contd (SET-2) SAY Date: 23-07-15 (P-1)

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) deposition / 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 (by bath temp & stirring) and deposition of ions

and deposition of ions due to current density / cathodic current density

~~principle of aqueous Electrolysis 2.01~~

~~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 gives such high grade pured metal powders.

No Need

Advantages of these process

- High purity powders can be obtained (99.95%)
- The metal powders have excellent pressing and sintering properties
- cheap raw materials can be used ie 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 surfae area making the powder very surface-active. So, after electrodeposition intensive washing of the powder and thorough drying are needed. Othe

there will be too much oxidation and corrosion in the products. 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 :→ or Thermodynamics of aqueous Electrolysis :→

Elements	Zn^{++}	Fe^{++}	Ni^{++}	Sn^{++}	Pb^{++}	H^{+}	Sb^{++}	Cu^{++}	Ag^{+}
Electrode potential (Volt) (E°)	-0.76	-0.44	-0.25	-0.14	-0.126	0	+0.11	+0.34,	+0.799

- 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 ie increasing pH of the bath or increasing metal ion concentration.

Mechanism /Reaction of Ni-plating

At anode:

$Ni \longrightarrow Ni^{++} + 2e$

Cathode:

$H^{+} + H^{+} + 2e \rightarrow H_2$ (H-H) ↑

oxygen reduction (Acid solⁿ) $O_2 + 4H^{+} + 4e = 2H_2O$ or O_2

oxygen reduction (Neutral or basic solⁿ) $O_2 + 2H_2O + 4e = 4OH^{-}$

Metal ion reduction $Ni^{++} + 2e = Ni$

- 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. Thus this H_2 gas evolution will not allow to powder particles to bind together, & it remains as loose. Due 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 electrodeposit: →

(I) Current density (CD): Here current density refers to the cathode, which is of interest to the electro deposition of metals.

Coarser and denser deposit
at Cathode.

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

$I = 0.2\,Kc$ → ~~For~~ ~~dense posit~~ course ~~&~~ structure & dense deposit

Where I = Cathodic current density
k = is a constant depending on the electrolute & varies b/w = 0.5 & 0.9
C = Concentration of bath ie Metal ions Concentration

$I = kc$ → for ~~loose powdery deposit~~ fine structure & loose deposit

Thus fine & very loose deposit $I >$ or $= kc$
Coarse and dense deposit $I <$ or $= 0.2\,kc$

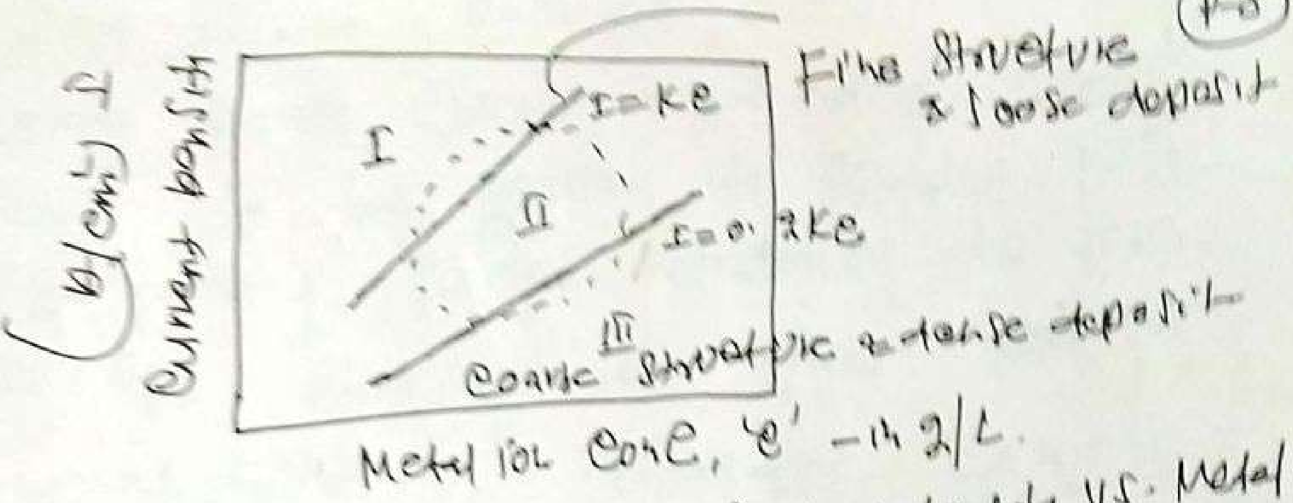

Fig (A) Plot of cathodic current density vs. Metal ions concentration (c).

- The intermediate zone as shown in Fig (A) by dotted ~~line~~ 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 gets into solution again and decreases the current efficiency.

'50 - 55 %'

- <u>At Zone-III</u> :→ 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, <u>Zone-II</u> is preferred i.e. within the dotted circle.

(iii) <u>Bath temperature</u> :→ It increases the mobility of ion by diffusion and convections 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) <u>Hydrogen ion concentration</u> :→ At the cathode, there is evolution of hydrogen gas at the same time, there is deposition of metal ~~powder gas~~. Due to evolution of hydrogen gas ie bubbling of hydrogen,

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it does not allow the bonding together of the metal particles. thus loose powderly with coherent & dense deposit is obtained. According to the ~~Accord~~ 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 powdery 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 ie increasing pH of the bath, in order to avoid much lowering of current efficiency due to much hydrogen evolution and yet sufficient high powdery deposit in case of -ve side of H^+ in electrochemical series.

(v) Different additives to the electrolyte :-

- In organic | additive such as H_2O_2, nitrates
  ↓
  oxidizing
  etc are used to cause slight surface oxidation on particles which retards the growth rate and we obtain finer deposit

- organic additive such as colloidal agent ie 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:

[illegible]

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 antimoney. Sulphate bath is used. The copper powder obtained is dendrite shape. These powder has good compachbility (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_2SO_4 in electrolyte	120 to 130 g/L	100 to 200 g/L
CD (cathodic)	120 to 200 A/m²	1000 to 2000 A
Bath temp	45 to 60° C	45 to 60° C

- 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 filteration in a rotating 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 are taken to maintain the metal ion concentration of the bath.

(i) 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 hydrogen evolution at cathode in an acidic sulphate bath.

- In order to 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 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 obtained dense deposit.

(3) Din-sh = $\overset{30-35\%}{NDT}$

Table: Conditions for electrodeposition of Iron in aqueous bath

Conditions	Spongy semi ~~Coherent~~ Coherent deposit
$FeSO_4$ in electrolyte	120 to 140 g/L
NaCl in Electrolyte	40 to 50 g/L
H_2SO_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) Dinyan = 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 and 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 ~~[illegible]~~ 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:

$$2FeSO_4 + \frac{1}{2}O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O$$

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

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4$$

By adding these two eqn, we get

$$2FeSO_4 + \frac{1}{2}O_2 + 5H_2O = 2Fe(OH)_3 + 2H_2SO_4$$

(3) Din-gen = 30–35% NDT

All these reactions of self rectification of the composition of electrolyte all 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 ~~adsor~~ 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 contain 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) Din-ow = 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 mill 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) Dinesh = 30-35%.
NDT