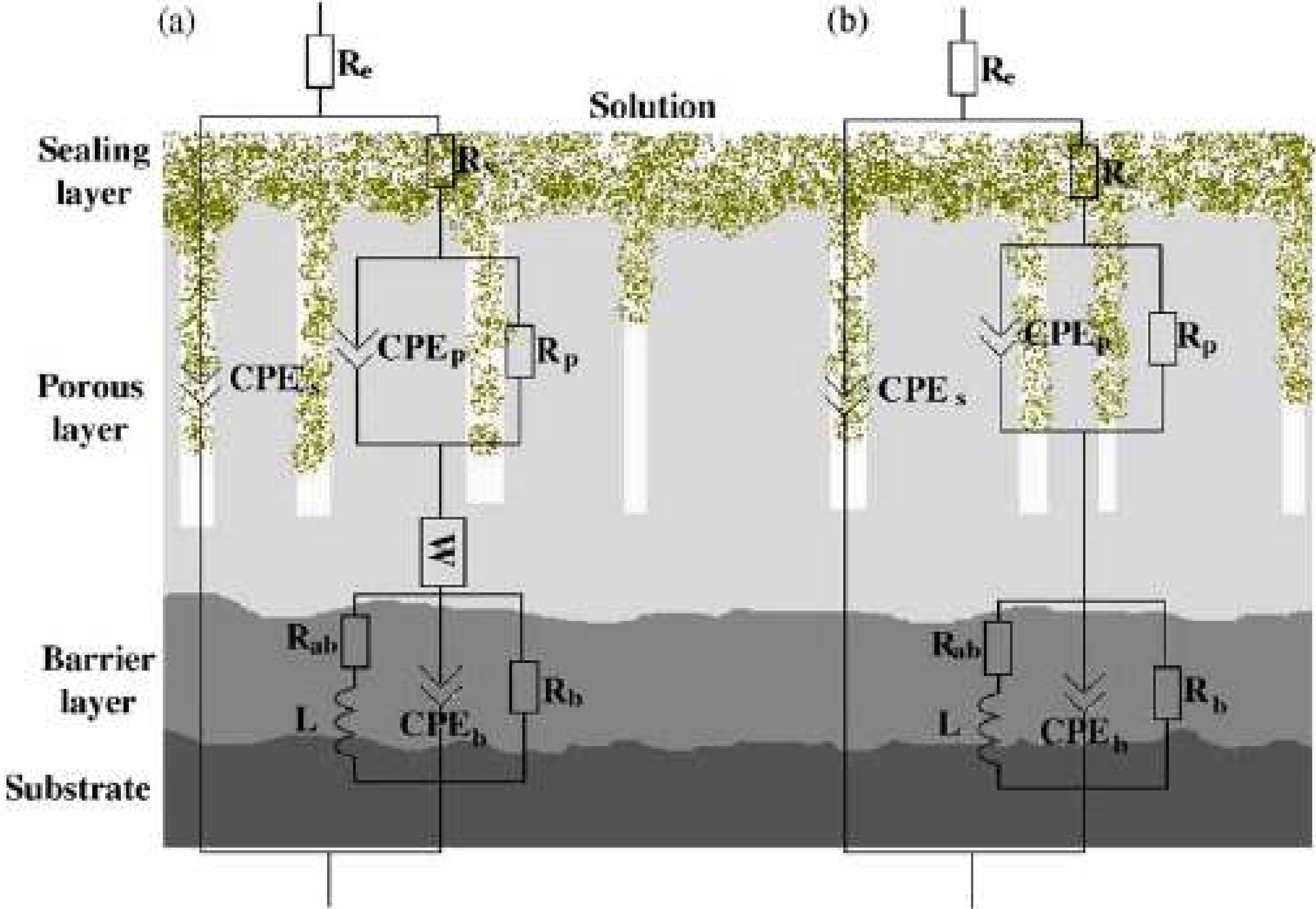
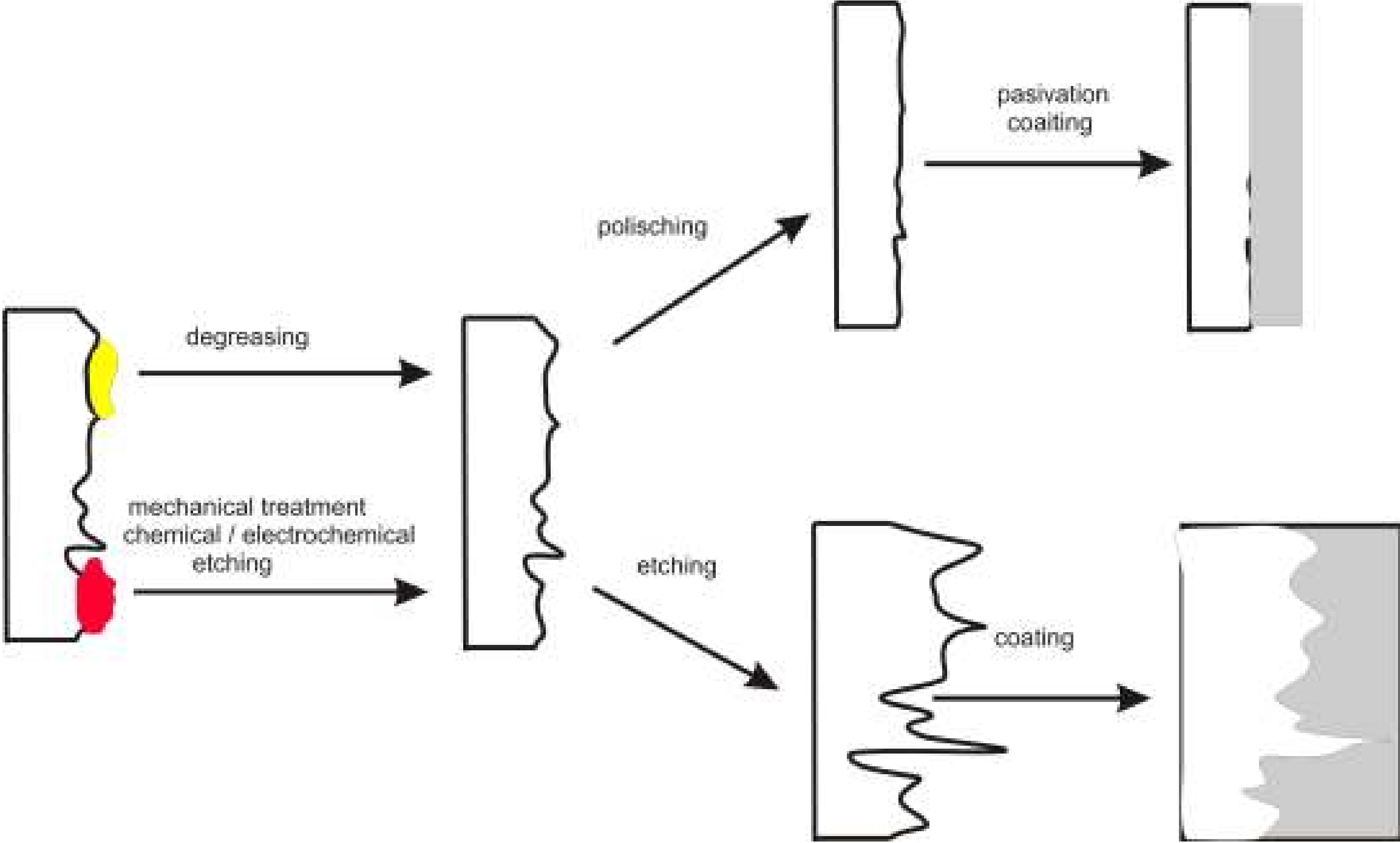
COATINGS



COATINGS
Coatings of metallic, inorganic and organic materials can provide a satisfactory barrier between metal and its environment and can protect the metal surface against corrosion.
The following kinds of anticorrosion coatings can be distinguished:
metallic coatings
inorganic coatings
organic coatings
composite materials

Surface preparation



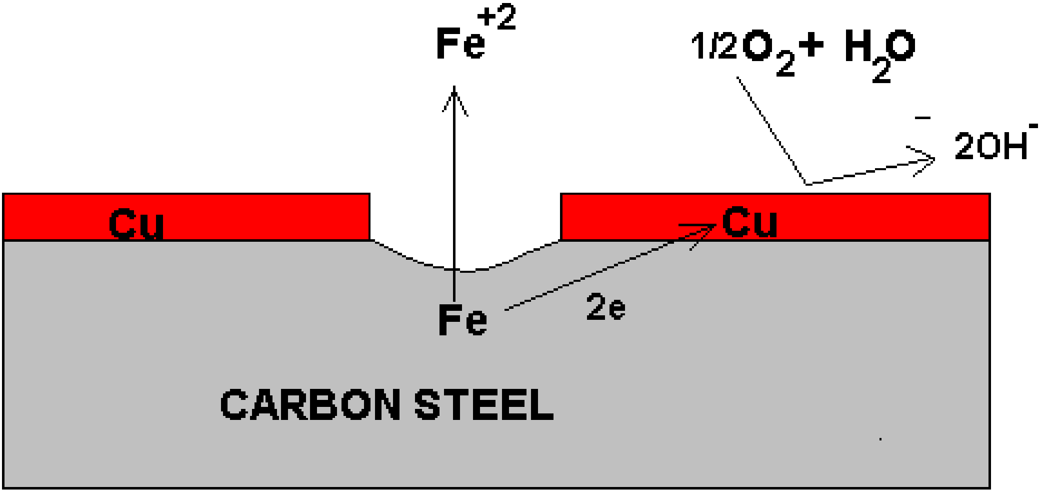
Metallic coatings:

-cathodic (Ni, Cr, Cu and copper alloys, noble metals - Au, Ag, Pt)

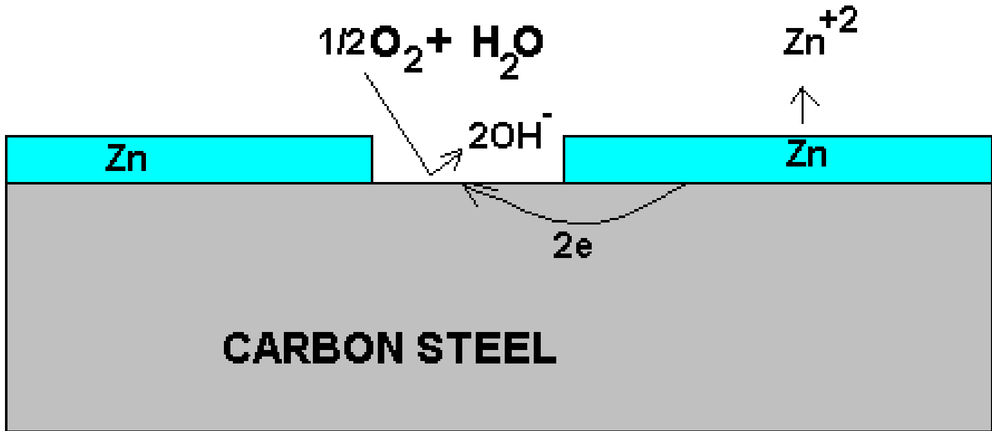
These coatings are composed from corrosion resistant metals and in corrosive medium, are nobler than underlying metal surface (are cathodic in reference to the protected metal).
The damage of the layer creates the corrosion macro galvanic cell with the anodic underlying metal surface and cathodic metal coating.

anodic (Zn, Cd, Al)

Composed from metals which show more negative stationary potential in corrosive medium (are anodic in reference to the underlying metal surface). These coatings can prevent underlying metal surface even by the damage or perforation of the layer - cathodic protection.



Fe^{+2}
$1/2O_2 + H_2O$
$2OH^-$
Cu
Cu
Fe
2e
CARBON STEEL

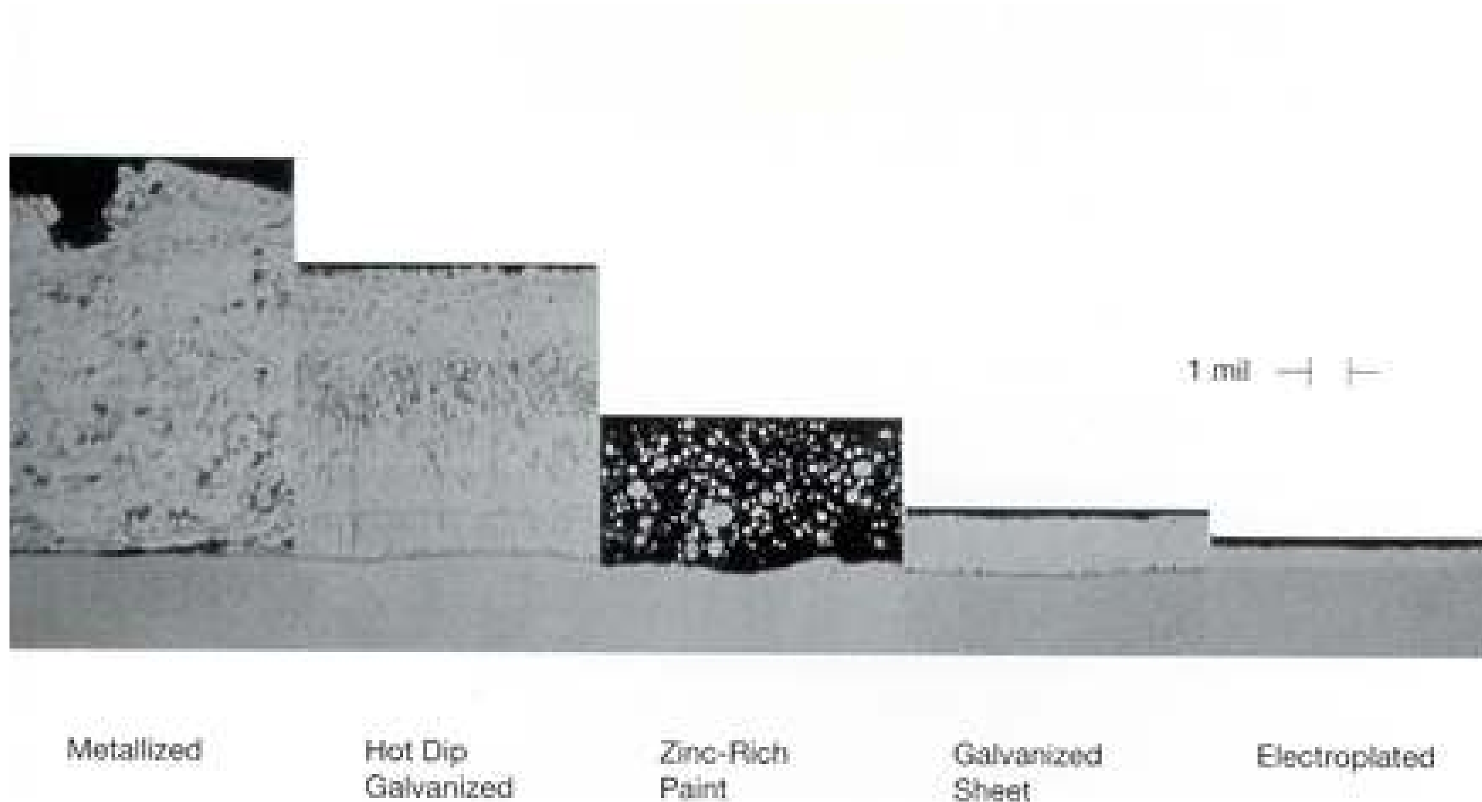


$1/2O_2 + H_2O$
Zn^{+2}
$2OH^-$
Zn
Zn
2e
CARBON STEEL

Methods of preparation:

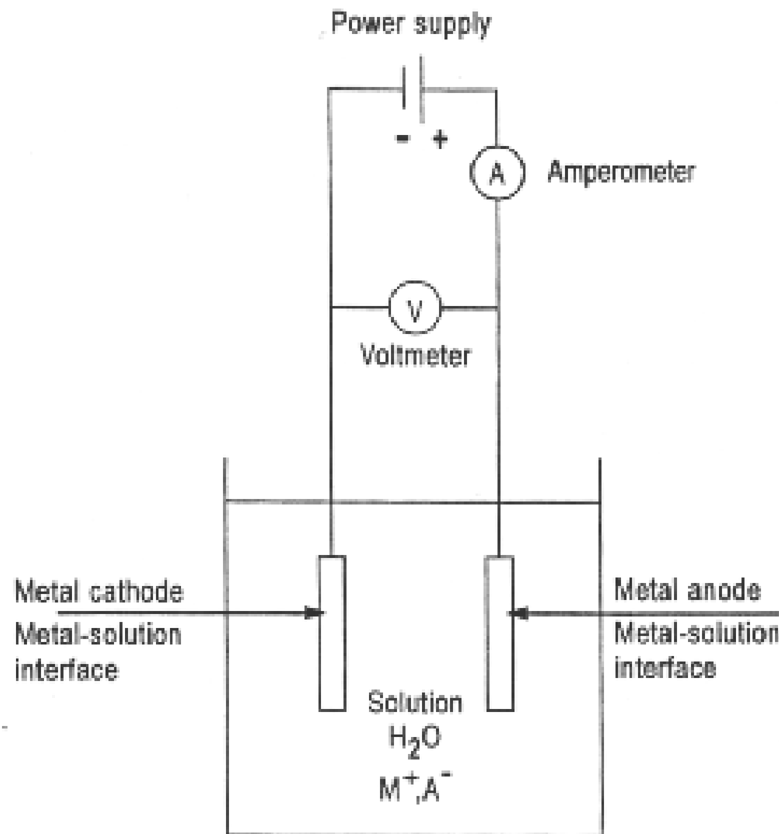
- electrodeposition $Zn^{+2} + 2e \rightarrow Zn$
- cementation $Fe + Cu^{+2} \rightarrow Fe^{+2} + Cu$
- chemical reduction $Ni^{+2} + H_2PO_2^- + H_2O \rightarrow Ni + 2H^+ + H_2PO_3^-$
- metalizing - flame spraying
- cladding
- hot dipping
- vapor deposition
- diffusion
- surface modification (laser surface alloying, ion implantation).

Zinc Coating



This figure shows five different cross section views of zinc coated steel. Each view depicts a different zinc coating method. The corrosion protection provided by each of these methods depends on the amount of zinc present in the coating.

Electroplating



Schematics of an electrolytic cell for plating metal "M" from a solution of the metal salt "MA"

$M^{+n} + ne^- \rightarrow M$

$$m = \frac{1}{n\,F} \int I\,dt$$

D = w / V = w / (A T)

$$T = \frac{w}{A\,D} = \frac{M_w}{n\,F\,A\,D} \int I\,dt$$

"D„is the density of the metal (gram/cm^3):

"w" is the weight of the deposit (gram)

"V" is the volume of the deposited metal in cm^3,

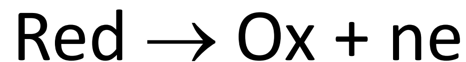
"A" is the area of the deposit in cm^2,

"T" is its thickness in cm.

Chemical deposition of metals

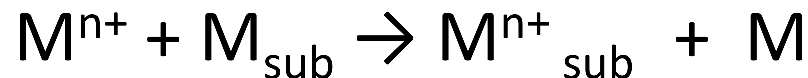
Autocatalytic process of metal deposition on surface of substrate without external current (current-free deposition). Deposited metal catalyses the crystallization and growth of metal layer (even when the surface is completely covered by the layer).

$$M^{n+} + ne \rightarrow M$$



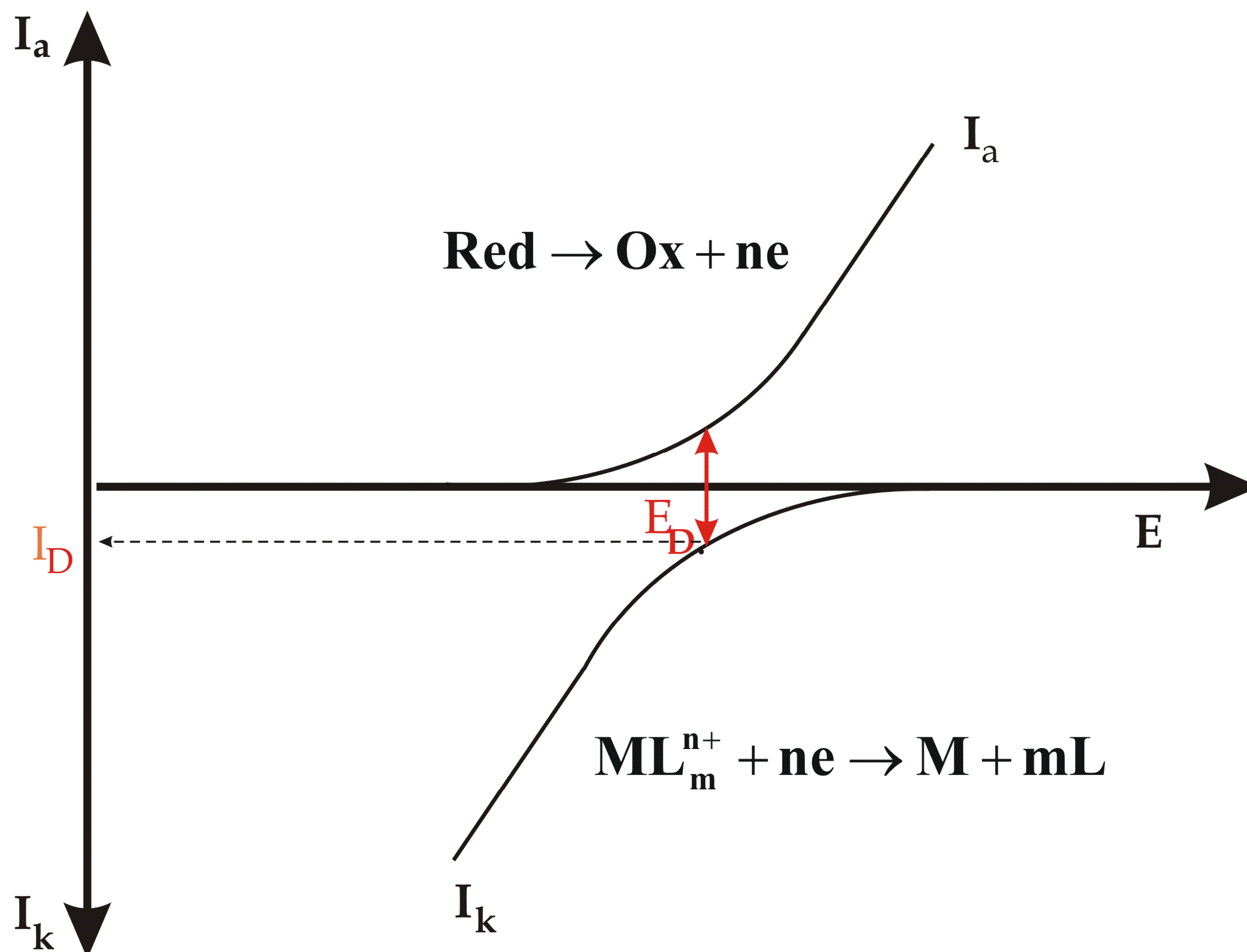
$$Red \rightarrow Ox + ne$$

Metal dismutation is very often called chemical deposition however it is an electrochemical process. The dismutation process is stopped when the surface of substrate is totally covered by deposited film.



$$M^{n+} + M_{sub} \rightarrow M^{n+}_{sub} + M$$

Polarization diagram for current-free deposition of metal



Chemical deposition

Bath composition	Role of the component
Metal salt	Metal source
Reductant	Reduction of metal ions
pH stabilizing agent	Stabilizing of pH
Complexing agent	Complexing of metal ions
others	Bath stabilization, Improving of coating quality

Effectiveness of reducing species

NaH_2PO_2 : Au > Ni > Pd > Co > Pt

HCHO : Cu > Au > Ag > Pt > Pd > Ni > Co

$NaHB_4$: Ni > Co > Pd > > Pt > Au > Ag > Cu

DMAB > Ni > Co > Pd > Au > Pt > Ag

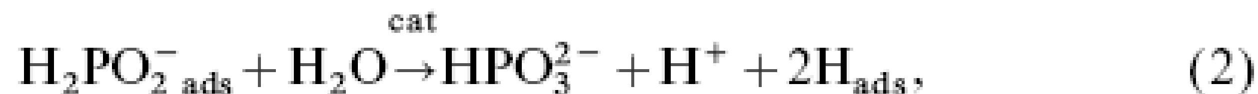
NH_2NH_2 : Co > Ni > Pt > Pd > Cu > Ag > Au

Chemical nickel plating

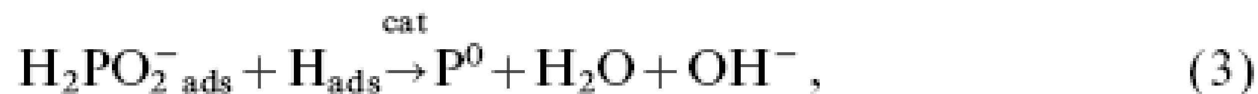
Chemical nickel plating using sodium hypophosphite as reductant leads to deposition of Ni-P layers. The phosphorus content depends on pH of the bath. With decrease of pH increases the P content and corrosion resistance of the layer.

Autocatalytic deposition of nickel can be applied for deposition of Ni-Co and Ni-Fe alloys and composite materials Ni-SiC.

$$Ni^{2+}_{ads} + H_2PO^-_{2\,ads} + H_2O \xrightarrow{cat} Ni^0 + 3H^+ + HPO_3^{2-}, \qquad (1)$$



$$H_2PO^-_{2\,ads} + H_2O \xrightarrow{cat} HPO_3^{2-} + H^+ + 2H_{ads}, \qquad (2)$$



$$H_2PO^-_{2\,ads} + H_{ads} \xrightarrow{cat} P^0 + H_2O + OH^-, \qquad (3)$$

$$2H_{ads} \xrightarrow{cat} H_2. \qquad (4)$$

Chemical nickel plating

Component	Concentration [mol/dm^3]
NaH_2PO_4* H_2O	0.15
$(NH_4)_2SO_4$	0.50
$Na_3C_6H_5O_7$	0.20
$NiSO_4$* $6H_2O$	0.10
temperature: 90^0C pH : 9.0 (NaOH stabilization)	

The effect of pH on phosphorus content and properties of NiP layer Osaka i inni 1988)

pH	P [%]	ρ [μΩ cm]	Ms [emu/g]	structure
10.0	4.6	60.6	15.5	crystalline
9.5	5.3	73.5	9.5	crystalline
9.2	6.6	82.7	4.0	crystalline
9.0	8.0	95.2	1.4	crystalline
8.6	10.4	117.6	0.0	amorphous
8.3	12.3	127.8	0.0	amorphous
8.0	12.8	132.2	0.0	amorphous
6.0	14.0	140.2	0.0	amorphous

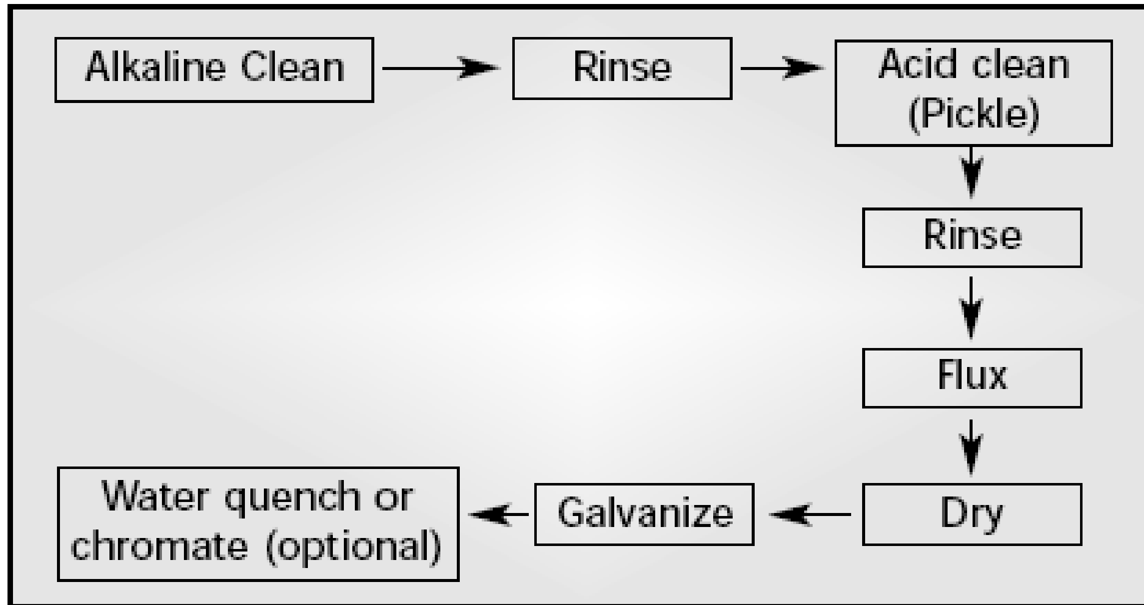
Chemical nickel plating

	Kąpiel		
	acidic	alkaline	borane
Ni source	25g/l $NiCl_2 \cdot 6H_2O$ + 25g/l $Ni_2SO_4 \cdot 6H_2O$	30-40g/l $NiCl_2 \cdot 6H_2O$ + 30g/l $Ni_2SO_4 \cdot 6H_2O$	93g/l $NiCl_2 \cdot 6H_2O$
Reductant	25g/lNa_2HPO_2	10-30g/lNa_2HPO_2	37g/l dimethylaminoborane
Lactic acid g/l	27	-	25
Sodium acetate g/l	-	100	-
Ammonium chloride g/l	-	50	-
Stabilizing components	1-3 mg/l Pb, Sb or 0.1-0.2 g/l carbamide	–	1 g/l tiodiglikole acid
pH			4 - 4.5
temperature ^0C	85 – 95	60	30

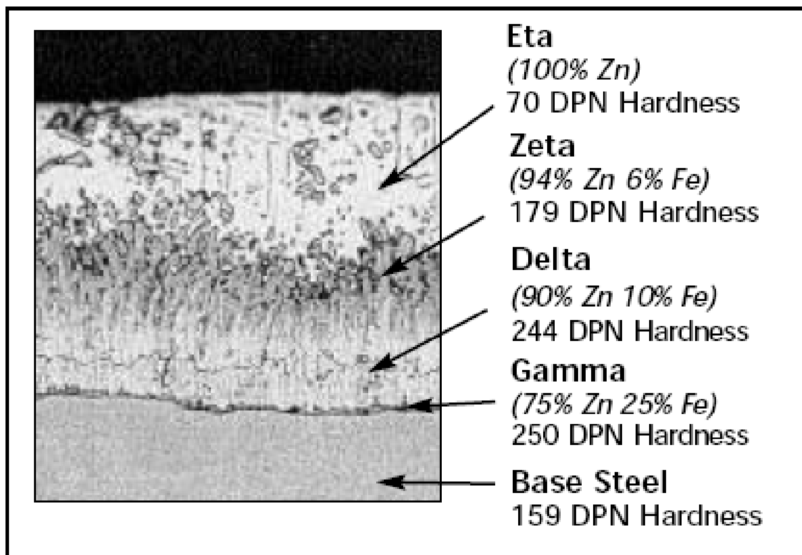
Chemical deposition of copper

Bath composition	Content
$CuSO_4 \cdot 5H_2O$	15 g/l
Sodium-potasium tartrate	40 g/l
Formaldehide 37%	6 m/l
Stabilizator V_2O_5	1-3 mg/l
pH	10 - 13
Temperature	70 – 75^0C
Deposition rate	1 – 5 μm/godz

THE HOT-DIP GALVANIZING PROCESS



Dry galvanizing process



Photomicrograph of galvanized coating

Metalizing - flame spraying

Aluminum wire or zinc wire is continuously melted in an electric arc spray or gas flame spray gun. Clean, compressed air strips droplets of molten metal from the wire depositing these particles onto the steel forming the protective coating. This sprayed metal coating is both a barrier coating and a galvanic coating in one. A single metalized coating protects steel for 30 years or longer depending upon the application, coating thickness and sealing.

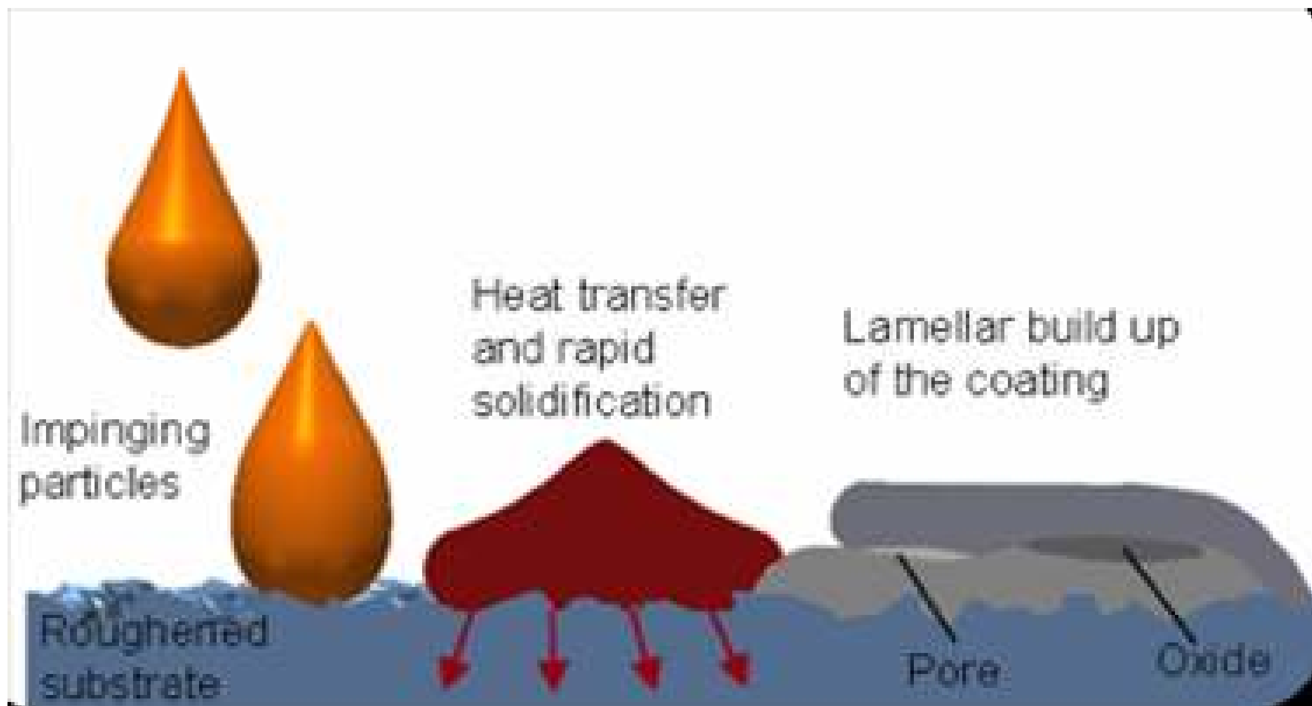
Metallizing is considered a cold process in that the aluminum or zinc is deposited onto steel by spraying rather than by dipping the steel into a bath of molten zinc as with galvanizing. The steel remains relatively cool. There is virtually no risk of heat distortion or weld damage by metalizing.

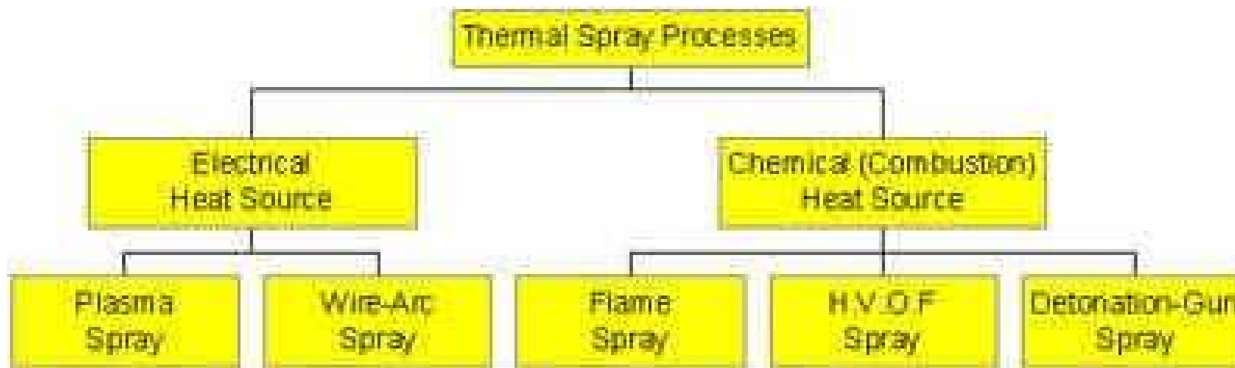
Any steel structure that can be blast cleaned may be metalized. Applications include:

- Bridges
- Piers & shore facilities
- Lock & dam gates
- Pipelines
- Offshore oil platforms
- Communication or power transmission poles

Thermal Spray

- ***Arc Wire Spray***
- ***Combustion/Flame Spray***
- ***High Velocity Oxy-Fuel (HVOF)***
- ***Plasma Spray***





Wire Spraying With this process, a specially designed gun is used, having a nozzle (similar to a welder's heating torch) which burns Oxygen and Acetylene achieving temperatures up to 5500°F. A wire is fed through the center of the nozzle into the flame where it is melted. Compressed air is concentrated around the flame atomizing the molten material into fine spherical particles and propelling these particles at high velocity onto a specially prepared substrate. By controlling the rate of feed of the wire through the flame, we can control the melt and atomization of metals with various melting points. With this gun, any wire may be sprayed which has a melting point below 5500°F.

Powder Spraying In this process, the basic principle of the heat source is the same as for wire spray except that powders are fed through the flame and propelled by high velocity Oxygen or air onto a Substrate. As with metallizing, any powdered metal or ceramic having a melting point below 5500°F. can be sprayed. This gun is mainly used for Hard Surfacing.

Electric Arc Spraying This equipment is comprised of DC Power Supply combined with a specially designed Spray Gun. Two wires are fed simultaneously through the gun at an angle so as to meet as they exit from the gun. The wires are insulated from each other but at the point where the wires exit from the gun, one wire is charged positive and the other negative, causing them to throw a molten arc between each other. Just behind this point we inject high velocity air or inert gas which atomizes the molten arc and propels the atomized particles onto the substrate. The temperature of the arc is controllable to a maximum of approximately 10,000°F. With this equipment, we can spray any type of metals which have melting points below 10,000°F.

HVOF The High Velocity Oxygen Fuel (HVOF) process was developed to produce high quality metal, carbide and various specialty coatings. A complete line of powders are available, which are specifically engineered for application with the HVOF System. The commercialization of this coating technology now affords industry the ability to get unique coating properties and extend the range of applications which previously could only be performed by proprietary coating processes.

Plasma Spray When Plasma spraying, the plasma is created by an electric arc burning within the nozzle of a plasma gun. The arc gas is formed into a plasma jet as it emerges from the gun nozzle. Powder particles are injected into this jet where they melt and then strike the surface at high velocity to produce a strongly adherent coating. Almost any material can be sprayed including metals, ceramics and plastics. The work piece remains cool because the plasma is localized at the gun. Applications for plasma sprayed coatings can be found in all industries - ranging from scuff resistant coatings on piston rings to thermal barriers on turbines and abrasion resistant coatings in the textile and paper industries.

Metalizing

Flame Spray

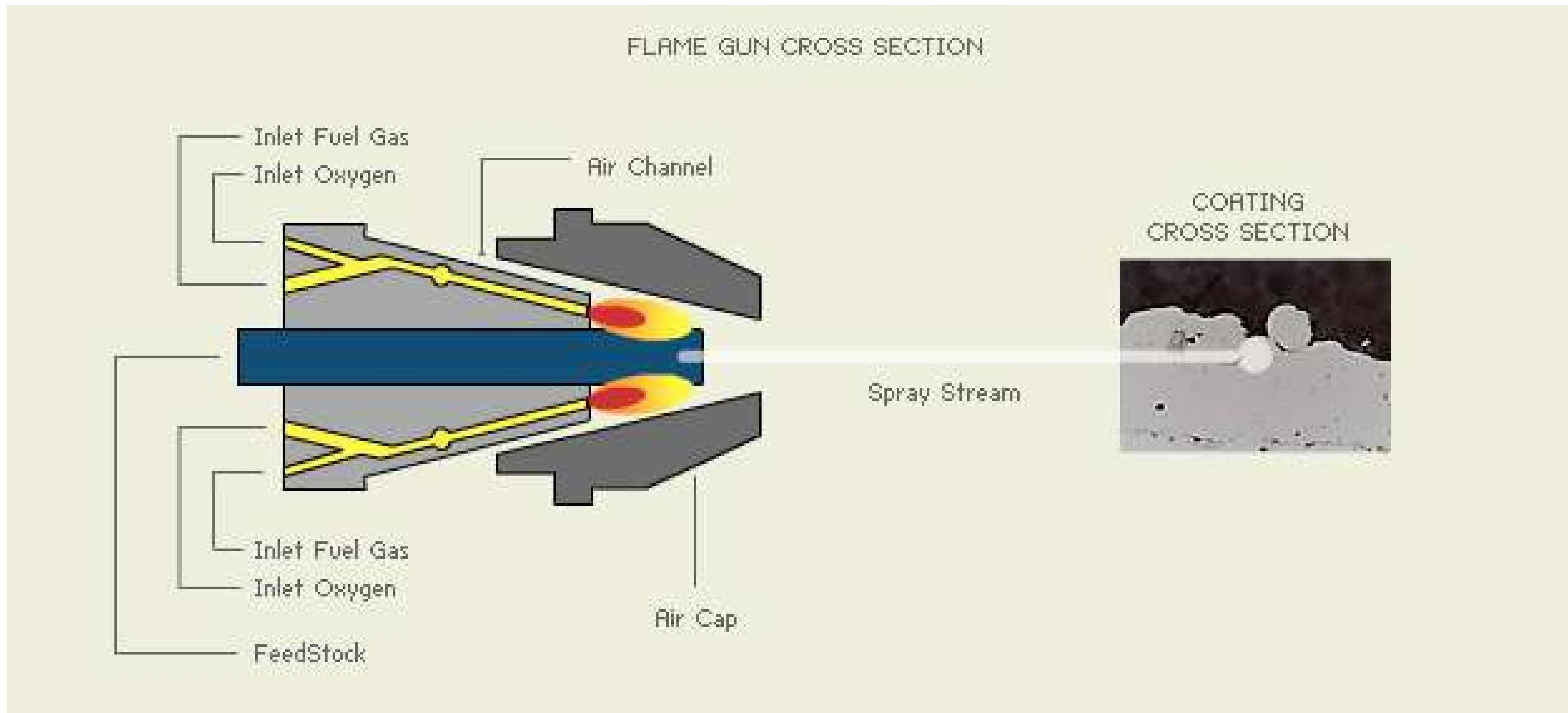
Arc Spray

Thermal Spray Overview

Thermal spray is a process of depositing molten, semi-molten, or solid particles onto a substrate to form a functional coating or a freestanding part. The particles travel at high velocity, causing them to flatten on impact with the substrate.

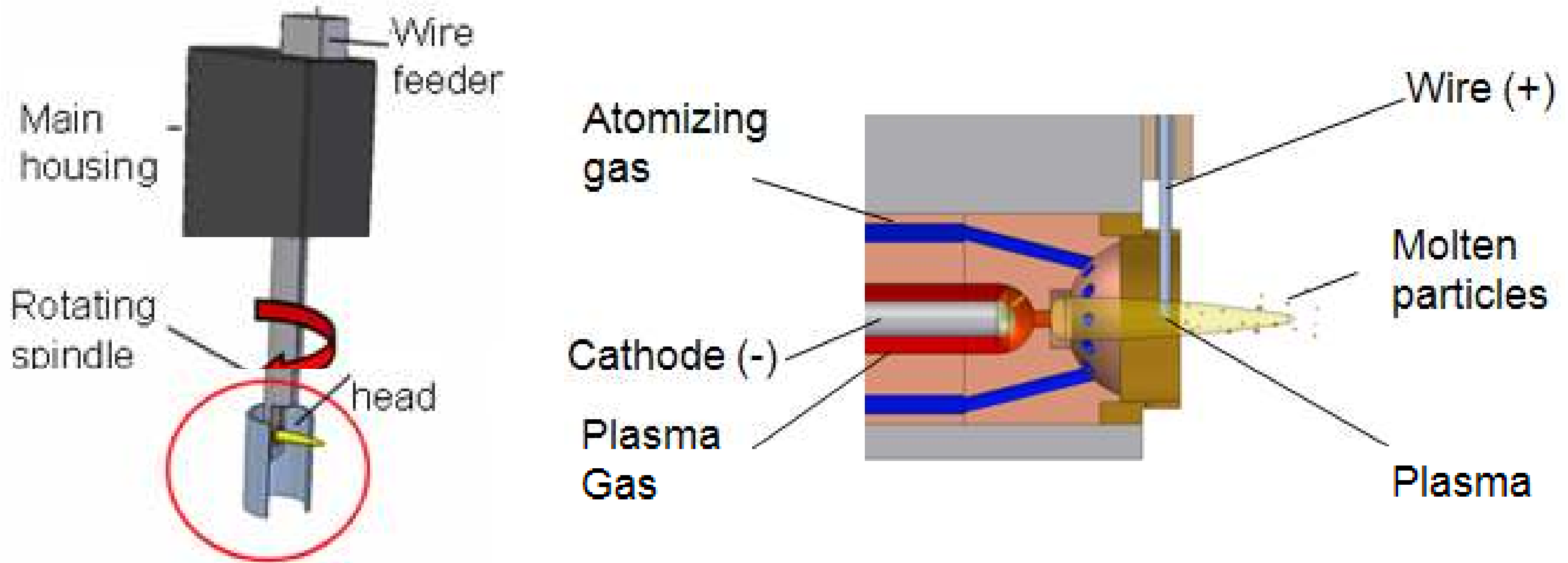
These flattened particles, known as "splats," build up to form the final coating or part. Thermal spray coatings are used in a number of industries because they offer benefits including corrosion resistance, increased conductivity, wear reduction, repair of damaged surfaces, thermal insulation, electrical insulation and biological functions such as bio-activity.

Flame Spray

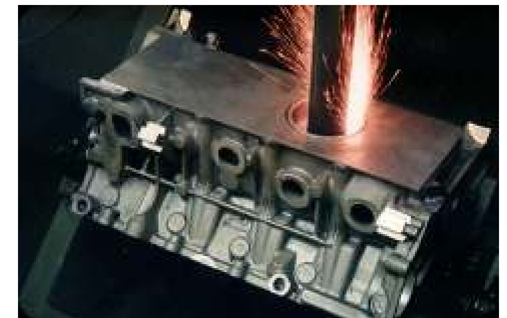


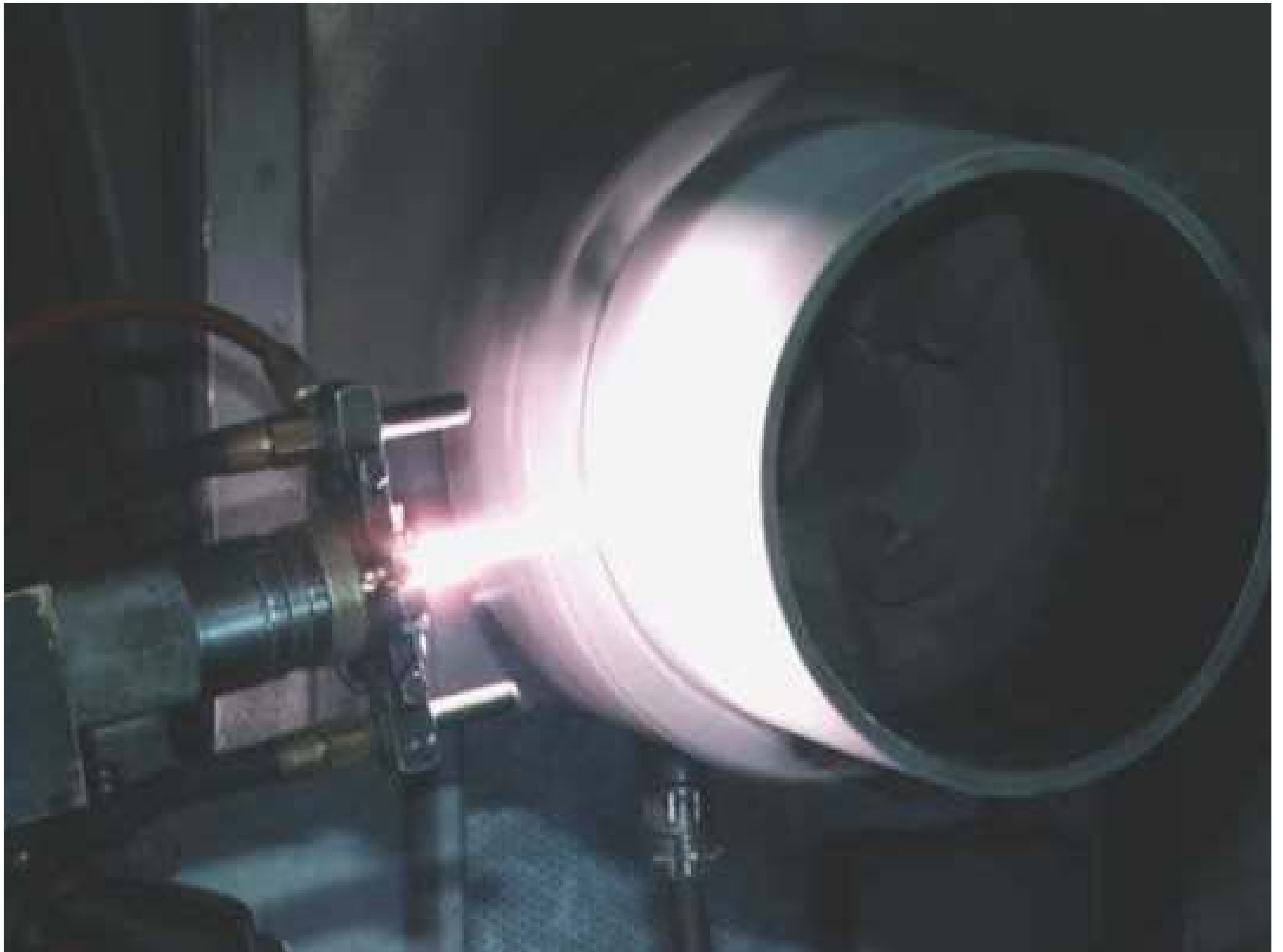
Flame spray is divided into three subcategories, based on the form of the feedstock material, either powder-, wire-, or rod-flame spray. Flame spray utilizes combustible gasses to create the energy necessary to melt the coating material. Combustion is essentially unconfined, in that there is no extension nozzle in which acceleration can occur. Common fuel gases include hydrogen, acetylene, propane, natural gas, etc. The lower temperatures and velocities associated with conventional flame spraying typically result in higher oxides, porosity, and inclusions in coatings.

Plasma Transferred Wire Arc

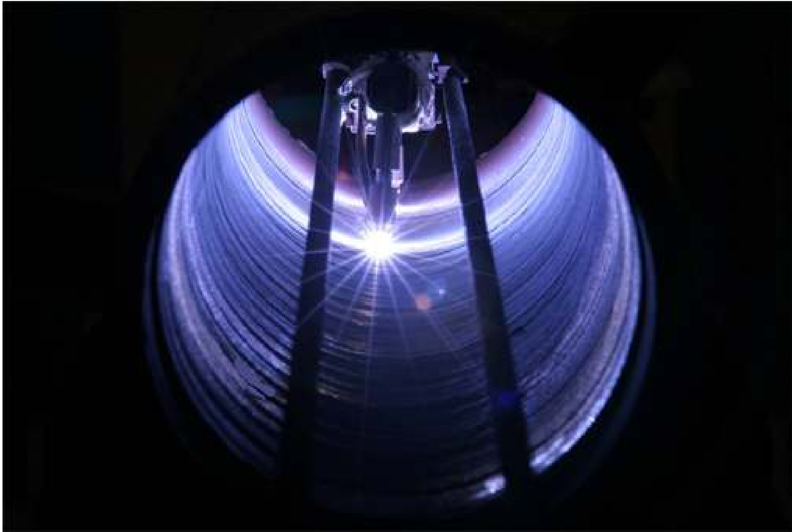


The PTWA thermal spray process utilizes a single wire as the feedstock material. All conductive wires up to and including 0.0625" (1.6mm) can be used as feedstock material, including "cored" wires. The wire is melted, atomized and propelled to the substrate by a supersonic plasma jet that is formed by a transferred arc between a non-consumable cathode and the tip of the wire.

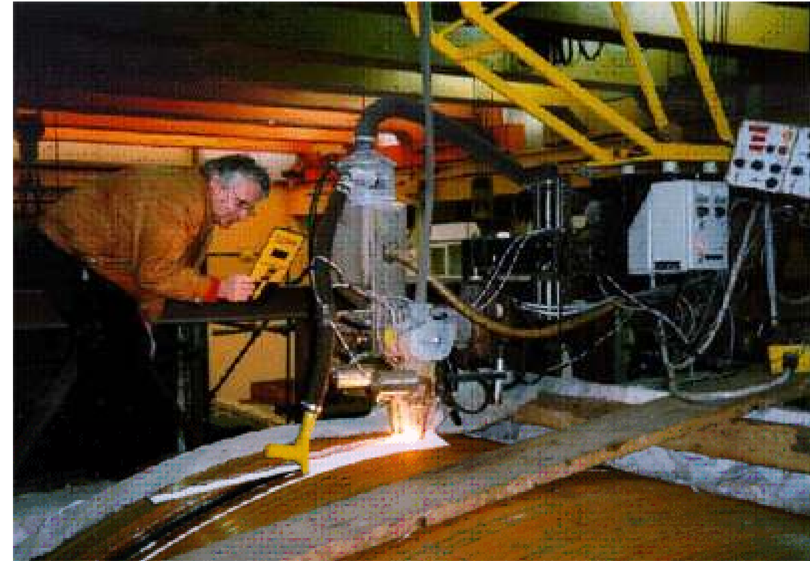




Weld Cladding



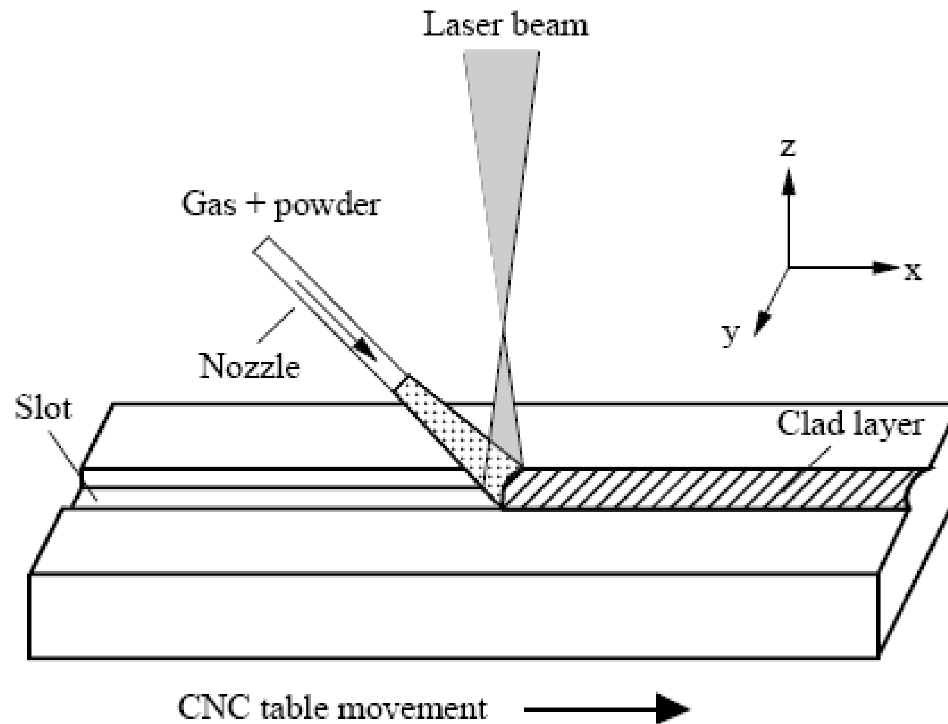
Internal weld clad pipe using Inconel 625.



The Electro Slag Strip Electrode Process applying ER 347 clad welds.

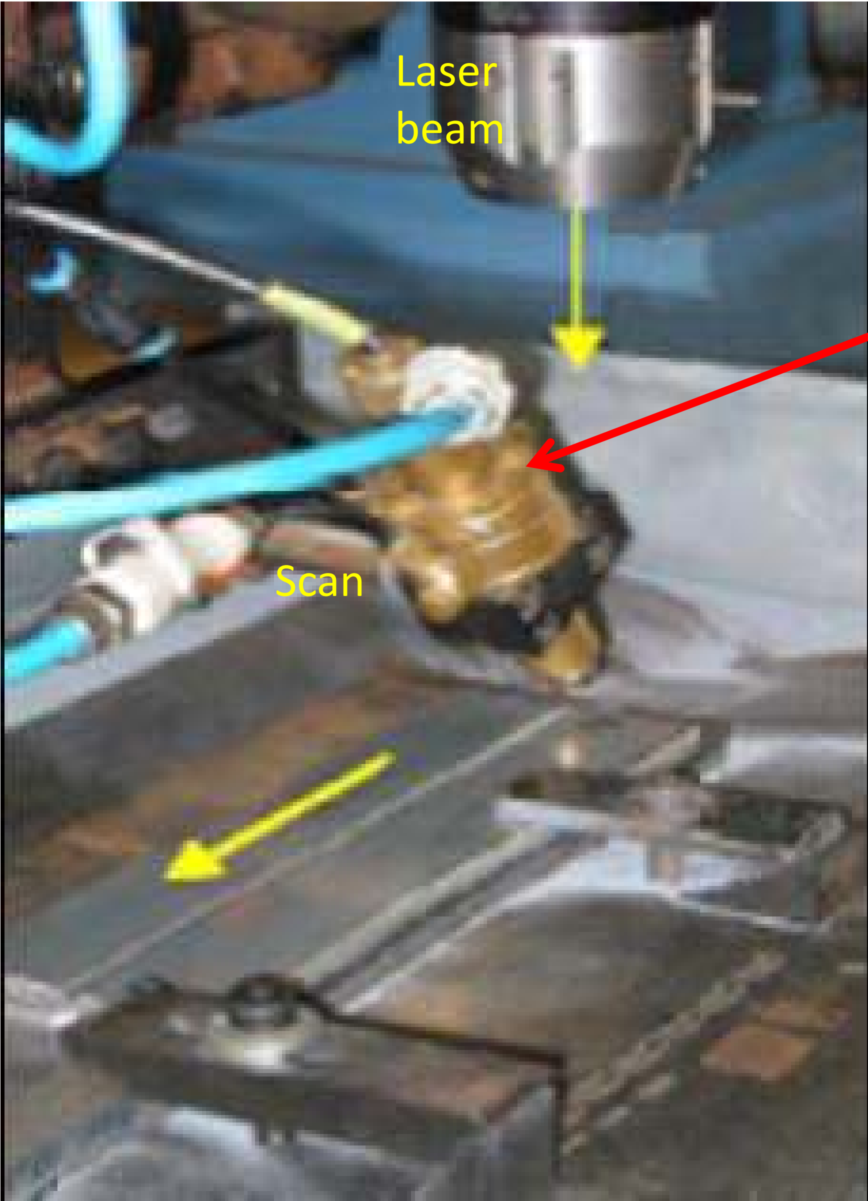
Laser cladding

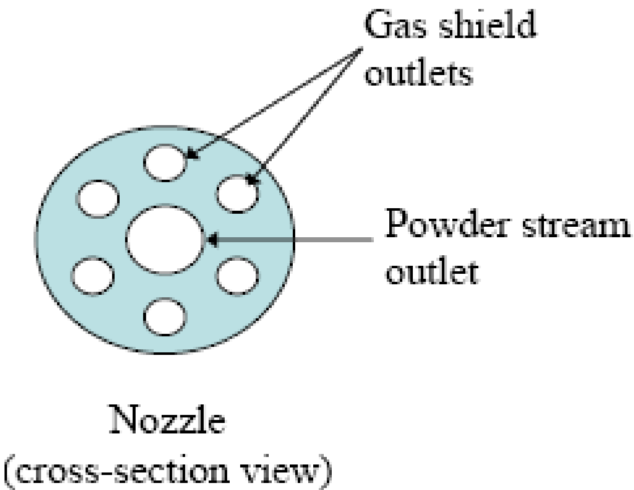
Anti-corrosion cladding :
Nickel Alloy: INCONEL 625 INCOLOY 825 INCONEL 725?INCONEL C-276 C22
Stainless Steel: 3, 4 series, 904L, Duplexes, Copper Nickel Alloy Others.



Schematic diagram of laser cladding process with side powder injection

Laser cladding

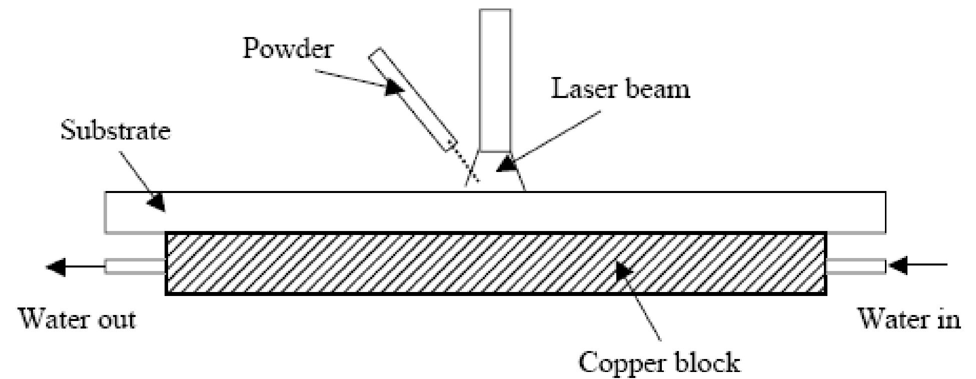




Schematic of cooling system for laser cladding on a thin aluminium plate

Laser cladding as a repair technology to improve structural integrity in aluminium alloy aircraft structures in terms of corrosion reduction and geometrical restoration

Macrograph of clad layers at the cross-section of clad specimen of AA7075-T6



Schematic of cooling system for laser cladding on a thin aluminium plate

Substrate: Al-1.6 Cu-2.5 Mg-5.6 Zn
Clad powder: Al-12%Si and 7075 Al

High energy density fusion cladding process

CermaClad™ is a high energy density fusion cladding process for large area applications where corrosion and/or wear limit the life of metal structures. CermaClad™ technology utilizes a high intensity light source, which is effectively an artificial sun captured in a reflector to rapidly fuse metal and cermet coatings on steel pipes and tubes (both internal and external surfaces), plates, sheets, and bars. CermaClad™ offers high-speed fusion cladding that is faster, better, and cost-competitive with other processes used to clad metal surfaces with corrosion resistant alloy (CRA), wear resistant alloy, cermet, ceramic, and metal powders.

3 mm Inconel 625 applied on API X65 Base

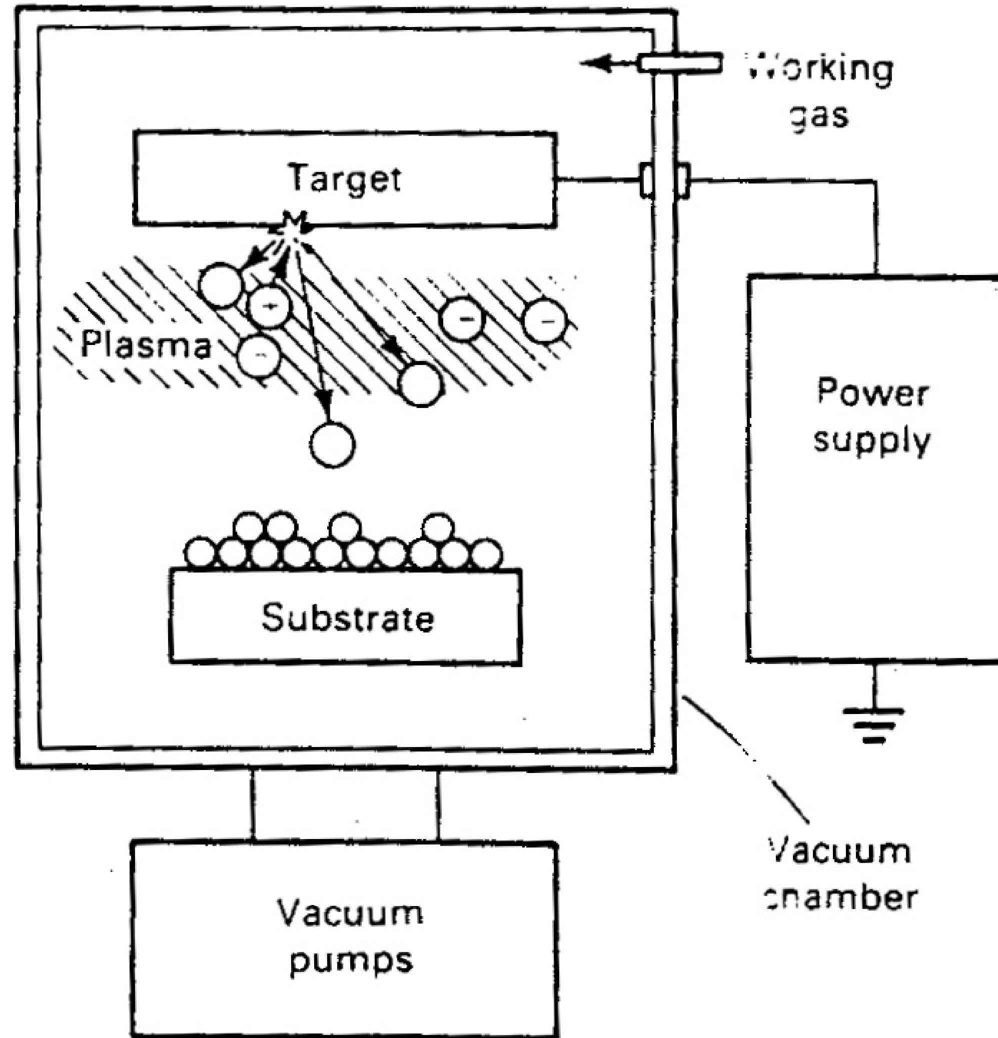
CermaClad™ is a patented process that uses high energy density IR fusion to metallurgically bond a layer of API compliant metal alloy such as 625, 316L, and nickel tungsten carbide or similar to a steel substrate.

PComP stands for **Particulate Composite Powders**.

These materials are nano-structured ceramic-metal composites formed with a nanocomposite core and binder coating, which are made using combination of low friction, high wear resistance and excellent corrosion resistant materials.

PComP™ offers high wear and corrosion resistance, high deposition rates, low spallation, low density, and easily grindable thermal spray coating compositions to replace Tungsten Carbide Cobalt (WC-Co) and hard chrome plating in high corrosion and wear applications

Vapor deposition (PVD, CVD)

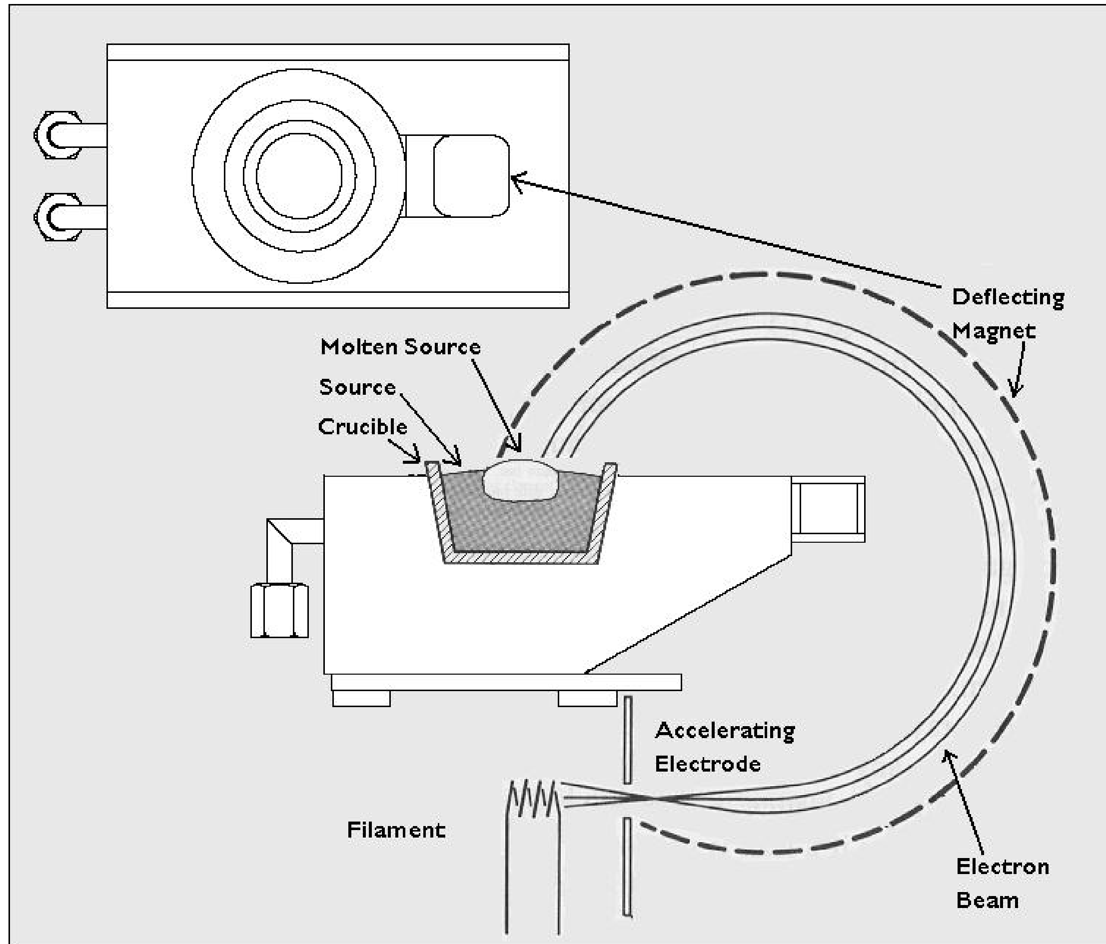


Physical vapour deposition PVD

Variants of PVD include, in order of increasing novelty:

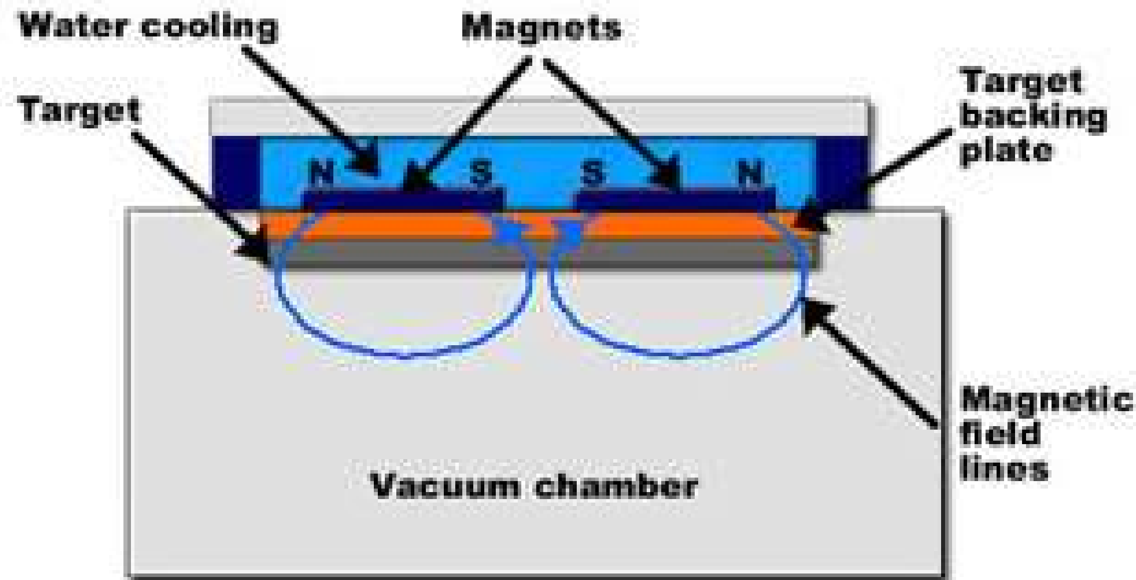
Evaporative deposition: In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "low" vacuum.
Electron beam physical vapor deposition: In which the material to be deposited is heated to a high vapor pressure by electron bombardment in "high" vacuum.
Sputter deposition: In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor.
Cathodic Arc Deposition: In which a high power arc directed at the target material blasts away some into a vapor.
Pulsed laser deposition: In which a high power laser ablates material from the target into a vapor.

E-Beam Evaporation



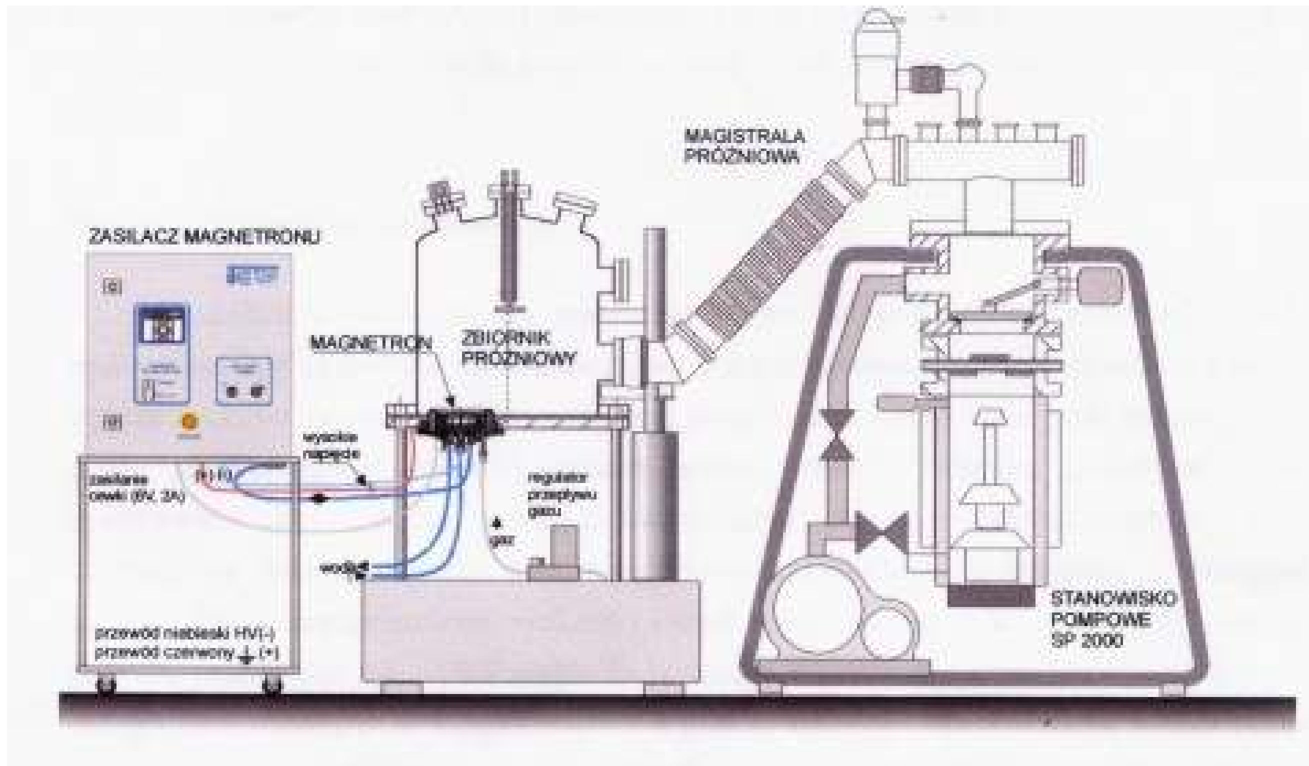
1.thermal emission of electrons from a filament source (usually tungsten) is used to heat samples to high temperatures.
2.Typically, electron beams are used when required temperatures are too high for thermal evaporation.
3.Magnetic fields and rastering are used to steer the electron beam 270º into metal source. (This is done to allow shielding of tungsten filament and prevent contamination. See image.)
4.Electrons striking metals can produce X-rays which sometimes causes damage to CMOS material layers on a wafer. An annealling step takes care of these problems.

Magnetron Sputtering



Magnetron sputtering is a powerful and flexible PVD coating technique which can be used to coat virtually any workpiece with a wide range of materials - any solid metal or alloy and a variety of compounds. Prior to the magnetron sputtering coating procedure a vacuum of less than one ten millionth of an atmosphere must be achieved. From this point a closely controlled flow of an inert gas such as argon is introduced. This raises the pressure to the minimum needed to operate the magnetrons, although it is still only a few ten thousandth of atmospheric pressure. A magnetron consists of a plate of the material of which all or part of the coating is to consist (referred to as the target) with magnets arranged behind it with alternating polarity.

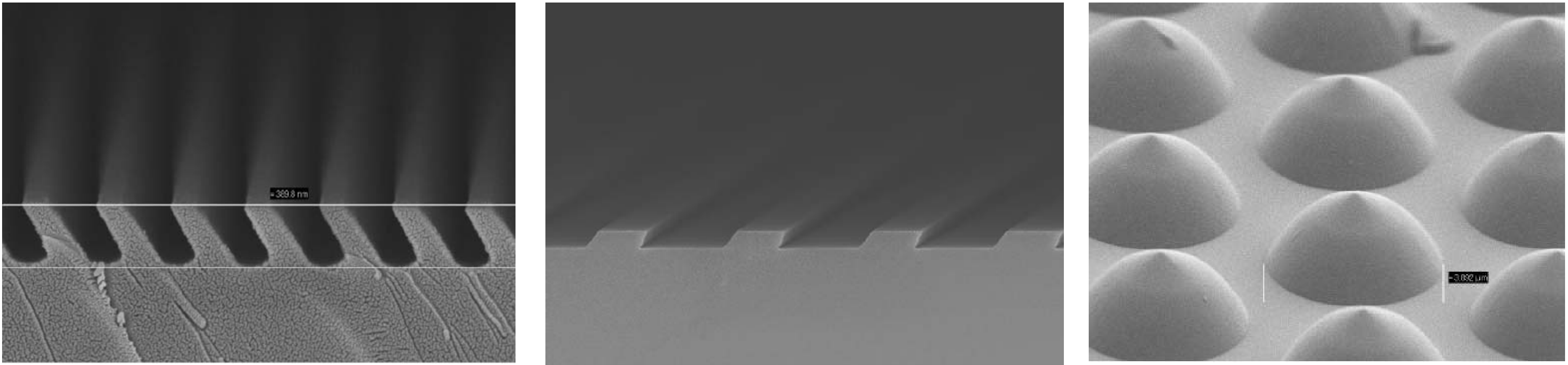
When power is supplied to the magnetron a negative voltage of typically -300V or more is applied to the target. This attracts argon ions to the target surface at speed. When they collide with the surface two important processes take place: Atoms are knocked out of the target surface with mean kinetic energies of 4 to 6 eV- this is sputtering. These sputtered atoms are neutrally charged and so are unaffected by the magnetic trap.



Magnetron

Ion Beam Etching and Reactive Ion Beam Etching

Ion beam etching is a versatile etch process in which the substrate to be etched is placed in a vacuum chamber in front of the broad-beam ion source. Ions (typically argon) are generated inside the ion source and are accelerated into a broad beam, and to a defined energy, by the extraction grids on the front of the source.

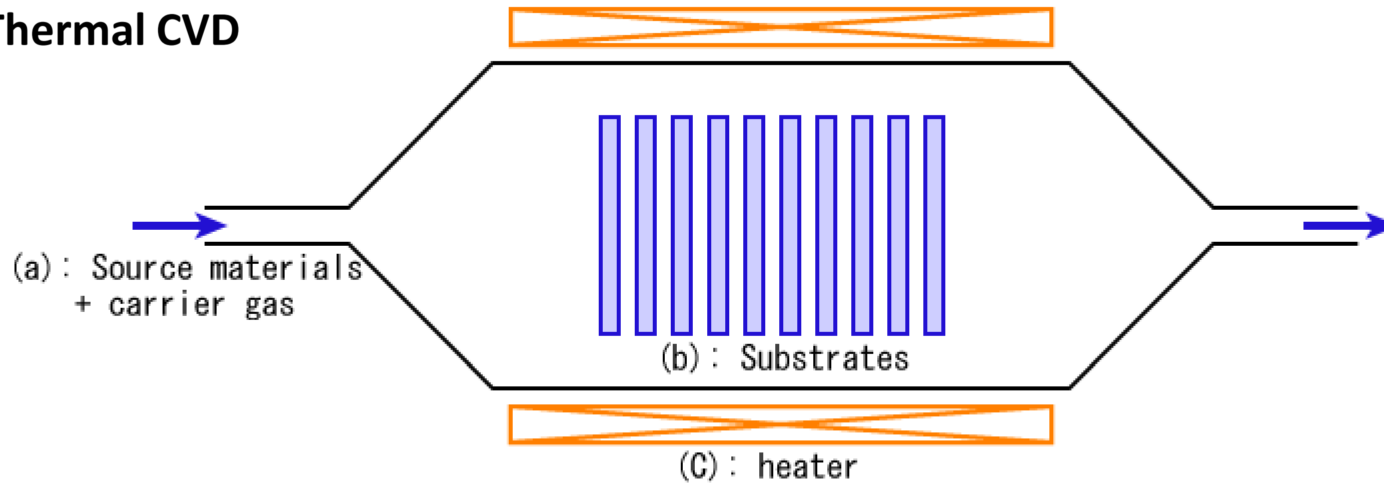


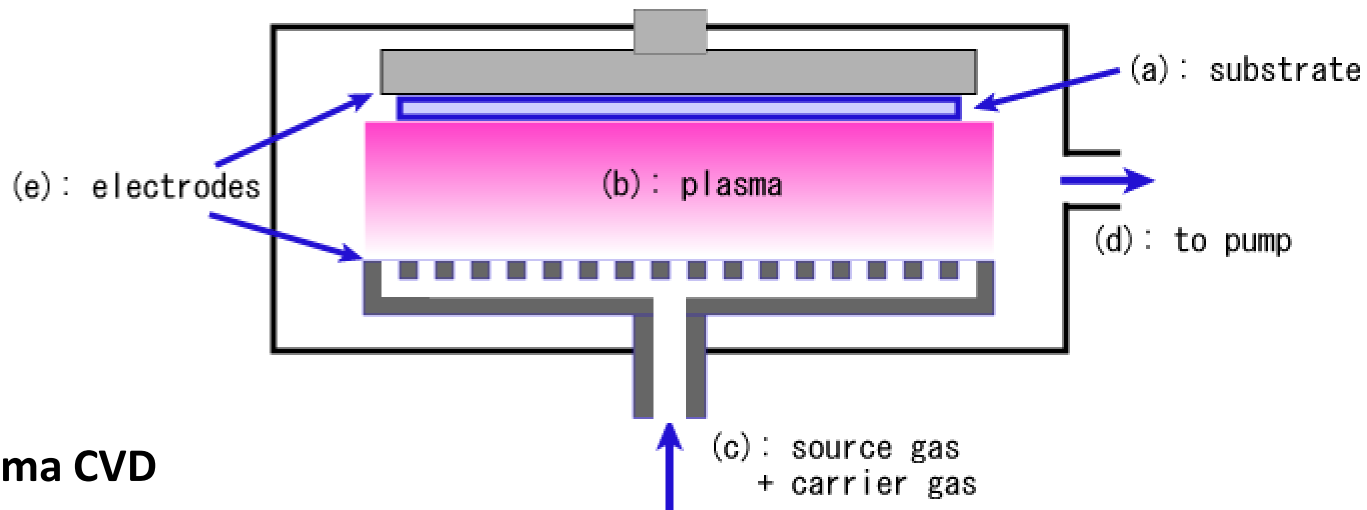
As the ion beam etches the surface, the substrate is tilted to an angle in the beam and continuously rotated in order to optimize the uniformity of the etch. If a pattern is being etched by the use of a photomask, the use of tilt and rotation allows the user to adjust the wall angles in the resulting etch. If one uses an inert gas such as argon, the process is relatively slow, (typically 50 - 100nm/minute,) and the heat that is generated must be removed with care, via He back cooling.

Adding reactive gas such as CHF_3, CF_4 or Chlorine to argon in RIBE mode enables better control over selectivity between a mask and an etched material as well as an increase in the material etch rate. Increasing selectivity offers even more possibilities of etch structure with better control over sidewalls.

Chemical vapour deposition CVD

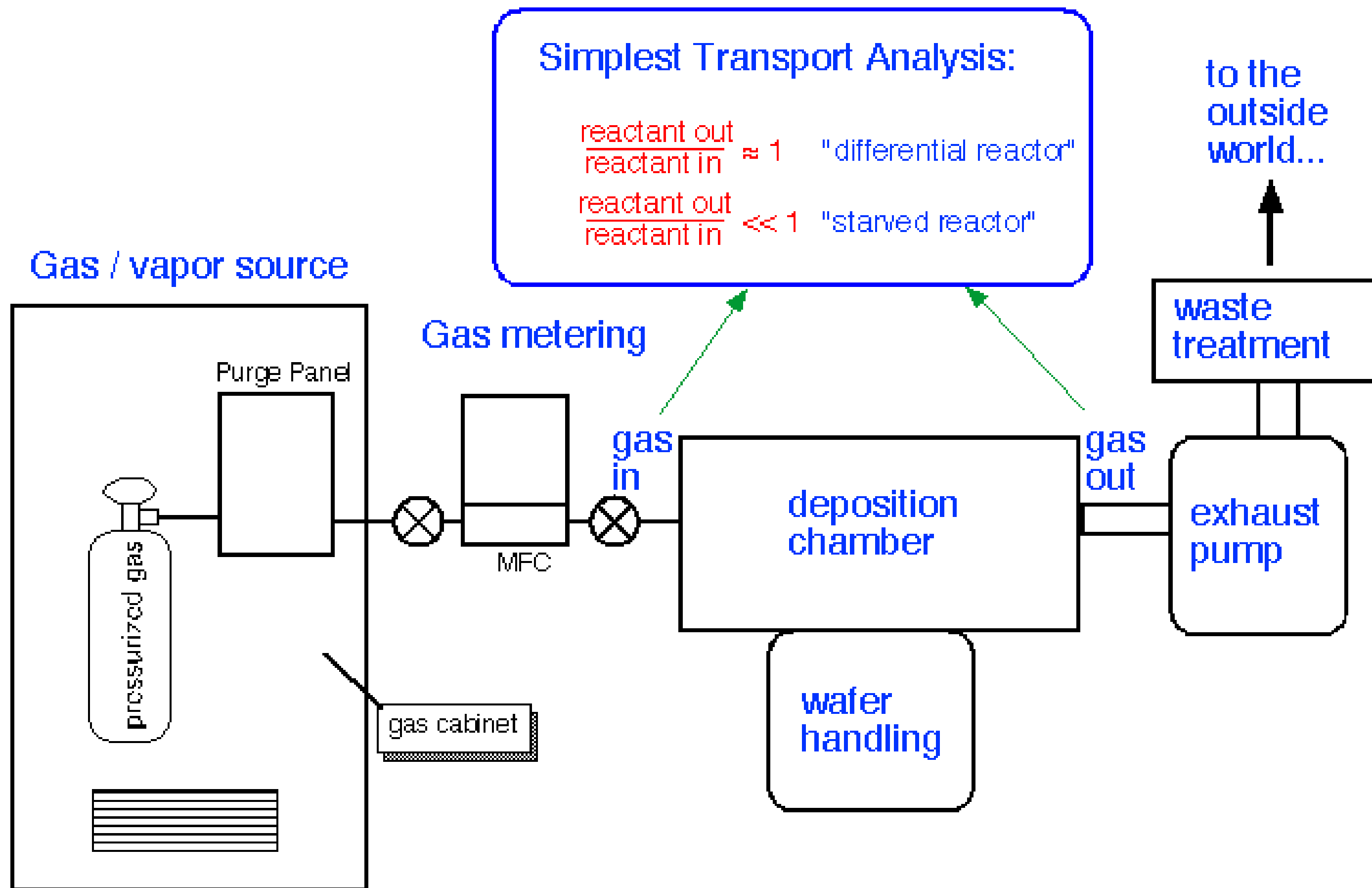
Thermal CVD





Plasma CVD

Chemical vapour deposition CVD



Types of chemical vapor deposition

Classified by operating pressure ***Atmospheric pressure***

APCVD - CVD processes at atmospheric pressure.
Low-pressure CVD **(LPCVD)** - CVD processes at subatmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.
Ultra high vacuum CVD **(UHVCVD**) - CVD processes at a very low pressure, typically below 10^{-6} Pa (~ 10^{-8} torr). Caution: in other fields, a lower division between high and ultra-high vacuum is common, often 10^{-7} Pa.

Classified by physical characteristics of vapor

Aerosol assisted CVD **(AACVD)** - a CVD process in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. This technique is suitable for use with involatile precursors.
Direct liquid injection CVD **(DLICVD)** - a CVD process in which the precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). Then the precursors vapors are transported to the substrate as in classical CVD process. This technique is suitable for use on liquid or solid precursors. High growth rates can be reached using this technique.

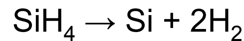
Plasma methods

Microwave plasma-assisted CVD **(MPCVD)**
Plasma-Enhanced CVD **(PECVD)** - CVD processes that utilize a plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors.
Remote plasma-enhanced CVD **(RPECVD)** - Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.

Substances commonly deposited for ICs

Polysilicon

Polycrystalline silicon is deposited from silane (SiH_4), using the following reaction:

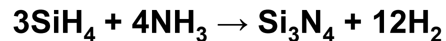


$$SiH_4 \rightarrow Si + 2H_2$$

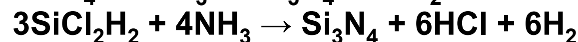
This reaction is usually performed in LPCVD systems, with either pure silane feedstock, or a solution of silane with 70-80% nitrogen. Temperatures between 600 and 650 °C and pressures between 25 and 150 Pa yield a growth rate between 10 and 20 nm per minute. An alternative process uses a hydrogen-based solution. The hydrogen reduces the growth rate, but the temperature is raised to 850 or even 1050 °C to compensate. Polysilicon may be grown directly with doping, if gases such as phosphine, arsine or diborane are added to the CVD chamber. Diborane increases the growth rate, but arsine and phosphine decrease it.

Silicon nitride

Silicon nitride is often used as an insulator and chemical barrier in manufacturing ICs. The following two reactions deposit nitride from the gas phase:

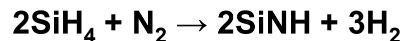


$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$$

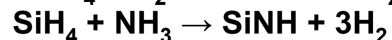


$$3SiCl_2H_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$$

Silicon nitride deposited by LPCVD contains up to 8% hydrogen. It also experiences strong tensile stress (physics), which may crack films thicker than 200 nm. However, it has higher resistivity and dielectric strength than most insulators commonly available in microfabrication (10^{16} Ω·cm and 10 MV/cm, respectively).
Another two reactions may be used in plasma to deposit SiNH:



$$2SiH_4 + N_2 \rightarrow 2SiNH + 3H_2$$

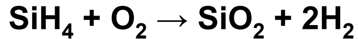


$$SiH_4 + NH_3 \rightarrow SiNH + 3H_2$$

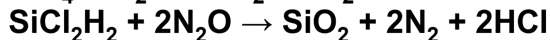
These films have much less tensile stress, but worse electrical properties (resistivity 10^6 to 10^{15} Ω·cm, and dielectric strength 1 to 5 MV/cm).

Silicon dioxide

Silicon dioxide (usually called simply "oxide" in the semiconductor industry) may be deposited by several different processes. Common source gases include silane and oxygen, dichlorosilane ($SiCl_2H_2$) and nitrous oxide (N_2O), or tetraethylorthosilicate (TEOS; $Si(OC_2H_5)_4$). The reactions are as follows:



$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$$

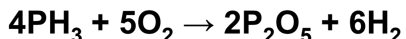


$$SiCl_2H_2 + 2N_2O \rightarrow SiO_2 + 2N_2 + 2HCl$$

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + \text{byproducts}$$

The choice of source gas depends on the thermal stability of the substrate; for instance, aluminium is sensitive to high temperature. Silane deposits between 300 and 500 °C, dichlorosilane at around 900 °C, and TEOS between 650 and 750 °C, resulting in a layer of **Low Temperature Oxide** (LTO). However, silane produces a lower-quality oxide than the other methods (lower dielectric strength, for instance), and it deposits nonconformally. Any of these reactions may be used in LPCVD, but the silane reaction is also done in APCVD. CVD oxide invariably has lower quality than thermal oxide, but thermal oxidation can only be used in the earliest stages of IC manufacturing.

Oxide may also be grown with impurities (alloying or "doping"). This may have two purposes. During further process steps that occur at high temperature, the impurities may diffuse from the oxide into adjacent layers (most notably silicon) and dope them. Oxides containing 5% to 15% impurities by mass are often used for this purpose. In addition, silicon dioxide alloyed with phosphorus pentoxide ("P-glass") can be used to smooth out uneven surfaces. P-glass softens and reflows at temperatures above 1000 °C. This process requires a phosphorus concentration of at least 6%, but concentrations above 8% can corrode aluminium. Phosphorus is deposited from phosphine gas and oxygen:



$$4PH_3 + 5O_2 \rightarrow 2P_2O_5 + 6H_2$$

Glasses containing both boron and phosphorus (borophosphosilicate glass, BPSG) undergo viscous flow at lower temperatures; around 850 °C is achievable with glasses containing around 5 weight % of both constituents, but stability in air can be difficult to achieve. Phosphorus oxide in high concentrations interacts with ambient moisture to produce phosphoric acid. Crystals of BPO_4 can also precipitate from the flowing glass on cooling; these crystals are not readily etched in the standard reactive plasmas used to pattern oxides, and will result in circuit defects in integrated circuit manufacturing.

Besides these intentional impurities, CVD oxide may contain byproducts of the deposition process. TEOS produces a relatively pure oxide, whereas silane introduces hydrogen impurities, and dichlorosilane introduces chlorine.

Lower temperature deposition of silicon dioxide and doped glasses from TEOS using ozone rather than oxygen has also been explored (350 to 500 °C). Ozone glasses have excellent conformality but tend to be hygroscopic -- that is, they absorb water from the air due to the incorporation of silanol (Si-OH) in the glass. Infrared spectroscopy and mechanical strain as a function of temperature are valuable diagnostic tools for diagnosing such problems.

Inorganic coatings:

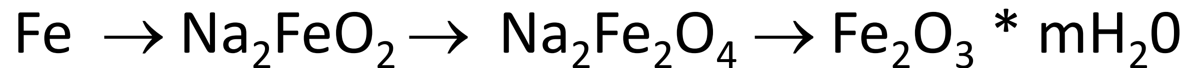
oxide films – anodization

anodization of aluminum

$$Al + 2H_2O \rightarrow AlOOH + 3H^+ + 3e$$

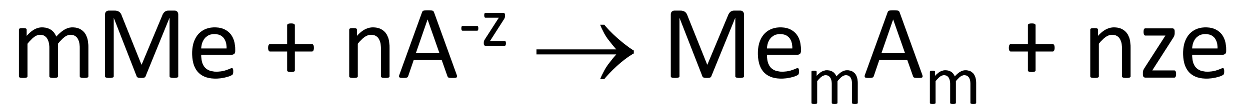
oxidation of iron

$$NaOH + NaNO_3 + NaNO_2 \ (140 - 145°C)$$



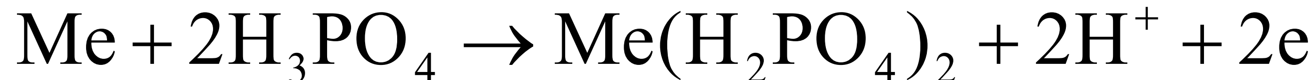
$$Fe \rightarrow Na_2FeO_2 \rightarrow Na_2Fe_2O_4 \rightarrow Fe_2O_3 * mH_20$$

Conversion layers



$$mMe + nA^{-z} \rightarrow Me_mA_m + nze$$

chromate layers
phosphate layers



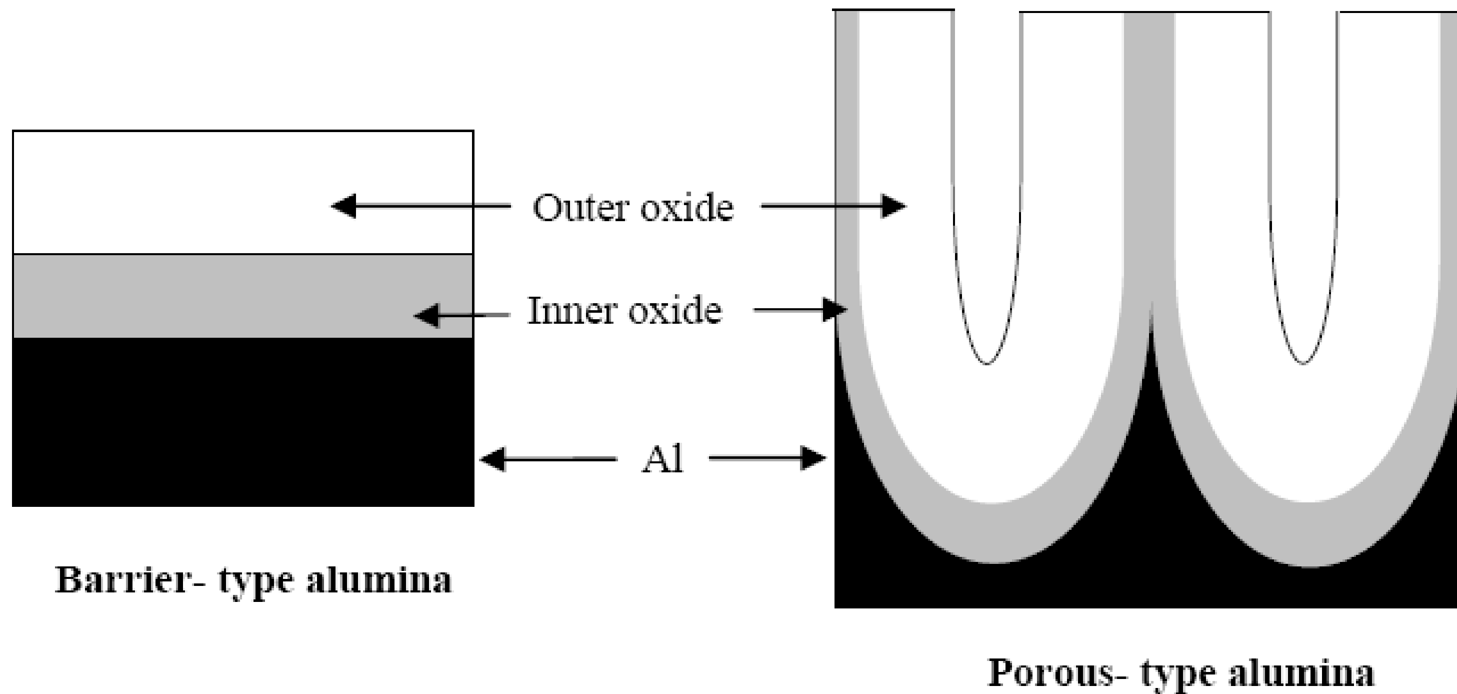
$$Me + 2H_3PO_4 \rightarrow Me(H_2PO_4)_2 + 2H^+ + 2e$$

$$Me(H_2PO_4)_2 \Leftrightarrow MeHPO_4 + H_3PO_4$$

$$3Me(H_2PO_4)_2 \Leftrightarrow Me_3(PO_4)_2 + 4H_3PO_4$$

$$3Me_3PO_4 \Leftrightarrow Me_3(PO_4)_2 + H_3PO_4$$

Anodizing



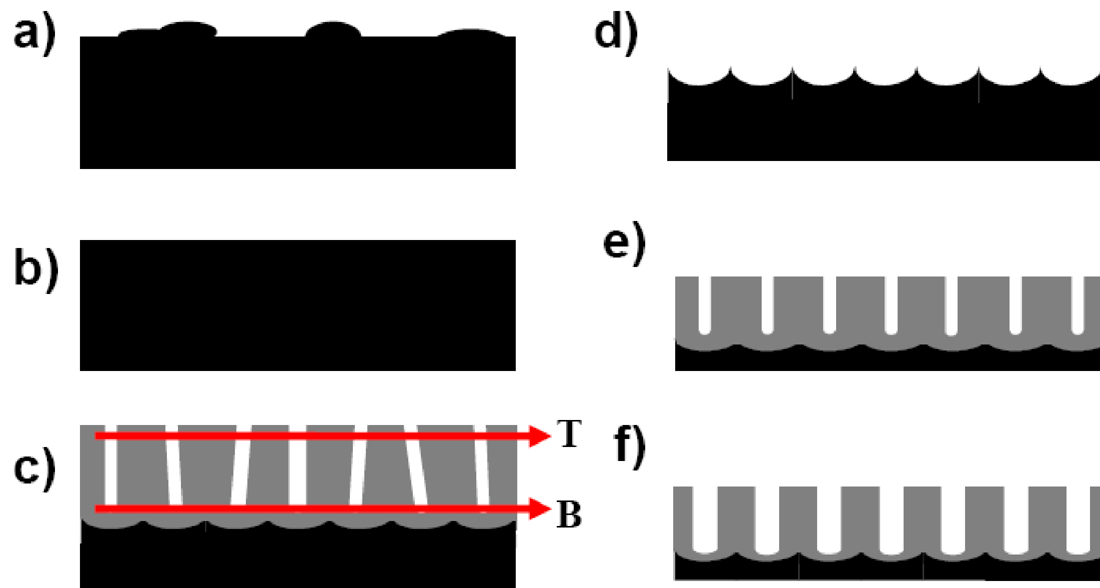
Schematic diagram for barrier type alumina and porous type alumina. The aluminum metal, an inner oxide consisting of pure alumina and an outer oxide consisting of an anion-contaminated alumina are indicated.

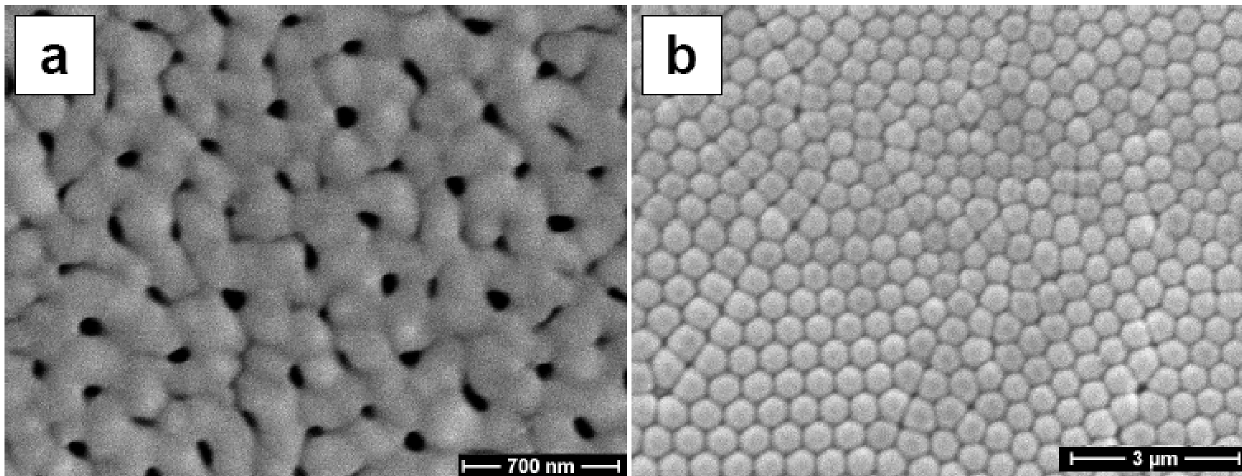
Depending on several factors, in particular the electrolyte, two types of anodic films can be produced. Barrier type films can be formed in completely insoluble electrolytes (5 < pH < 7), e.g., neutral boric acid, ammonium borate, tartrate, and ammonium tetraborate in ethylene glycol. Porous type films can be created in slightly soluble electrolytes such as sulfuric, phosphoric, chromic and oxalic acid .

Anodizing

Metal	Anodizing ratio (ÅV^{-1})
Tantalum	16.0
Niobium	22.0
Zirconium	20 ~ 27
Tungsten	18
Silicon	4 - 8
Aluminum	10.0 in 15 % sulfuric acid
	11.8 in 2 % oxalic acid
	11.9 in 4 % phosphoric acid
	12.5 in 3 % chromic acid
	13 ~ 13.7 in barrier-type electrolytes

Anodizing ratios for barrier film formation on valve metals. Note that in the case of aluminum anodized in sulfuric, oxalic, phosphoric, and chromic acid, anodizing ratios of the barrier layer formed beneath the porous alumina are indicated





Scanning Electron Microscopy (SEM) images of a porous alumina sample produced by a first anodization (in 0.1Mphosphoric acid at 195 V). (a) the surface, and (b) the bottom of the membrane after selective removal of Al,

Anodized titanium

Enamels

Table 2 Melted-oxide compositions of frits for ground-coat enamels for sheet steel

Constituent	Composition, wt%			
	Regular blue-black enamel	Alkali-resistant enamel	Acid-resistant enamel	Water-resistant enamel
SiO_2	33.74	36.34	56.44	48.00
B_2O_3	20.16	19.41	14.90	12.82
Na_2O	16.74	14.99	16.59	18.48
K_2O	0.90	1.47	0.51	...
Li_2O	...	0.89	0.72	1.14
CaO	8.48	4.08	3.06	2.90
BaO	9.24	8.59	...	...
ZnO	...	2.29	...	...
Al_2O_3	4.11	3.69	0.27	...
ZrO_2	...	2.29	...	8.52
TiO_2	...	...	3.10	3.46
CuO	...	...	0.39	...
MnO_2	1.43	1.49	1.12	0.52
NiO	1.25	1.14	0.03	1.21
Co_3O_4	0.59	1.00	1.24	0.81
P_2O_5	1.04	...	...	0.20
F_2	2.32	2.33	1.63	1.94