Electroplating*
(Electrolytic Deposition (ELD) Coating)

***Coating in a solution with electric current**

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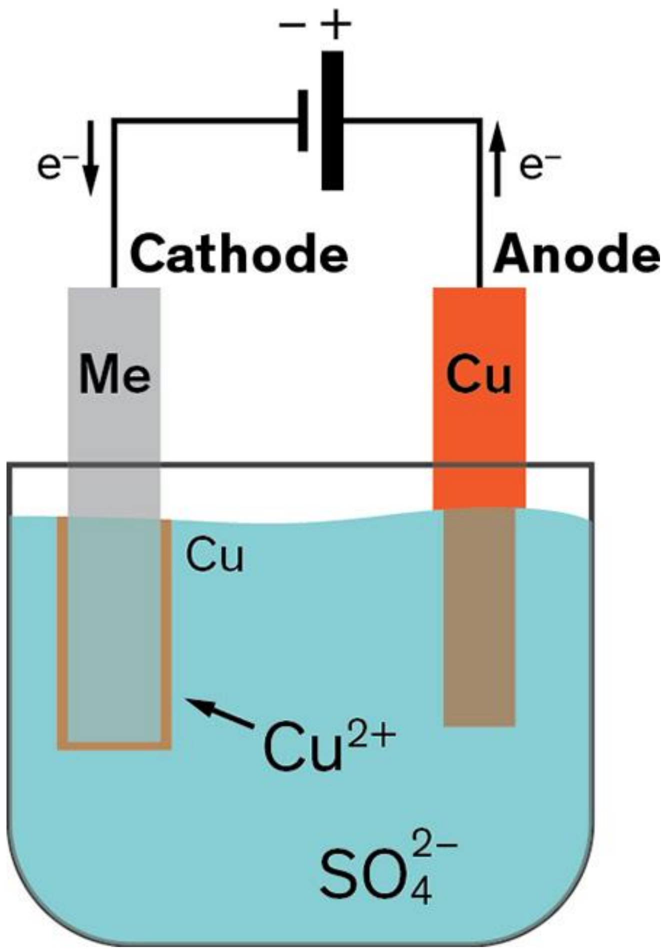
- The workpiece (cathode) is plated with a different metal (anode) while both are suspended in a bath containing a waterbase electrolyte solution. Although this process involves a number of reactions, the basic procedure is that the metal ions from the anode are discharged (under the potential from the external source of electricity), they combine with the ions in the solution, and are deposited on the cathode.



Cathode reaction

$Cu^{+2} + 2e \rightarrow Cu$

Anode reaction

$Cu \rightarrow Cu^{+2} + 2e$

* Coating thickness is directly proportional with coating time and current.

Pre-treatments before coating:

- There is not any film or oxide layer exist on the surface of base material.
- Right surface cleaning provides high bonding strength.

Factors effects coating quality:

- Bath composition, bath type, additives (moisturizer, shiner) and hardness of water. (Hard water is water that has high mineral content.)
- Current density, concentration, mixing, temperature, structure of base material, nature of electrolyte, pH.

- The volume of the plated metal can be calculated from the expression

$$\text{Volume of metal plated} = cIt$$

where I is the current in amperes, t is time, and c is a constant that depends on the plated metal, the electrolyte, and the efficiency of the system, being typically in the range of 0.03 to 0.1 mm^3/amp-s.

- For the same volume of material deposited, the deposited thickness is inversely proportional to the surface area. The time required for electroplating is typically long, because the deposition rate is generally on the order of 75 μm/hr. Thin electroplated layers are typically on the order of 1 μm, and thick layers can be as much as 500 μm.

- The plating solutions are either strong acids or cyanide solutions. As the metal is plated from the solution, it has to be periodically replenished. This is accomplished through two principal methods: (a) salts of metals are occasionally added to the solution; or (b) a sacrificial anode of the metal to be plated is located in the electroplating tank, which dissolves at the same rate that metal is deposited.
- There are three main methods of electroplating:

a) In rack plating, the parts to be plated are placed on a rack, which is then moved through a series of processing tanks.

b) Barrel plating is used to plate small parts, such as bolts, nuts, gears, etc., that are placed in a container, or barrel, often constructed of polypropylene. Electrolytic fluid flows through the barrel and provides the plating metal. Electric current is provided by contacts in the barrel; current is provided to every part through contact with the barrel and other parts. During barrel plating, the barrel rotates to ensure plating uniformity.

c) In brush processing, the electrolytic fluid is pumped through a hand-held brush with metal bristles. It is suitable for plating of very large parts, and can be used to apply coatings on large equipment without the need for disassembly.

- Common plating materials include chromium, nickel, cadmium, copper, zinc, silver, gold, and tin. Chromium plating is carried out by plating the metal first with copper, then with nickel, and finally with chromium. Hard chromium plating is deposited directly on the base metal, and has a hardness of up to 70 HRC.
- Typical electroplating applications include copper plating of aluminum wire and phenolic printed circuit boards, decorative chrome plating of automotive parts, tin plating of copper electrical terminals (for ease of soldering), and plating of various components for enhanced appearance and resistance to wear and corrosion.

- Because they do not develop oxide films, noble metals (gold, silver, and platinum) are important electroplating materials for the electronics and jewelry industries.
- Plastics, such as ABS, polypropylene, polysulfone, polycarbonate, polyester, and nylon, can have metallic coatings applied through electroplating. Because they basically are not electrically conductive plastics must first be preplated by such processes as electroless nickel plating (see below).
- Parts to be electroplated may be simple or complex, and size is not a limitation; complex shapes may, however, develop varying plating thicknesses.

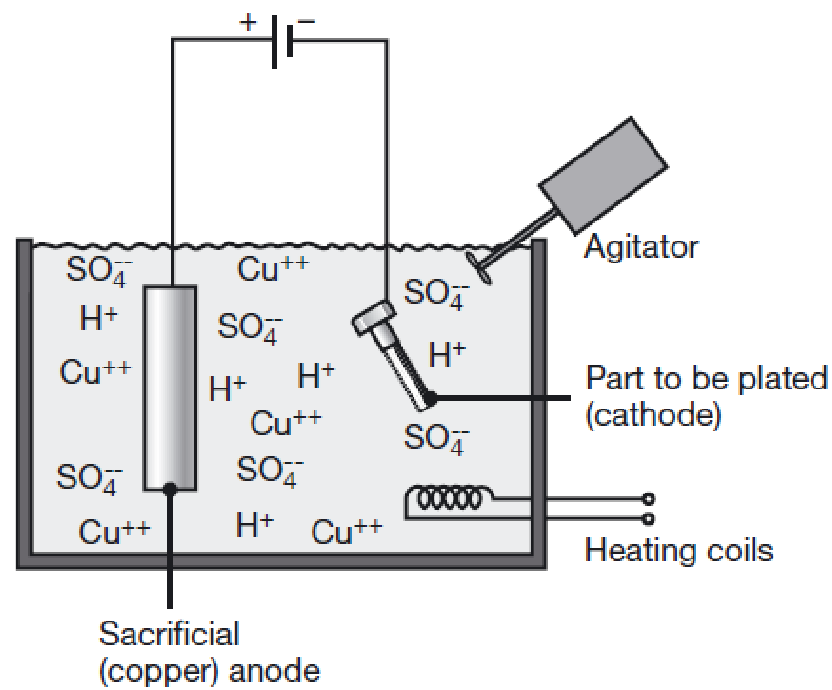
Advantages of electroplating

- There is not any shape distortion or metallurgical change in work piece because bath temperature is less than 100 °C.
- Coating conditions can be set for modify coating hardness, internal stress and metallurgical properties.
- Denser coatings are obtained.
- Coating thickness is directly proportional with coating time and current.
- Deposition rate rarely exceed 75 μm/h however it can be accelerated with mixing and reaches 150-200 μm/h for some metals.
- Process is suitable for automation and it has economical advantages to other coating processes.

Electroplating of copper

It has wide spread of applications because of:

- Fills surface roughness
- Coating brightly
- Provide corrosion protection
- To obtain continuous ductile surface
- For excellent electrical properties
- Accordance (coherence) with Ni or Cr plating



Bath types for copper coating:

- Acid-sulphate solutions.
- Acid free cyanide or alkaline solutions.
- Pyrophosphate, fluoroborate solutions.

* Adhesion strength of acid-copper solution coating is low.

* Adhesion strength of cyanide solutions is better.

* Cyanide is so toxic that it must be completely separated from waste water.

Alkaline copper coating baths

- In cyanide baths copper ions has +1 degree.
- Alkaline cyanide copper solution provides easy control of coating thickness and homogeneously dispersed fine grains to whole surface.
- Cyanide is very harmful for environment and human health, because of this cyanide free alkaline solutions were developed for many applications.
- Cyanide free systems give cleaner surfaces and they are used for produce thick coatings as a result of high deposition rates.

- The most significant properties of dilute cyanide are performance and appearance of coatings.
- 3-8 µm copper coatings on to steel surfaces must be carried out in cyanide solutions.
- When 10 µm coatings are desired, additional thickness is provided with acidic solutions in high concentrations.
- High concentrated cyanide baths give thicker and faster coatings. Moreover, with appropriate additives depositions can be brighter and more ductile.
- High current density may cause corrosion of the anode. Addition of Rochelle salt* prevents this effect.

(*Rochelle salt: potassium, sodium tartrate tetrahydrate $KNaC_4H_4O_6 \cdot 4H_2O$)

Acidic copper coating baths

- In acidic baths copper ions has +2 degree.
- They are the simplest baths for electroplating of copper.
- Applied as a first coat before bright nickel plating.
- Because of perfect dispersion power in micro scale, it effectively fills scratches, grooves and pores.
- Its advantages:

  - high deposition rate

  - Low cost

  - Easy control

  - Low toxic effect

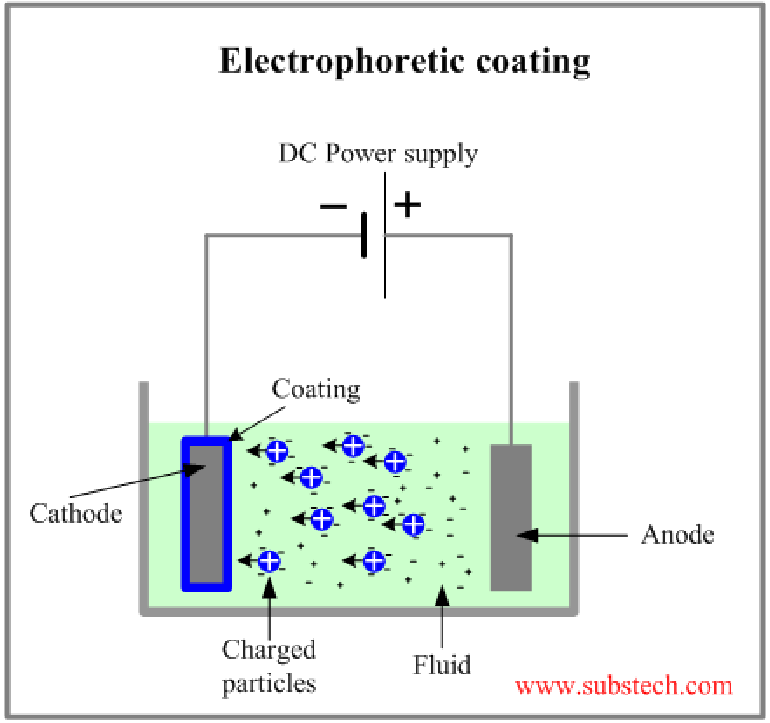
  - Good homogeneity in strength and ductility.


Electroplating



Electrophoretic Deposition (EPD) Coating

- EPD is another form of electrodeposition that provides thicker coating layers with a colloidal nature.
- Using an electric field in a unit cell, similar to that of electroplating, thin films form on substrates by coagulation of colloidal particles.



- EPD is a multi-phase technique, in which:

1. External electric field forces suspended particles in electrolyte toward one electrode called electrophoresis.
2. The moving particles gather in one electrode and form a larger coagulated particle.
3. The larger particles deposit on the surface of the electrode, which is a to be coated substrate.

- Finally, a thick coating layer will be created on the substrate having a powder-shaped structure.

- Densification processes (e.g., furnace curing, light curing, sintering, etc.,) are recommended to increase the quality of the protective layer.
- Up to now, numerous applications have been introduced for EPD that include coating, selective deposition, graded material deposition, porous structure deposition and biomedical applications.
- The materials used in EPD are commonly borides, carbides, oxides, phosphates and metals.

- Table summarizes ELD and EPD processes regarding their characteristics and

Property	ELD	EPD
Coating elements	Ions	Solid particles
Surface charge	Medium	High
Preferred electrolyte	Water	Organic
Ionic electrolytic strength	High	Low
Electrolytic conductivity	High	Low
Approximate rate of deposition	0.1 μm/min	1000 μm/min

Video links

- https://www.youtube.com/watch?v=BZGDxL9pBC4
- https://www.youtube.com/watch?v=OdpvTr-7bYI
- https://www.youtube.com/watch?v=FnJ0V7B7nKo
- https://www.youtube.com/watch?v=Q8Xo43sfLgY
- https://www.youtube.com/watch?v=ggDITboNBm4
- https://www.youtube.com/watch?v=f89_ZxVFn1w
- https://www.youtube.com/watch?v=e7HfC8Ct5tI

Electroless coating (plating)*

*** Coating of some metals to substrates in appropriate solutions without using any external current source.**

- This process is carried out by chemical reactions and without the use of an external source of electricity. In electroless nickel plating, nickel chloride (a metallic salt) is reduced (with sodium hypophosphite as the reducing agent) to nickel metal, which is then deposited on the workpiece.

Electroless coatings can be divided into three groups:

- Alloy coatings
- Composite coatings
- Metallic coatings

- Electroless coatings have superior physicochemical and mechanical properties. Thus their applications are increasing.

Some properties of electroless coatings:

- Uniformity ($\pm$ 2.5 micron tolerance).
- Excellent corrosion resistance.
- Wear resistance.
- Soldering ability.
- High hardness.
- Amorphous, microcrystalline deposition.
- Low friction coefficients.
- High reflection.

Electroless nickel coating

- They are not pure Ni layers. Mostly Ni-P and Ni-B alloys.
- When a material with conductive and catalytic surface is dipped into solution which contains nickel salts. Reduction of Ni ions occur on the material surface and at this time Ni makes alloys with P and B.
- Reduction goes on surface of coated Ni which also shows catalytic effect.

Advantages of electroless nickel coating

- Coatings can be produced in desired thickness.
- Coating happens on all regions contacted with solution. Equivalent thickness is produced even on irregular (rough) surfaces.
- It has wear resistance. High hardness can be produced with heat treatments.
- It can be easily coated to metallic and non-metallic surfaces after certain pre-treatments.
- It is a suitable technique both for mass and hanging production.
- Expensive current source and hanger system are not necessary.

Comparison of electro and electroless Ni coating

Properties	Electro	Electroless
Composition	99 % Ni	2-15 % P + 98-85 %Ni
Appearance	Opaque to bright	Semi gloss (yarı parlak)
Structure	Crystalline	Amorphous
Density	8.9 g/cm^3	7.9 g/cm^3
Melting Temp.	1455 °C	890 °C
Hardness	40-150 HV	500-600 HV
Hardness after heat t.	40-150 HV	1000 HV
Wear resistance	Medium	Excellent
Corrosion resistance	Good (porous)	Very good (low porosity)

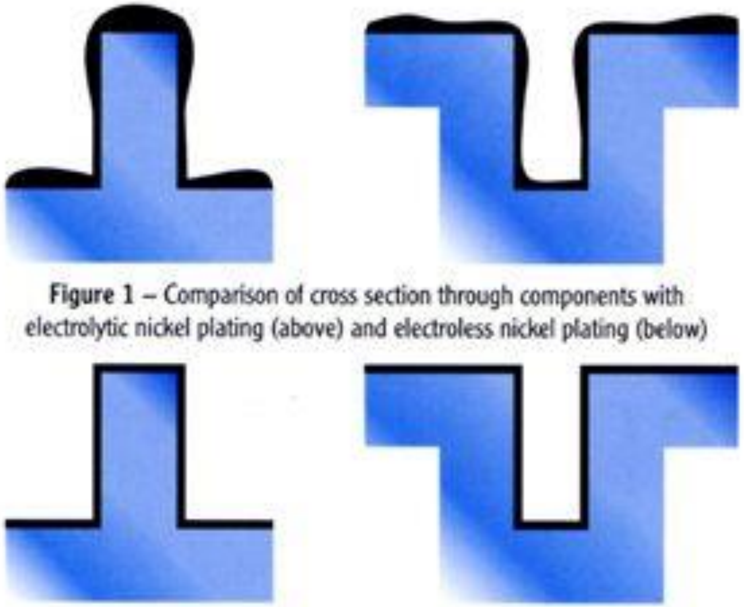
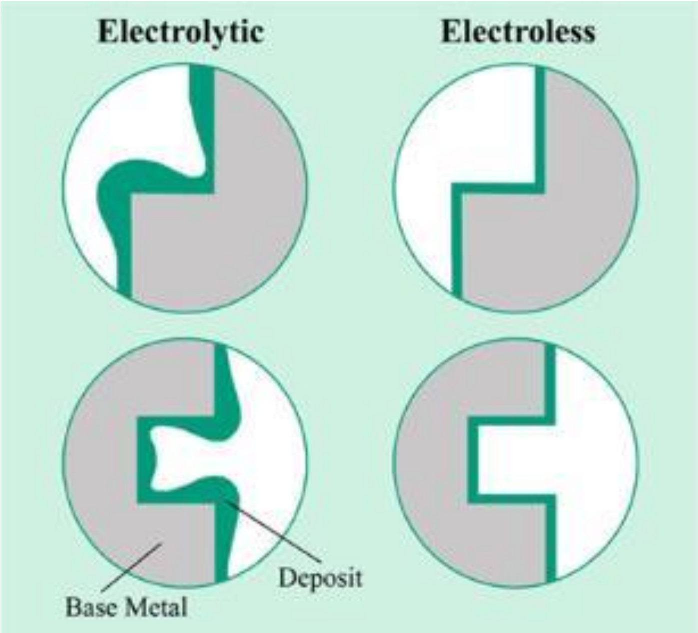


Figure 1 – Comparison of cross section through components with electrolytic nickel plating (above) and electroless nickel plating (below)



- If surfaces are not catalytic or conductive (like polymers) they can be transformed with special treatments.
- First step of electroless Ni plating of plastics is treatment in chromic and sulfuric acids. Then process goes on in solutions contain Sn and Pt group metals.

(Pt group metals: Ruthenium (Ru), Rhodium (Rh), Osmium (Os), Iridium (Ir), and Platinum (Pt).

- To obtain a certain reaction flow rate (coating rate), solutions should be heated up.
- Acceptable coating rates can be obtained above 65 °C.
- The most common temperature range in applications is 85-95 °C.

- $NiSO_4 + NaH_2PO_2 + H_2O \xrightarrow[\text{(Temperature: 85-90°C)}]{\text{coating}} Ni + NaHPO_3 + H_2SO_4$

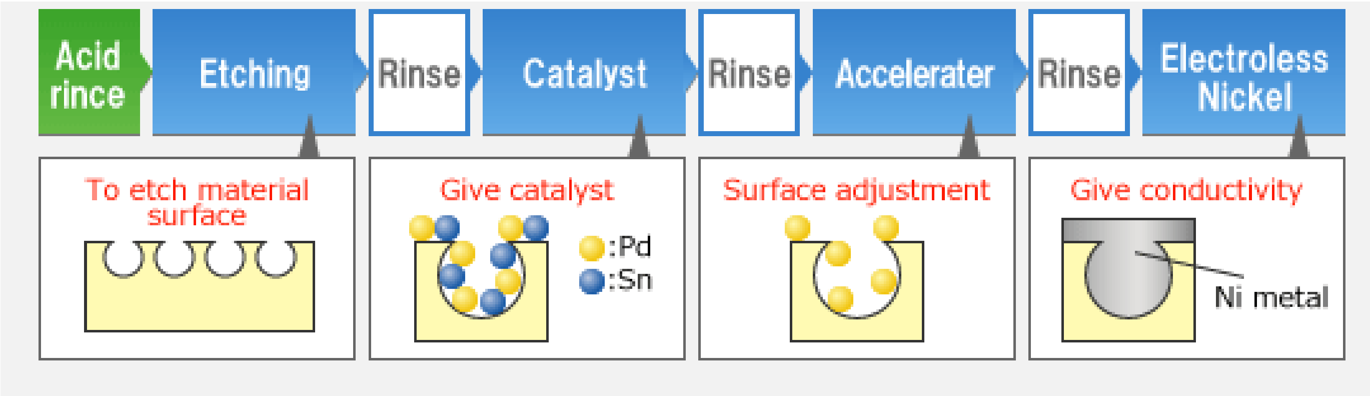
- At 100 °C segregation (decomposition) starts in solution.
- Coatings on plastics are carried out in lower temperatures.

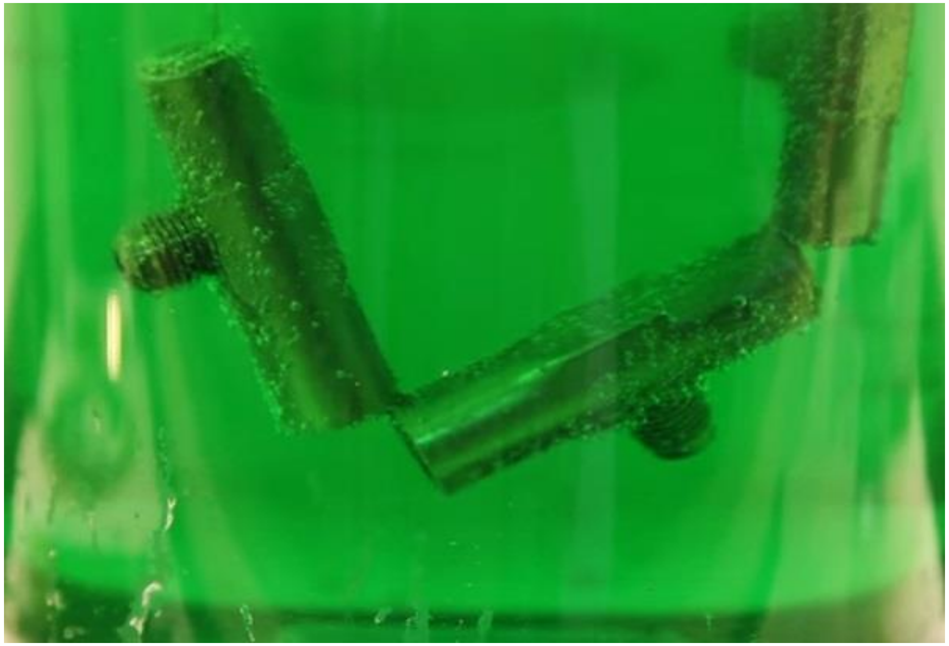
Coating thicknesses:

- 20 – 60 μm most common thicknesses.
- 2 μm for electronics.
- 200 μm for Al mirrors.

Examples for application areas:

- Pressured vessels (steel).
- Valves (stainless steels).
- Landing gears of some aeroplanes (aluminium).
- Pipes (copper/steel).
- Memory discs (aluminium)
- Polypropylene and ABS parts.
- Surgical instruments.
- Fuel rails of alcohol engines.
- Petrol engine pistons.


Acid rince
Etching
Rinse
Catalyst
Rinse
Accelerater
Rinse
Electroless Nickel
To etch material surface
Give catalyst
:Pd
:Sn
Surface adjustment
Give conductivity
Ni metal



Video links

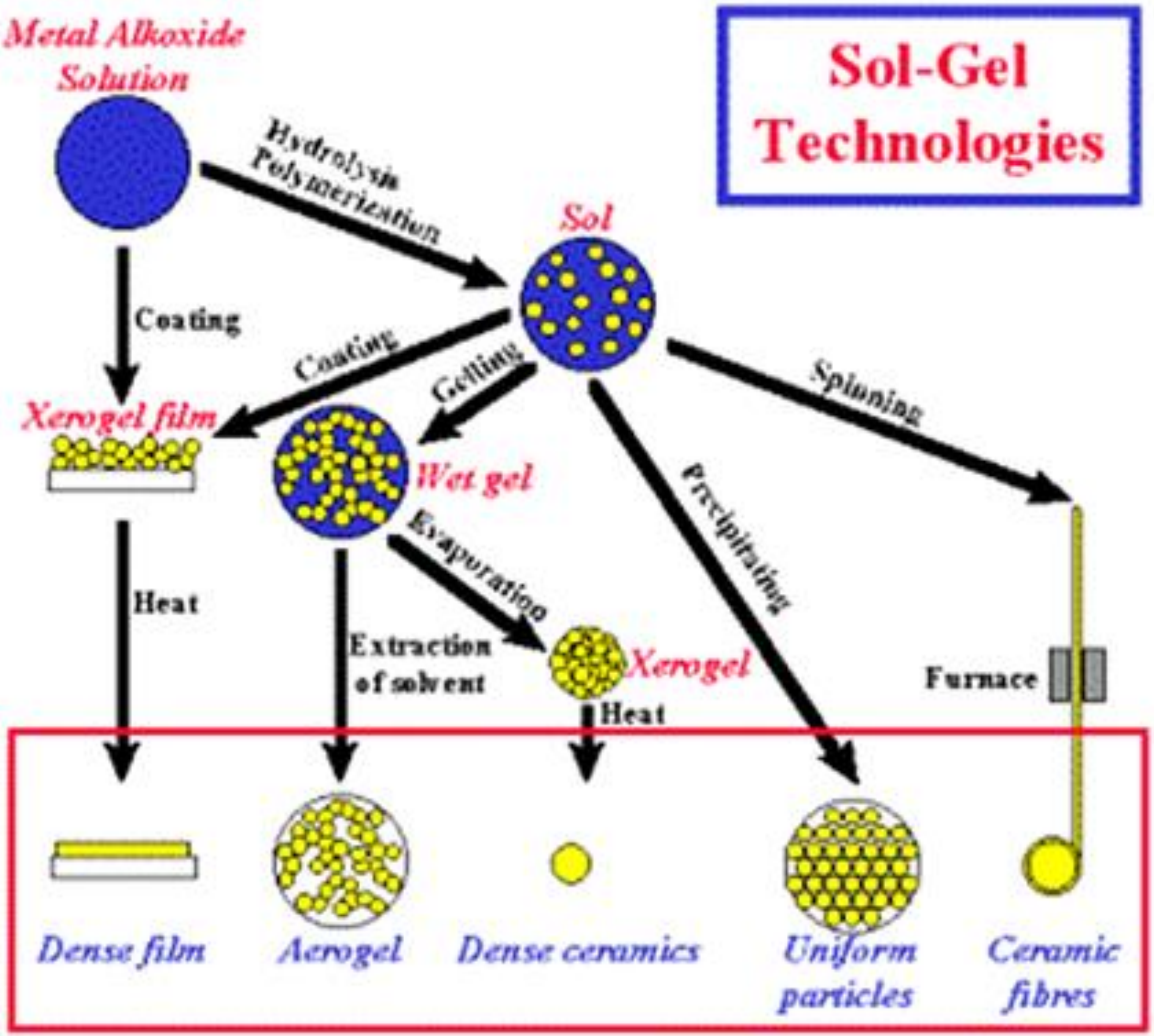
- https://www.youtube.com/watch?v=s1kn5rk8EyE
- https://www.youtube.com/watch?v=WRcf2LO23Fg
- https://www.youtube.com/watch?v=EuKhSUtlJg8
- https://www.youtube.com/watch?v=CVzMNzI6mV8
- https://www.youtube.com/watch?v=M_fWf6h6rEo

Sol–Gel* Coatings

*** Sol-gel is a general name of a technology producing ceramic, glass or composite materials starting from a solution.**

In this technique ceramic or glass materials can be produced in various shapes:

- Ultra fine or spherical shaped pure powders.
- Thin film coatings.
- Ceramic fibers.
- Microporous inorganic membranes.
- Monolithic porous aerogel materials.
- Extra porous aerogel materials.


Sol-Gel Technologies
Metal Alkoxide Solution
Hydrolysis Polymerization
Sol
Coating
Coating
Gelling
Spinning
Xerogel film
Wet gel
Precipitating
Evaporation
Heat
Extraction of solvent
Xerogel
Heat
Furnace
Dense film
Aerogel
Dense ceramics
Uniform particles
Ceramic fibres

- Sol-gel technique is a kind of chemical process and it can be applied to all kinds of solutions and suspensions which can get gel.
- Sol-gel process express transformation from liquid «sol» to solid «gel».
- **Sol-gel:**
  - Gelation of colloidal suspensions.
  - Gelation of 3D solid inorganic network structures from continuous liquid phase.

*Colloidal particle: grain size lower than 500 nm.

Process stages of Sol-Gel

- Preparing homogeneous solution.
- Hydrolysis.
- Polymerization.
- Densification.
- Gelation.
- Rinsing (washing).
- Aging (curing).

<u>Coating techniques:</u>

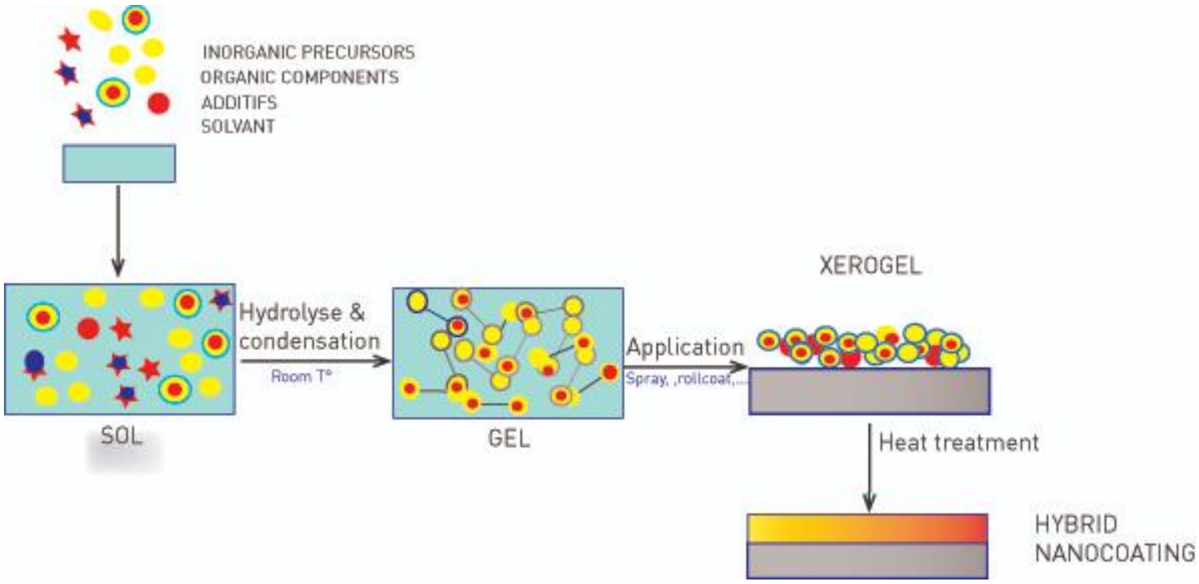
- Dip coating.
- Spin coating.
- Spray coating.

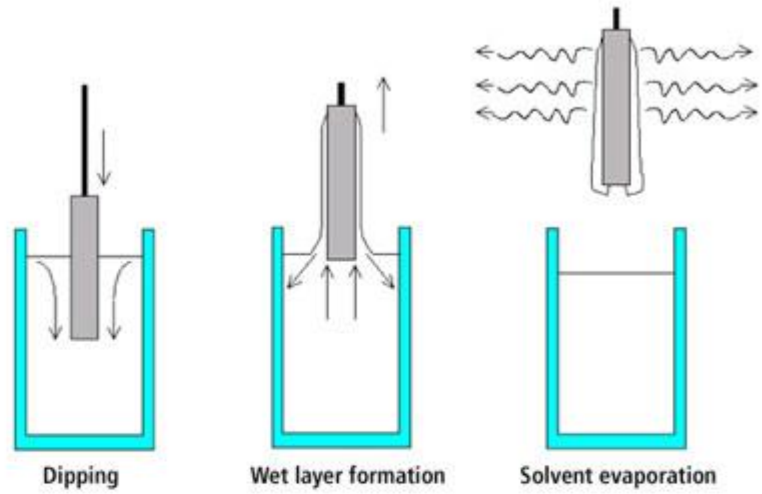
Applications of Sol-Gel coatings

- To increase corrosion resistance of steel, surfaces are coated with ceramic based SiO_2, ZrO_2 layers.
- Sol-gel process is used to coat galvanized surfaces, high Si steel sheets and magnetic steel sheets with protective silicate or chromate layers.
- Ferroelectric PZT (lead-zirconate-titanate) coatings.
- High temperature superconductors (Y-Ba-Cu oxide)
- In-Sn oxide conductive coatings.
- Optical and protective coatings of complex oxides.

Advantages of Sol-Gel process

- Easy operation.
- Economical technique.
- Easy production of complex oxides and coatings.
- Easy control of composition and microstructure.




Dipping
Wet layer formation
Solvent evaporation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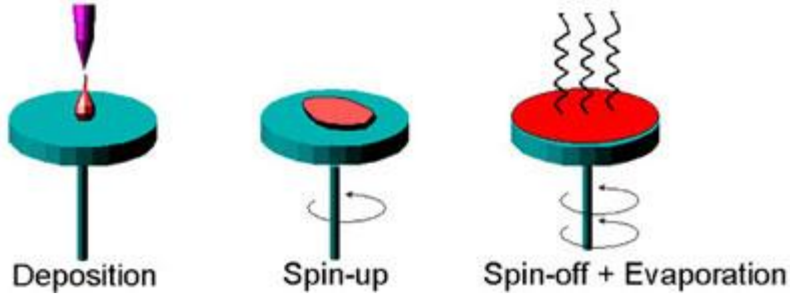
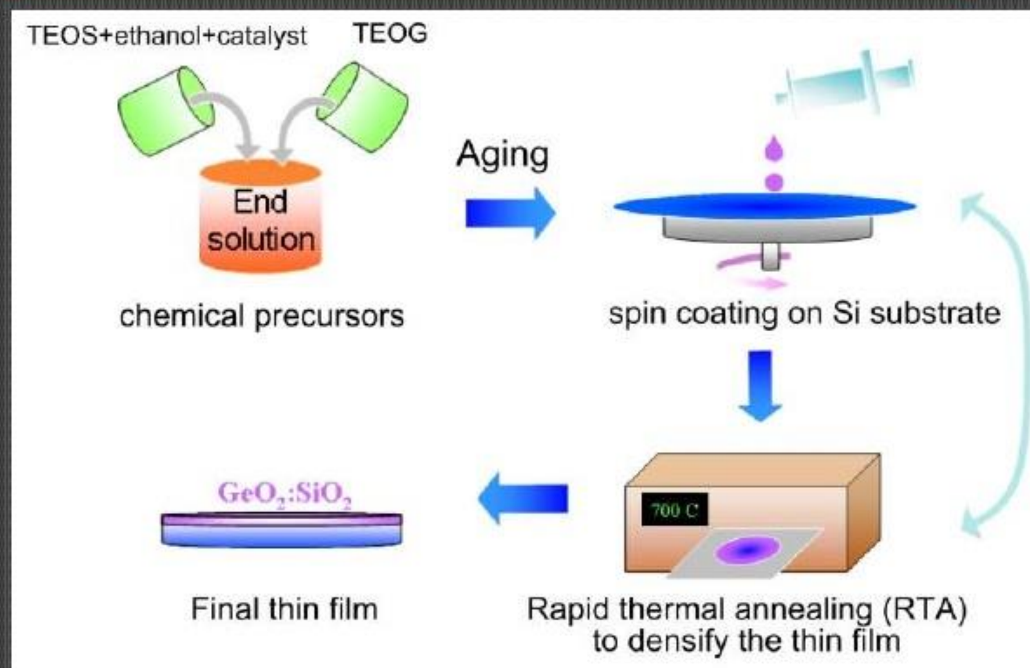
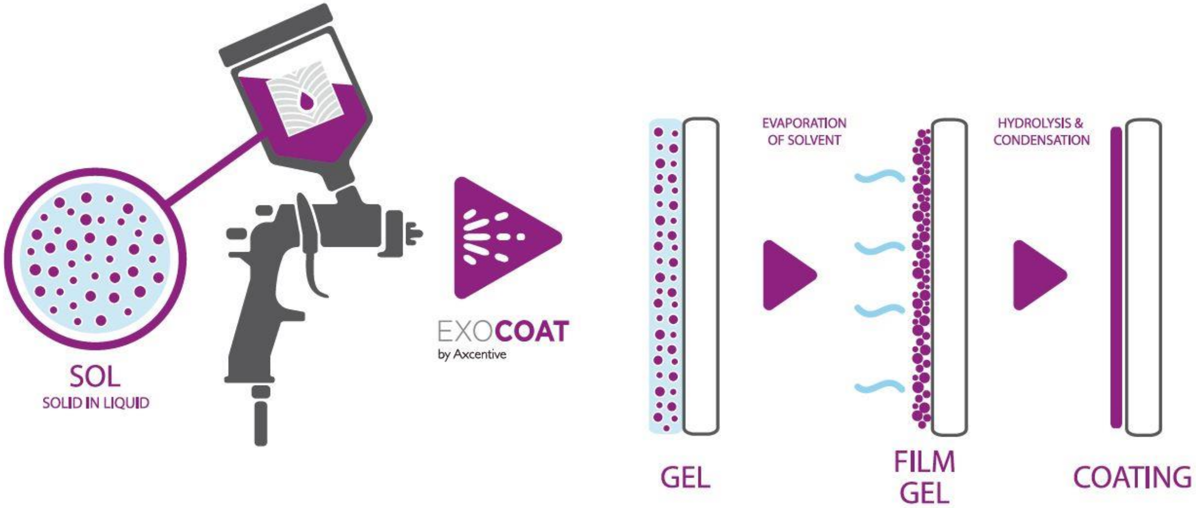
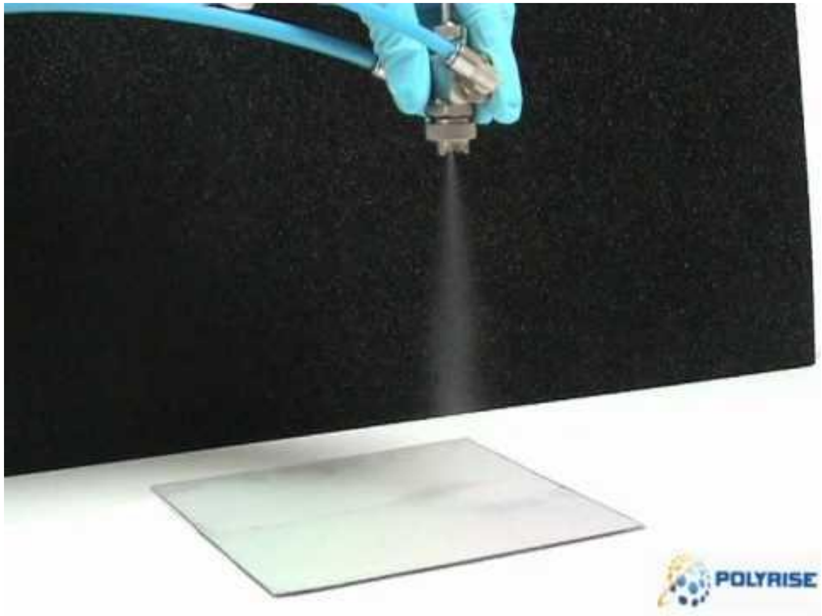


SOL GEL PREPARATION



TECHNOLOGY : SOL-GEL





Video links

- https://www.youtube.com/watch?v=nZgN40EJbAQ
- https://www.youtube.com/watch?v=KirDBLMWhkM
- https://www.youtube.com/watch?v=9s-8-j90zhY
- https://www.youtube.com/watch?v=v178jtHsfFM
- https://www.youtube.com/watch?v=Nf7_bAIZHDU