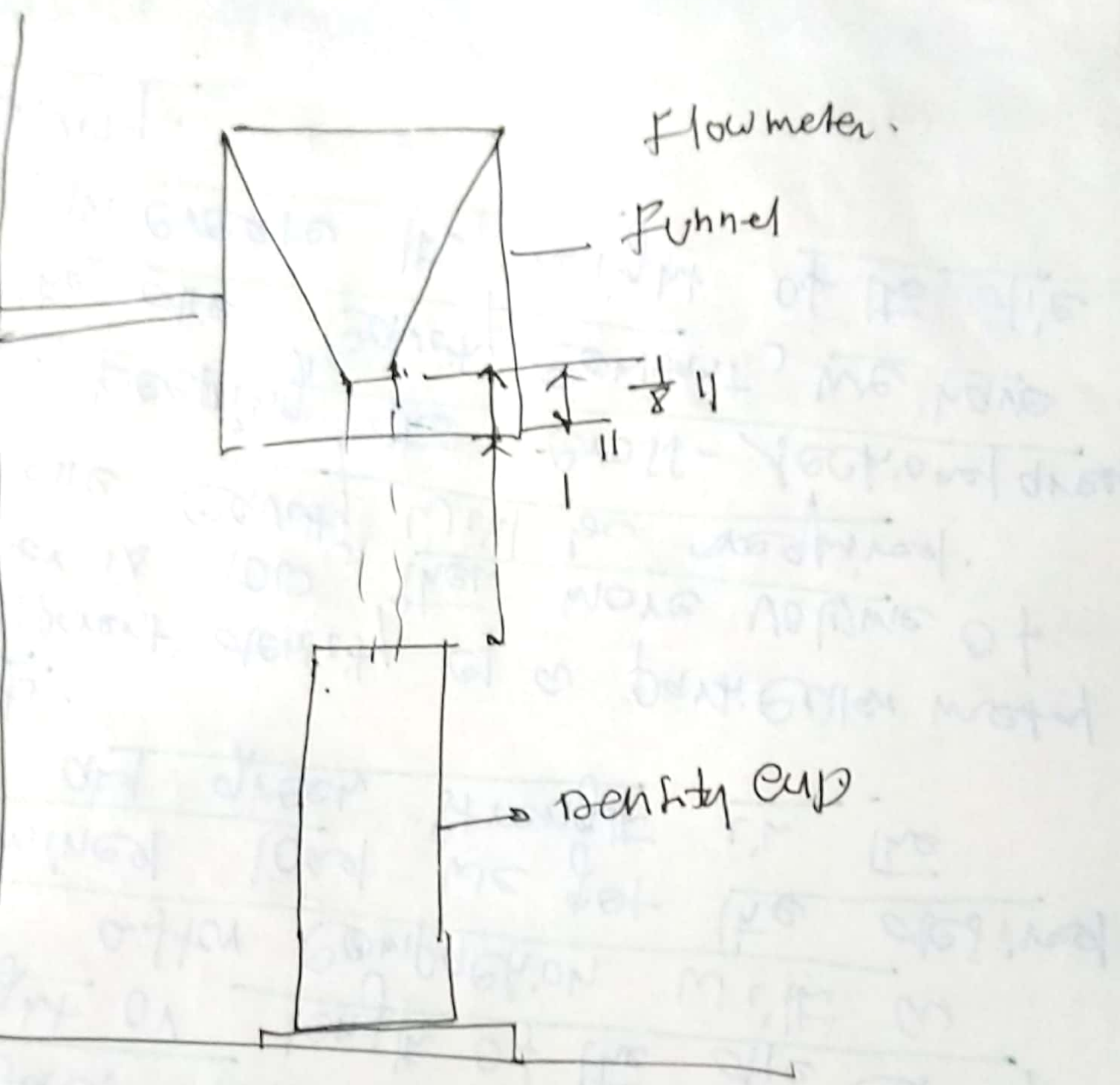
(C) Technological characteristics :-

(I) Apparent density and tap density :-

— Apparent density is the density of loosely packed powder expressed as weight per unit volume (g/cm^3). Its importance lies in the fact that we have to adjust the height or length of the die cavity so that after compaction with a predetermined load we get the desired density and green strength in the compacts.

— If apparent density of a particular metal powder is low, then more volume of the die cavity will be required.

— Thus, keeping the cross-sectional area of the die cavity constant, we have to increase the height of the die cavity.



Flowmeter.

Funnel

$\frac{1}{8}$ 11

Density cup

- (P-19)
- According to the MPIF test, a Hall flow meter is used.
 - It is a simple funnel type apparatus made of brass.
 - A density cup of 25 cm^3 volume is placed one inch below the bottom of the funnel.
 - ~~A powder is a free flowing~~
 - A powder, which is free flowing type is poured in the funnel keeping its orifice closed with finger.
 - Then by removing the finger the powder is let fall into the density cup.
 - After filling the cup a heap is formed, which is very carefully scraped off ~~the~~ with the help of a knife, thus levelling off the surface.
 - Weight of this powder is taken and on dividing it by 25, we get the apparent density of the powder in g/cm^3 .

- Apparent density of ~~the~~ fine size Hoganas reduced iron powder is 2.4 to 2.6 g/cm³. This density of metal powders is usually 20 to 50% of the theoretical density of solid metal.
- Apparent density is depend on:-
 - i) the particle density, ii) particle size and distribution, iii) particle shape and iv) surface roughness.
- porous powder particles have low apparent density.
- Free settling ability of the fine powder particles is low/poor, which results into low packing density, due to large particle-to-particle contact area, where frictional forces are ~~prevent~~ more during particle-to-particle sliding.
- In a mass of fine powders, there are more chances of formation of bridges and arches inside the loosely packed powder mass, thus creating voids.

The porosity of loosely packed powder can be estimated as:-

$$\text{fractional porosity} = 1 - \text{packing factor}$$

$$= 1 - \frac{\text{Volume of Solids}}{\text{Volume of loose powder}}$$

$$\text{fractional porosity} = 1 - \frac{\text{apparent density}}{\text{density of solid}}$$

$$= 1 - \text{relative density.}$$

Tap density: It is another important powder property related to apparent density.

This is estimated simply by tapping the density cup filled with powder up to the brim and tapping manually on the base of apparatus.

The level of powder goes down due to collapsing of all bridges and arches inside the powder mass as well as much increase in the packing density by rotation and jumping of particles inside the cup and the

(P-18)

Smaller particles occupying the interstices and voids in b/w the large particles. So an appropriate size distribution can give high packing density. This process of tapping is repeated until we find no further decrease in volume of the powder in the density cup.

- After, finally levelling off the cup, weight of the powder is taken and dividing it by 25 to get the tap density (in g/cm^3).

This is more than apparent density.

- The tap density can be measured in a more scientific way by taking 100 gm powder in a measuring cylinder and placing it securely on a vibrating machine. Tapping is done at certain frequency and amplitude until the volume, as read on the cylinder, is minimum. Dividing 100 by this volume,

we get tap density in g/cm^3 . (P-19)

— Because of taking a large quantity of sample the measurement error is minimum.

① Flow rate: The measurement of the flowability of a powder is very important— industrially.

— Rate of compacting in presses depends on how fast the die cavity is filled with powder and how well the powder gets into the intricacies in the die cavity.

— Low flow rate of powder results into lower production rate and also causes poor feeding into the intricacies in the interior of the die cavity, as a result of which the thin sections of the green compact will not be properly densified because of insufficient filling of powder in these sections.

P-20

and there may be breaking during handling.

— Moreover, there may be deshraping or Warpage of the Compacts during Sintering ~~due to~~ due to density differences.

— According to MPIF Standard, 50 gm of dry powder sample is taken in the funnel of the HALL Flow meter, keeping the orifice closed with a finger.

— Then powder is let fall and with the help of a stop watch the time of flow of the entire powder is recorded as the flow rate of the powder in terms of seconds/50 g.

— This can be repeated several times until a steady value is reached.

— For sieve grade iron powder (D-22)
this value is around 30 seconds.

— All factors affecting apparent density affect flow rate.

— Spherical, rounded or granular powders have highest flow rate and apparent density. Here particle-to-particle sliding is much more easy than

the dendritic powder (by electrodeposition) where the interlocking of the particles or high frictional effect restricts the movements of the neighbouring particles, whereas smooth spherical powder particles give least frictional effect.

— Hall flow meter is useful to measure the flow rate of free falling powders. That means that the powder must flow spontaneously through the orifice of the Hall funnel.

(P-22)

- for non free falling flowing powder like powders having highly irregular shaped particles (ie dendrite shaped particles), very fine particles size or considerable moisture content, a different funnel, known as Carney funnel is used. In this funnel the size of orifice dia is 5mm.

- Another term angle of repose is used.

- This is nothing, but the angle made by a heap of powder formed on a flat surface by pouring slowly a stream of powder.

- This is entirely dependent on the interparticle friction.

- for smooth and spherical particles this angle is almost nil.

- With increase of interparticle

Compression ratio,

defined as the ratio of the volume of the loose powder to the volume of the green compact made from it.

- This ratio is important for a powder or a mixture of powder in order to correctly design the

Compacting tools.

- The weight of powder filling the die cavity for every step of compaction at a constant pressure must be the same in order to obtain the same density and porosity and similar dimensions in each and every product of the same kind.