2.1. HIGH SPEED DEPOSITION:

High-Speed Deposition (HSD) has been the target for many researchers in the past few decades. All of the work in this area required high flow rates of electrolyte near the cathode surface. In general high-speed deposition is the term used to describe, solutions with greater than traditional deposition rates because of increased solution efficiency and higher limiting current densities. Some of the mechanisms suggested to improve solution efficiencies are:

- High solution flow rate
- Direct solution impingement
- High velocity spray
- Increased chemical concentration
- Close anode placement
- High solution agitation

High-speed plating was initially introduced in small commercial equipment in the early 1940's. At that time, thin tin deposits of thickness 0.75 μm were applied in 2 to 3 seconds on continuous steel strip at a current density of 30 to 50 A/dm² (1). In high-speed deposition, metal concentrations and solution conductivity are higher than the conventional solutions, normal operating temperatures and solution agitation rates are specified. (2) (3)

High-speed deposition technique is used mostly in electronic industrial components which can be divided into two areas like connectors and semiconductors; the latter utilizes most of the products, produced by strip plating. The major components like connector contacts, lead frames, various connecting devises, leads, headers of the strip materials from which contacts and components are subsequently formed. For all these parts, before the precious metal deposition, some base metals are usually plated. In most
cases, copper and its alloys particularly phosphor bronze, brass, beryllium copper and similar alloys are plated as a base deposit in semiconductor components.

Some of the high-speed techniques on strips suggested are: (1)

1. Controlled depth or Tip plating
2. Moving belt.
3. Drum and mask selective plating
4. Tape masking
5. Spot plating cell
6. Selective brush plating

Westey and his team (4) published their work in 1949, describing a cell in which nickel was deposited at a rate of 1.56 micron per second using a current density of 458 A/dm². This is about 10 times the average rate that was commonly used in rack plating. The cell contained two parallel electrodes with provisions to pump nickel solution between them. In their work they never reached a maximum current density because they exceeded the current capacity of the direct current generator when the flow rate was 2.7m/sec. However they arrived a direct relationship between flow rate and current density, which defined the boundary between sound and unsound deposits.

Some investigations during the 1950 to 1960 explained the inclusions of high frequency pulsing, mechanical agitation with abrasives, ultrasonic agitation, brushing, jet plating in high-speed deposition process but none of these methods supported high current densities, as effective as turbulent solution flow or rapid cathode motion. W.H. Safranek (6) discussed their work on the better deposition rates, achieved on turbulent flow of the electrolyte, and a deposition rate of 150 μm/minute compared with 50 μm/minute on jet plating. W.H. Safranek (7) also reported in his book, on the practical current densities adopted and maximum deposition rates for plating 50 to 75μm thick
coating or foil and described the practical current density used and maximum plating rate to plate 50 to 75 μm thick foil (7).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solution</th>
<th>Practical current density, A/cm²</th>
<th>Deposition rate μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>2.0M NiSO₄ or Ni CI₂</td>
<td>3.0</td>
<td>60</td>
</tr>
<tr>
<td>Copper</td>
<td>2.0M CuSO₄</td>
<td>3.1</td>
<td>75</td>
</tr>
<tr>
<td>Cobalt</td>
<td>2.5M CO (BF)₂</td>
<td>6.2</td>
<td>125</td>
</tr>
<tr>
<td>Chromium</td>
<td>3.0M CrO₃</td>
<td>6.2</td>
<td>20</td>
</tr>
<tr>
<td>Iron</td>
<td>2.3M Fe (NH₂ SO₃)₂</td>
<td>6.9</td>
<td>150</td>
</tr>
<tr>
<td>Gold</td>
<td>0.05M Au CN (citrate)</td>
<td>0.3</td>
<td>18</td>
</tr>
<tr>
<td>Lead</td>
<td>2.5M Pb (BF₄)₂</td>
<td>1.6</td>
<td>100</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.0M Cd (BF₄)₂</td>
<td>3.0</td>
<td>120</td>
</tr>
<tr>
<td>Tin</td>
<td>1.0M Sn (BF₄)₂</td>
<td>3.0</td>
<td>140</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.0M ZnSO₄</td>
<td>3.0</td>
<td>80</td>
</tr>
</tbody>
</table>

J.P. Hoare and co-workers (8) studied on air pressure flow system on high-speed plating which required a higher volume of electrolyte. Although this system could accept many of the production units, it was not convenient for research in plating, where lower operating volumes are desirable particularly if the chemicals involved are expensive one. He described by using flow channel fixture, much higher solution flow could be attained. La Boda and his team (9) reported that the rate of nickel deposition by high-speed deposition at three temperatures 325, 330, 345K and three flow rates 5, 7.5 and 10m/sec; the Reynolds number for this system ranged from 20,000 to 40,000, so that the flow was always turbulent in nature. According to their report, the deposition rate increases linearly with the current to a critical point after which a precipitous drop in the rate occurs in most of the cases. He further investigated that the flow rate of the electrolyte (velocity) must be greater than 1m/sec before high speed plating of nickel can take place and the critical current density is shifted to higher values with an
increasing flow rates. The narrow gap between the anode and cathode during high-speed plating allows higher current without excessive voltage and with the higher rate of solution flow, the temperature in the gap can be controlled.

Eisner (10) reported that high rates of deposition compared with normal procedures as a result of abrading the cathodic surface during plating with inert hard particles. This rapidly removes the cation depleted electrolyte layer on the cathode surface and replaces with the fresh solution thus raising the limiting current density. This abrasion may also serve as activating and smoothening operation while plating proceeds. Reichard (11) described a new method for high rate of deposition that combines electroplating and honing. The honing process removes the cation depleted electrolyte layer much as in the other process and it is further claimed to provide particle size control and surface conditioning concurrent with electro deposition. WH. Safranek (6) investigated that limiting current density and deposition rate could be increased by increasing ion transporting rate and reducing diffusion layer thickness by fast solution flow rate.

Moreover Der Tau Chin (12) described chromium deposition at current densities of 7 to 70 A/cm² in a small flow cell employing steel cathodes and a platinum anode at a flow rate of 2 lit/min (Reynold’s number of 9000). However La Boda (13) described the high-speed plating of chromium and made a devise based on narrow gap spacing and rapid electrolyte flow between anode and cathode. In this experiment, the anode–cathode distance was kept as 2.5mm, and a gear pump has been used to pump the electrolyte at a rate of 78 lit/min at a pressure of 2.1x10² KPa with the velocity of 3.9 m/second. He summarized that bright adherent chromium has been plated at a rate of 5 µm/minute at a current density of 134 A/dm² using a high-speed plating system.

Enicott and his team (14) discussed about high-speed selective gold plating for the semiconductor industries. He developed a special plating system to plate gold on a lead frame of a Motorola small signal transistor.
device to conserve the cost of the precious metal investment cost. He described the mechanism of lead frames, transported vertically in a plating cell and pay put real to take up real. During the experiments the concentration of bath has been reduced to 10 ± 1.5gpl than the conventional one of 25 to 50gpl. He explained that the dilute gold plating solution developed for thermo compression wire, bonding to lead frames contains 10 gpl of gold and has a specific gravity of 8° Be, operated at 60 to 80A/dm² and produced a semi bright gold at a thickness of 1μm over the nickel base.

Steve Eisner (15) suggested in his paper entitled an ultra high speed plating process, utilizing small hard particles that, copper and nickel can be plated using High Speed Deposition technique and the following bath compositions were suggested.

For Copper

\[
\begin{align*}
\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} & \quad 264 \text{ gpl} \\
\text{H}_2\text{SO}_4 & \quad 100 \text{ gpl} \\
\text{Temperature} & \quad 298 \text{ K}
\end{align*}
\]

For Nickel

\[
\begin{align*}
\text{NiSO}_4 \cdot 5 \text{H}_2\text{O} & \quad 40 \text{ gpl} \\
\text{NiCl}_2 & \quad 8 \text{ gpl} \\
\text{H}_3\text{BO}_3 & \quad 4 \text{ gpl} \\
\text{Temperature} & \quad 333 \text{ K}
\end{align*}
\]

He reported that 7.6 μm of copper deposit plated from acid copper sulphate baths at a current density of 53 A/dm² using an activator speed of 305 meter per minute with an activator pressure of 21 g/m² & a knoop hardness of 172 to 175 and a plating speed of about 25 to 50 μm per minute could be achieved at a current density of 108 – 216 A/dm². In high-speed deposition of copper, additive will have considerable grain refinement. He concluded that ultra high speed electroplating has been attained using multiple hard activator particles the properties of the deposit can be varied from burnt to ductile and coherent to hard, brittle and coherent depending on the plating rate and activation rate.
A. Waymeersch (16) reported on high current density electroplating of Zinc-nickel and Zinc-iron alloys on the anode cathode distances. An anode to cathode spacing of less than 25mm keeps voltage and energy requirements at low levels. He suggested that high current densities can be used effectively for plating zinc alloys on continues steel strip: both uniform current density and hydrodynamic conditions over the entire cathode surface are necessary to achieve high productivity and has employed a current of 300 A/dm². James and his team (17) explained in their report about study on high rate deposition of chromium about the flow of the chromium bath and gap width. For high rate of deposition, the electrolyte must flow through the narrow gap between anode and cathode at a higher rate. To increase the chromium deposition rate to a maximum for a given flow rate, raising the temperature of the system would increase both the mobility of ions in solution and solution conductivity. They reported that at 341K and at a current density of 7A/cm² bright hard Chromium was deposited on Copper substrates at a rate of 26 μm/minute with a current efficiency of 52 percent. In conventional decorative Chromium plating, the lower limit in CrO₃ concentration was found 50gpl at which bright Chromium can be deposited at a rate of ~ 0.12 μm/min at 316K.

Schaer and co-workers (18) described an equipment design for fast rate of electroforming to make printing plates (stampers) for currency notes and stamps. In their experiment, they used to take the electrolyte from the tank itself at the bottom of the basket to with draw the solution adjacent to the anodes to prevent excessive concentration polarisation or passivation of the anodes at a current density of 20 A/dm². They reported that because of the fast solution flow between the anode and the cathode, the current densities could be increased up to four times without altering the physical properties of the nickel electroform. Current density could be raised to 20A/dm² which reduced the plating time to 4 hours compared with the 18 hours required to make the same printing plate / stamper. They discussed about the flow velocity of the electrolyte in their experiments. Stewart Hemsley (19)
discussed in brief on high-speed precious metal plating of gold, silver and palladium on nickel for electronics connectors; he further reported about problems on thickness distribution in high-speed reel to reel plating, vat plating and barrel plating. Ya suuo kota (20) reported about the high-speed silver and solder plating process for semiconductor lead frames and converters for electronic industrial applications. He further discussed on bath composition, production style and operational conditions of hi speed silver plating for lead frames. Kudrjavtzeva (55) reported about the high-speed plating in low concentrate baths by using colloids. He explained that the rational selection of high-speed plating solutions taking colloidal phenomena in to account can enable high quality metallic deposits with desired properties. ED. Winters and his team reported the characteristics of high-speed gold deposit (> 8mA/cm²) plated upon electroplated nickel in an in-line, conveyerised system. It further discussed with gold layer's microstructural characteristics, surface morphology, texture, crystalline size and micro-strain; if gold is deposited on heat treated nickel, the gold deposit has a texture of <111> and unsintered gold deposit is <100> of larger grain size (54).

2.1.2. FLUID DYNAMICS:

The science of hydraulics come into existence at the end of seventeenth century when the attention of philosophers was drawn to the problems involved in the design of fountains, which came into considerable use in Italian landscape gardens. Issac Newton was the first Englishman to have earned place in the field of hydraulics and he enunciated concisely the three basic laws of motion. Eighteenth and nineteenth centuries have seen a tremendous advancement in hydraulics and hydrodynamics. In this period only, most of the experimental hydraulics was developed at French, Italy, German by eminent scientists Bernoulli, Euler D’alembert, Darcy, Navier, Stokes, Lord Kelvin, Reynolds.
A fluid may be defined as substance, which deforms continuously under the action of shear stress, regardless of its magnitude. The time rate of deformation of the fluid will, however depend upon the magnitude of shear stress. Fluids are composed of molecules, which are separated by spaces usually much larger than the size of molecules themselves.

Fluids are characterized by such properties as density, specific weight, specific gravity, viscosity, surface tension, elasticity and vapor pressure. Among all these properties, viscosity is important one in the study of fluids. According to Newton’s law of viscosity, for a given shear stress acting on a fluid element, the rate at which the fluid deforms is inversely proportional to the value of viscosity. Any fluid, which obeys above law, is known as a Newtonian fluid. Newtonian fluids have constant viscosity, i.e. the viscosity is independent of the shear stress. Many common fluids such as air, water, light oils and gasoline are Newtonian fluids under normal conditions. However, there are certain fluids which exhibit non-Newtonian characteristics i.e. the stress is not linearly dependent upon the velocity gradient. Non-Newtonian fluids, therefore, do not follow Newton’s law of viscosity and common examples are human blood, lubricating oils, clay suspensions in water, molten rubber, printer’s ink, butter and sewage sludge. There is however evidence to believe that Newtonian fluids may exhibit non-Newtonian characteristics under conditions of high shear stress, and hence the classification of a fluid may change with the conditions of flow. (21)

2.1.2.1. **Important properties of fluid.**

a) **Viscosity**

Viscosity of a fluid by virtue of which, it offers resistance to shear force. Newton’s law of viscosity states that for a given rate of angular deformation of fluid, the shear stress is directly proportional to the viscosity. Molasses and tar are example of highly viscous liquid; water and air have very small viscosities. The viscosity of a gas increases with temperature, but the viscosity of a liquid decrease with temperature. The unit of viscosity is N.sec/m².
b) Kinematic viscosity

Kinematic viscosity is the ratio between the absolute viscosity or dynamic viscosity and the mass density of the fluid. Viscosity is practically independent of pressure and depends upon temperature only. The kinematic viscosity of liquids and of gases at a given pressure is substantially a function of temperature.

The unit of Kinematic viscosity is $v = m^2/\text{sec}$.

The value of kinematic viscosity of water at 295 K is $8.315 \times 10^{-7} m^2/\text{sec}$.


c). Density

The density of a fluid is defined as its mass per unit volume. For water at standard pressure (760mm Hg) and at 313K, density is 1000kg/m$^3$.

d). Pressure

The normal force pushing against a planer area is the average pressure. The pressure at any point is the ratio of normal force to area, as the area approaches a small value enclosing the point. If a fluid enters a pressure, against the walls of a container will exert a reaction on the fluid, which will be compressive in nature. Liquids can sustain very high compressive pressure but unless they are extremely pure, they are weak in tension.

e). Reynolds Number

Reynolds numbers is the ratio of inertia forces to viscous forces. A critical Reynolds number distinguishes among flow regimes, such as laminar, transient and turbulent flow in pipes, in the boundary layer or around immersed objects. The specific Reynolds number value depends upon the situations.

2.1.2.2. Types of Fluid flow

Normally flows are classified in many ways but two are described of practical importance.
a) **Laminar flow**

In laminar flow fluid particle move along smooth paths in lamines or layer with one layer gliding smoothly over an adjacent layer. Laminar flow is not stable in situations involving combinations of low viscosity, high velocity and will breakdown into turbulent flow.

b) **Turbulent flow**

In turbulent flow, the fluids particles move in very irregular paths causing an exchange of momentum from one portion of the fluid to another portion. Nearly all the fluid flow problems encountered in engineering cases have a turbulent in nature.

2.1.2.3. Flow in pipes:

The continuity equation states that "The mass within a system remains constant with time", thus for a fluid flowing through the pipe at all the cross-section is constant. The quantity of fluid flowing is constant with respect to time.

Let us consider two cross section of pipes 1 & 2 and

\[ v_1, v_2 \text{ - Average velocities at section 1&2 respectively,} \]
\[ A_1, A_2 \text{ - Area of cross section at 1&2 respectively and} \]
\[ \rho_1, \rho_2 \text{ - Density at section 1&2 respectively} \]

Then

\[ \text{Mass flow rate } m = \rho_1 A_1 v_1 = \rho_2 A_2 v_2 \]
\[ \text{Volume flow rate } Q = A_1 v_1 = A_2 v_2 \]

Thus for incompressible, steady flow,

Discharge \[ Q = A_1 v_1 = A_2 v_2 \]

As soon as the fluid comes in contact with the pipe wall, the boundary layer started forming over it. The retarding effect of the wall, where the velocity must be zero, at once operates so that the fluid nears the wall is slow down, in order to satisfy or compensate for the reduction in velocity near the wall. When the thickness of boundary layer becomes equal to pipe radius, the effect of retardation of flow reaches the central region of flow. In
case of laminar flow, the boundary layer starts as a laminar layer and remains through out its length (23).

If the Reynolds number is high, so that the flow in the pipe is turbulent, the boundary layer, which starts as a laminar layer a little distance downstream the transition occurs and the boundary layer becomes turbulent. This turbulent boundary layer from opposite side meet at the pipe axis much earlier and downstream of this section, the flow is fully developed a turbulent flow.

2.1.2.4. Flow through nozzles and orifices:

If a nozzle is fitted at the end of a long pipe, the total energy at the end of the pipe consists of pressure energy and kinetic energy. By fitting the nozzle at the end of the pipe, the total energy is converted into kinetic energy. Thus the nozzles are used, where higher velocities of flow are required. Orifice is a small opening of any cross suction (Such as circular, triangular, rectangular, etc.) on the side or at the bottom of a tank, through which a fluid is flowing.

2.1.2.5. Importance of Reynolds number:

Reynolds an eminent scientist worked on fluid flows and studied the conditions under which one type of flow changes into other. For fully developed flow, through a circular pipe, he found that the critical velocity at which laminar flow changes into turbulent flow depending on the following parameters.

1. The diameter of the pipe (d)
2. Viscosity of the fluid (μ)
3. Density of the fluid (ρ)
4. Average linear velocity of the fluid (v).

Further, he combined these four factors into one group and that determines the type of flow occurs at a definite magnitude of the group. The grouping of variables found by Reynolds (23) is
Re = \( \frac{\rho v L}{\mu} \)

In case of pipe flow, the length is considered as diameter and Reynolds number is

\[
Re = \frac{\rho v d}{\mu} \quad \text{or} \quad \frac{v d}{\nu}
\]

\( \rho \) - Density of fluid
\( v \) - Velocity of fluid
\( d \) - Diameter of pipe
\( \mu \) - Viscosity of fluid
\( \nu \) - Kinematic viscosity of fluid (\( \mu / \rho \))

2.1.3. Laminar Flow

In laminar flow, the fluid particles move along smooth regular paths, which can be predicted well in advance. The particles thus move in lamines or layers gliding smoothly over the adjacent layer. The flow through a small diameter tube at low velocity is generally a laminar one. The streamline flow is straight and therefore the laminar flow is called the streamline flow. The conditions favorable for laminar flows are high viscosity, low mass density, low mean velocity and small flow passage. Osborne Reynolds has explained that Reynolds number \( \frac{\rho v L}{\mu} \) is the criteria for determining the type of flow, whether laminar or turbulent in a circular pipe. The concept of Reynolds number is a useful one in demarcating the regions of laminar or turbulent flow. Applying this concept to circular pipes, one may predict that flow will be laminar if \( Re < 2000 \) and it will be turbulent if \( Re > 4000 \). It is noted that the Reynolds number generally defined as \( \frac{\rho v L}{\mu} \), is a function of geometry of flow area taken into account of characteristic length \( L \) and for circular pipes it will be taken as diameter \( d \).

2.1.3.1. Steady Laminar flow through a Circular Tube

The laminar flow of an incompressible fluid flowing under steady conditions may be completely analyzed using Newton’s law of viscosity and
Newton's second law of motion. Let us consider a horizontal pipe of radius $R_0$, and a concentric cylindrical fluid element of radius $r$ and length $dx$, as shown in figure. 2.1. (22)

The forces acting on the free body of the fluid elements are:

1. The pressure force, $p\pi r^2$, on the left face (acting from left to right).
2. The pressure force $(p + \frac{dp}{dx} \cdot dx) \pi r^2$ on the right face (acting from right to left).
3. The shear force $(\tau \cdot 2\pi r \cdot dx)$ acting on the surface of the fluid element opposing the motion (acting from right to left).

The flow is steady and the tube is of uniform diamensions i.e., the radius is same throughout the length, then the total acceleration is given by

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + u \cdot \frac{\partial u}{\partial t} = 0, \quad (\frac{\partial u}{\partial s} = \frac{\partial u}{\partial x})$$

Since the flow is steady, $\frac{\partial u}{\partial x} = 0$, and for uniform flow, $\frac{\partial u}{\partial s} = 0$.

By applying Newton's second law of motion in the direction of flow, thus

$$p\pi r^2 - (p + \frac{dp}{dx} \cdot dx) \pi r^2 - \tau \cdot 2\pi r \cdot dx = 0$$

which simplifies,

$$\tau = -(\frac{dp}{dx}) \cdot \frac{r}{2}$$

This equation gives the distribution of shear stress across a flow section. The pressure gradient, $\frac{dp}{dx}$, depends only on $x$ and hence, the above
equation provides a linear relationship between $\tau$ and $r$. It is evident from the equation that the shear will be maximum at the tube surface where $r = R_0$ and minimum at $r = 0$, where it has a value zero. It is to be noted that the above equation is applicable to any type of flow whether laminar or turbulent depending upon the conditions prevail.

Reynolds investigated in detail the circumstances leading the flow laminar to transition and then to turbulent in nature. The approximate numerical value of Re at which laminar starts becoming unstable and breakdown was noticed to be in order of 2000. i.e. Re critical $R_{cr} = 2000$. For the pipe flow if $R < R_{cr}$, the flow is laminar while $R > R_{cr}$, the flow may change over to turbulent in nature.

2.1.4. TURBULANT FLOW

The turbulent flow is characterized by random irregular and haphazard movement of fluid particles making it impossible to predict the motion of a fluid particle with respect to time and space. This type of motion gives rise to velocity fluctuation in all the directions. The velocity fluctuations in the transverse direction are responsible for the transverse mixing of small masses of fluid. This mixing process of turbulent has been clearly evinced in Reynolds work (22). In the process of turbulent mixing, the fluid with high kinetic energy is carried by the fluctuations towards the boundary, while the fluid moving with low kinetic energy near the boundary is carried away from the boundary into the region of high kinetic energy. This results in a more uniform velocity distribution in turbulent flow as compared with laminar flow. The transverse mixing of fluid tends to equalize the velocity except near the boundary where the mixing tends to vanish.

The figure 2.2 shows the velocity distribution in laminar and turbulent flow at the same Reynolds number in a circular pipe.
The most essential feature of a turbulent flow is that at a given point, velocity and pressure are not constant with time but exhibit very irregular fluctuations of high frequency. Turbulence occurs commonly in various forms of shear flow. Shear flow can be classified according to whether they occur along solid surface or at the interface between fluid zones having different velocities, such as boundaries of jet. The turbulence generated by the viscous effect due to the presence of a solid wall as known as the wall turbulence. The turbulence generated by the flow of fluid layers at different velocities, in the absence of a solid wall is termed as free turbulence.

2.1.5. Agitation in plating baths

Agitation of the electrolyte brings up a fresh supply of metal ions to the cathode, reduces the thickness of the cathode film, and thus facilitates replenishment of the metal ions at the cathode surface. Another advantage of agitation is that it sweeps away the gas bubbles, which may cause pits. Agitation is also desirable because it mixes the solution and prevents stratification of heavier solution toward the bottom of the tank. The net result is that agitation permits a higher current density to be used to produce a deposit with a given structure and it increases the limiting current density for dense deposits. In principle the relative motion is obtained by horizontally, vertically or rotational movement of the cathode or by splashing the solution.
near by the cathode by stirrer, pump or a jet of air. There are two categories of agitations possible in any liquids, which are laminar and turbulent flow. The creation of turbulence promotes, the limiting current density and mass transfer co-efficient of the electrolyte. Higher current density can be adopted because of enhance mass transfer conditions; increase in current density that increases the current efficiency, the production rate and reduces required building area and inventory.

DR. Gabe and Amedi et al discussed different types of vigorous agitation techniques given in plating baths to increase the limiting current densities (24-28), M Ward and Gabe reported the use of eductors for agitation of anodizing solution used in the production of hard anodized surfaces and discussed the advantageous of their agitation system (29).

2.1.5.1. Types of Agitation methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Cheap, easy, traditional widely used.</td>
<td>Generally inadequate current densities used.</td>
</tr>
<tr>
<td>movement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical</td>
<td>Cheap, reasonably effective</td>
<td>Requires careful positioning, may be highly localized.</td>
</tr>
<tr>
<td>Air</td>
<td>Cheap and readily available; visible pattern of agitation for process control.</td>
<td>Creates foam, losses of heat by air, limits to possible process enhancement, loss of solution conductivity.</td>
</tr>
<tr>
<td>Jetting</td>
<td>No air is used; so no oxidation can be directed at work. High opportunity for enhancement and optimization.</td>
<td>Power is used higher than other methods, heat input to solutions</td>
</tr>
</tbody>
</table>

In high-speed deposition system, fast solution spray technique by creation of turbulence near the electrode has been used. A spray is a quantity of liquid projected in fine droplets. Even though there are gamut of methods exist to produce sprays, one cannot yet be certain about their characteristics. The physical phenomena that are responsible for the formation of sprays, like the explosion of liquid into droplets, are still not well known. Yet they have a number of industrial and domestic applications. In cars, aeroplanes and rocket engines, which are run by heat engines, the fuel is injected in the form of a spray within the engine. The diameter of the fine droplet spray should be close to 5x10^{-6} m. The spray should have certain characteristics of size and speed in the electrolyte and create wild agitation. This agitation significantly alters the hydrodynamic conditions at the electrode-electrolyte interface, thus causing a reduction in diffusion layer thickness close to the electrodes. The concentration gradient is disrupted and this is increase in the mass transport of electrolyte in regions adjacent to the electrodes; more ions are available for discharge near the cathode. The electrode processes are thus accelerated and the limiting current density for metal deposition increases.

2.1.6. WHY ZIRCONIUM AS ADDITIVE

The use of additive in aqueous plating solutions is extremely important owing mainly to the interesting and important effects produced on the growth and structure of deposits. The potential benefits of additives include; brightening the deposit, reducing the grain size, reducing the tendency to tree, increasing current density range, promote leveling, changing mechanical properties, effects on stress and elimination of pitting on deposit. The additives can be organic or metallic, ionic or nonionic and are adsorbed on the plated surface and often incorporated in the deposit. (30) Additives are classified into four major categories.

(1). Grain refiners
(2). Dendrite and roughness inhibitors
(3). Leveling agents

(4). Wetting agents

If any one studies on effect of metal additives in plating bath they differ in their susceptibility and is roughly the same as the order of their melting points, hardness and strength and increases in the order of Pb, Sn, Ag, Cd, Zn, Cu, Fe. Lyons suggested that: "An atom which is capable of interacting strongly with other atoms of the same or other kinds, tends to form a strong crystal lattice with a relatively, high melting point, to co-ordinate strongly with ligands to de-coordinate water slowly and to catalyze conversion of atomic to molecular hydrogen". (31)

2.1.6.1. Additives for Oxygen scavenger

The electroformed copper used for fabricating the combustion chamber of NASA'S space shuttle main engine is an interesting story in the history of additives in Hi-Tech field. This copper deposit serves as a barrier between hydrogen coolant and electroformed nickel, preventing the embrittlement of the nickel by hydrogen. Electroformed copper deposits contain some oxygen and this can be deleterious when high temperature brazing is done since hydrogen can combine with oxygen and produce water. With the high temperature involved, steam pressure generated by the reaction, often exceeds the strength of copper and causes plastic deformation and tearing, frequently manifesting itself by grain boundary cracking or cavities (32) (33). This phenomenon is referred as hydrogen embrittlement in copper or steam embrittlement. Rocketdyne, NASA's contractor for space shuttle engine fabricator, started working on this type of low oxygen copper found that, sugar derivatives was the main cause for this effect. It turns out that all of the pentoses are suitable for use in acid copper bath ex. Xylose, arabinose, ribose, ryxose. These materials act as oxygen scavenger in the solution by picking up dissolved oxygen. This prevents the anodes from becoming oxidized and leading to this oxygen being incorporated in the deposit. John and Veeramani et al discussed about other
kind of additives, for lower dissolved oxygen in copper during the process of electroforming of cryogenic steering engine chamber (34). Zirconium's relativity with gases at elevated temperatures has found application in radio valves as a "getter" in the past years ie a substance employed in vacuum tubes to remove traces of gases. As ferro zirconium, it is used oxygen scavenger in steel manufacturing industries (35).

2.1.6.2. Copper – Zirconium deposition

Among the copper alloys, brass and bronze are two important alloys, which are widely used in engineering applications. Brass was the first along electrodeposited and still used extensively for decorative purposes and for promoting rubber adhesion to steel and other metals. The customary solutions for plating brass, bronze and other copper alloys are based on mostly cyanide complex, but some baths for copper tin alloy plating also contain pyrophosphate ions useful for complexing stannous tin (36) (37). Several non-cyanide baths for depositing brass or bronze, which are of little, no commercial impacts have been reported. (38)

Russian investigators reported that ceramic particles like corundum can be co deposited along with copper in acid sulphate bath. (39) (40). Copper containing 6.5 volume percent of 0.1 to 0.2 micron of alumina particles exhibited a hardness of 148 kg/sq mm in the acid sulphate deposits; for this magnetic stirrer was engaged (41). Graphite flakes incorporated in copper, deposited from acid sulphate solution, reduced the friction for a functional application (42). For a longer period, zirconium could not be deposited from aqueous solution. The cathodic deposition of zirconium from aqueous baths is very difficult, chiefly because of the high electronegative potential of zirconium (-1.53 V) and the low hydrogen over voltage on it. Pure zirconium coating should be deposited only from molten salts. Some of the reports suggested that zirconium, hafnium, niobium, molybdenum, tungsten should be deposited from a mixture containing 15-50 % by weight of a double
fluoride of the metal to be deposited and an alkalie metal 0.25-10 % water and the balance, halides of alkaline and alkaline earth metals.

Aqueous baths can be used for deposition of alloys of zirconium with other metals. Electro deposition of alloys of zirconium with zinc and cadmium recommends alkaline cyanide baths containing sodium zirconate. A zinc-zirconium of alloy was deposited from a bath containing Zn(CN)₂ 70 gpl, NaCN 40 gpl, NaOH 20 gpl and sodium zirconate 2 gpl at a temperature of 298K with a current density of 10Amp/ dm² and cadmium-zirconium from Cd(CN)₂ 30 gpl, NaCN 50gpl, NaOH 20 gpl and sodium perzirconate 5 gpl at a temperature of 298K and a current density of 2 Amp/dm².(43).

2.1.6.3. Application of Copper – Zirconium alloys

Copper rich alloys are of interest for application at elevated temperature of improved strength and conductivity (thermal and electrical) are prime considerations in Hi-Tech areas. Example. Resistance welding electrodes, high voltage switches, motor commuters, continuous casting moulds, heat exchanges are application of interest. Fusion reactor first walls (44), water-cooled gas turbine blades (45), targets for neutron irradiations (46) are some of the area where high performance copper alloys are required. The requirements include very high conductivity (better than 50 % IACS), ability to with stand high brazing temperatures (>1173K) and outstanding properties over a range of temperature 293 to 673 K. This finds application in nuclear fusion reactor –Tokomak- parts like, Water-cooled grids for lon source, Hypervapotran elements and some critical components for Neutral Beam Injector unit (47-51). The following are some of the copper-zirconium super alloys widely used in hi tech fields.

Dilute Cu – Zr (up to 0.15 w/o Zr) alloys are highly conductive (better than 90 % IACS) but the response to age hardening is small and strength is primarily developed through thermo mechanical treatments and age hardening is achieved by adding Cr (≈ 0.5 w/o) to Cu –Zr binary.
Copper – Zirconium alloy, which can achieve an increase in strength with a low additive concentration is the most suitable for high temperature and high conductivity applications and has the electrical conductivity almost equal to that of oxygen free high conductivity copper (OFHC). This Copper – Zirconium alloy, variations in magnetization studies shown a non-magnetic state, that is preferred for lead frame materials for audio and hall elements. Heat resistance of Copper Zirconium is in order of high and it can withstand the thermal effect and this alloys are sufficiently stiff and no reduction in stiffness.

The following table gives a view about some of the mechanical properties of the existing Copper Zirconium alloys, which are produced by powder metallurgy route.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Alloy</th>
<th>UTS (MPa)</th>
<th>Elongation (%)</th>
<th>Electrical Conductivity (% ICAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu Ni Ti</td>
<td>641</td>
<td>9</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Cu-Cr Zr-Al</td>
<td>517</td>
<td>9</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>Cu-0.06Mg-0.6Cr-0.1Zr (MZC)</td>
<td>497</td>
<td>18</td>
<td>52</td>
</tr>
</tbody>
</table>
Mechanical properties of Copper Zirconium alloys (53)

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Alloy Name- (commercial)</th>
<th>Zr %</th>
<th>Strength kg/mm²</th>
<th>Elong %</th>
<th>Hardnes (HV)</th>
<th>Elect. Cond % IACS</th>
<th>Thermal expansion ratio X 10⁻⁵°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2 Zr – OFC</td>
<td>0.015 0.030</td>
<td>30 to 37</td>
<td>3 to 8</td>
<td>105 to 120</td>
<td>97</td>
<td>17.7</td>
</tr>
<tr>
<td>2.</td>
<td>5 Zr – OFC</td>
<td>0.025 0.060</td>
<td>37</td>
<td>3</td>
<td>120</td>
<td>96</td>
<td>17.7</td>
</tr>
<tr>
<td>3.</td>
<td>C 151</td>
<td>0.050 0.150</td>
<td>35 to 40</td>
<td>5 to 8</td>
<td>105 to 120</td>
<td>95</td>
<td>17.7</td>
</tr>
<tr>
<td>4.</td>
<td>2 Zr – SH</td>
<td>0.015 –0.03</td>
<td>45</td>
<td>7</td>
<td>135</td>
<td>94</td>
<td>17.7</td>
</tr>
<tr>
<td>5.</td>
<td>C 151-SH</td>
<td>0.05 0.15</td>
<td>50</td>
<td>10</td>
<td>140</td>
<td>92</td>
<td>17.7</td>
</tr>
<tr>
<td>6.</td>
<td>OFC (Cu 99.6 min)</td>
<td>—</td>
<td>37</td>
<td>9</td>
<td>120</td>
<td>101</td>
<td>17.7</td>
</tr>
</tbody>
</table>

It is assumed that Zirconium present in copper can be yielded the following improved properties,

* Good strength at elevated temperature
* Very good conductivity
* Very good heat resistance
* Non-magnetic
* Excellent wire bond ability
* Chemical characteristics as oxygen free deposit.

Hence for this studies, zirconium has selected as an additive to be co deposited along with copper to achieve the improved strength, low dissolved oxygen content and improved conductivity for hi tech applications.
2.2. SCOPE OF WORK

Heavy deposition technique has been adopted for many applications. In this, copper deposits are normally used from consumer goods to space applications. Copper deposit is produced mostly from acid copper electrolyte by electroplating / electro forming process but consumes time with the limited mechanical properties. To achieve some improved mechanical properties for Hi-tech areas, with improved conductivity, tensile strength, elongation, hardness the conventional baths cannot be used. High-speed deposition work can be considered by increasing the current density to achieve the above desired properties. For increasing the cathode current density, forced electrolyte spray system is one among the parameters to be used and this only minimize the time of deposition. The forced spray of electrolyte, replenish the diffusion layer in the electrolyte near the cathode and reduce the deposition time. In this work the deposition is to be carried out in copper by adopting forced flow technique of the electrolyte by the right choice of nozzle / orifices.

Besides the flow conditions, metal ion concentration and current density are also critical factors in achieving High Speed Deposition (HSD). Towards the end, acid copper bath of various formulations are to be prepared and tried. Also some modified cyanide and pyrophosphate baths too are to be experimented for comparison of quality of the deposits. The usual Hull cell studies are to be resorted to fix the optimum current density with right choice of experiment temperature. Different orifices of various diameters on suitable PVC pipes are to be tried as orifice/nozzle and the Reynolds number for the effective turbulence conditions in the electrolyte are to be determined to quantify the flow pattern. With the optimized experimental conditions, copper foils of moderate thickness are to be developed, to be tested for some of the mechanical properties like strength, elongation, hardness, wear resistance besides their internal stress. The most striking property of copper namely its electrical resistivity is tried to be
measured as a function of some of the experimental parameters. A small concentration of zirconium is to be tried to be incorporated into the deposit for further improvement of the above mentioned properties besides its known oxygen scavenger ability in copper matrix. Hence a suitable incorporation of above element will be another thrust aspect of the present investigation. The usual XRD and SEM studies are to be carried out to study the texture as well as surface topography of the deposit that normally have a direct bearing on many of its mechanical properties. In short the present investigation is for High Speed copper-zirconium deposit development through the normal aqueous electrodeposition route.

* * * * *
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