Institute of Metallurgy and Materials Science
Polish Academy of Sciences

Electrochemistry for materials science

Ewa Bełtowska-Lehman

ELECTROCHEMISTRY FOR MATERIALS SCIENCE

Introduction, general information and overview of the phenomena

Part I

Ewa Bełtowska-Lehman

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ELECTROCHEMISTRY – PART OF PHYSICAL CHEMISTRY

Electrochemistry is a part of physical chemistry dealing with the properties of electrolytes in solution and in the molten state as well as the processes occurring at the interface electrode / electrolyte solution.

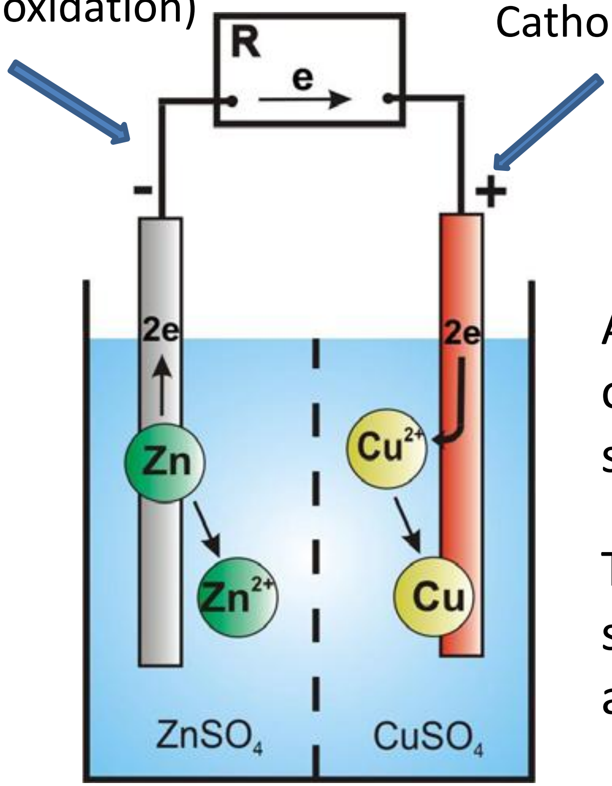
- in galvanic cells, in which occurs the conversion of chemical energy into electrical

- in electrolyser, where electrical work under the influence of externally applied electric field allows for a chemical transformation

(present lectures refer only to aqueous solutions)

CONVERSION OF CHEMICAL ENERGY INTO ELECTRICAL ENERGY GALVANIC CELLS

Cation - an ion or group of ions having a positive charge
Anion - any negatively charged atom or group of atoms



Anode (oxidation)

Cathode (reduction)

chemical transformation
⇓
electrical energy

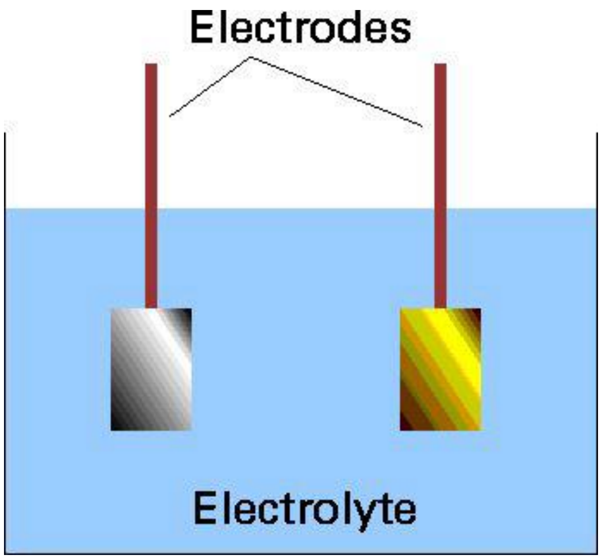
A system producing electrical energy as a result of chemical transformations is called a chemical source of electricity or galvanic cell.

The half-cell contains the metal in two oxidation states and the chemical reaction in the half-cell is an oxidation-reduction (redox) reaction:

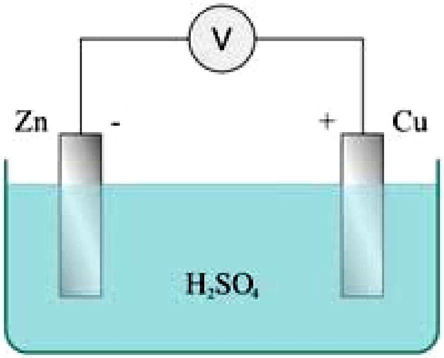
$$M^{z+}\,(\text{oxidized species}) + ze^{-} \rightleftarrows M\,(\text{reduced species})$$

M. Bełtowska-Brzezinska, Wprowadzenie do elektrochemii, UAM, Poznań 2009 (www.wbc.poznan.pl)

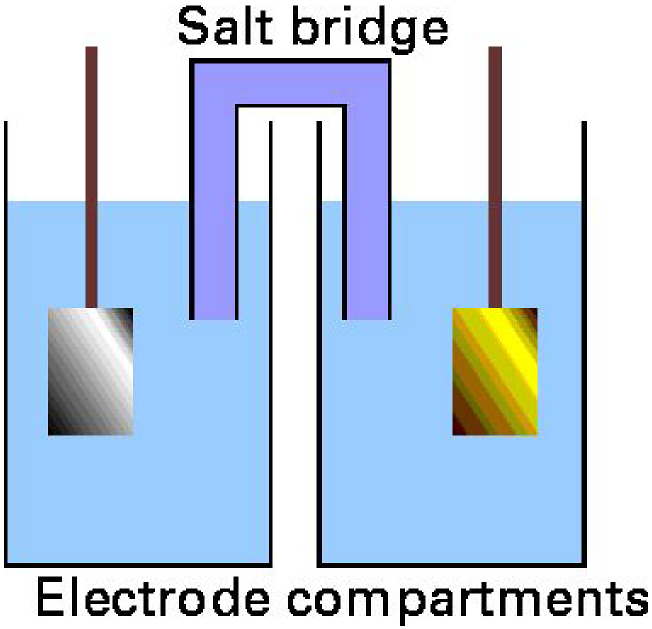
ARRANGEMENT FOR ELECTROCHEMICAL CELLS



Volta cell



(-) Zn | 5% H_2SO_4 | Cu (+)

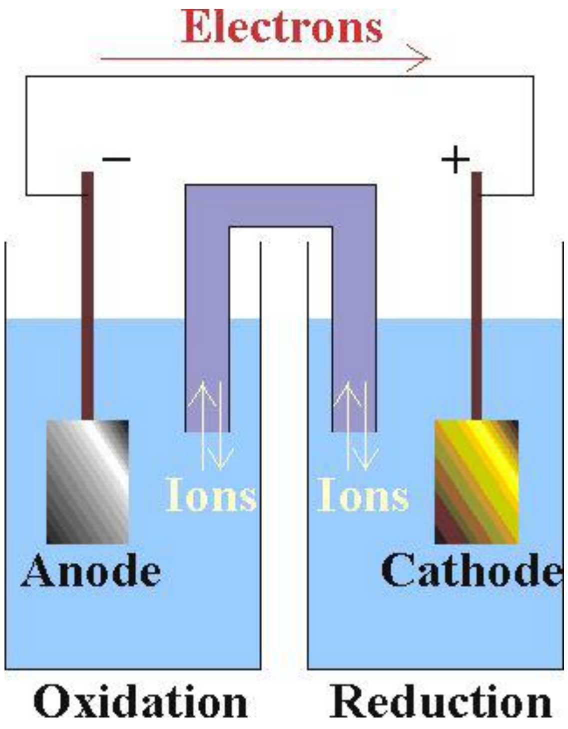


The arrangement for an electrochemical cell in which the two electrodes share a common electrolyte.

When the electrolytes in the electrode compartments of a cell are different, they need to be joined so that ions can travel from one compartment to another.
One device for joining the two compartments is a salt bridge.

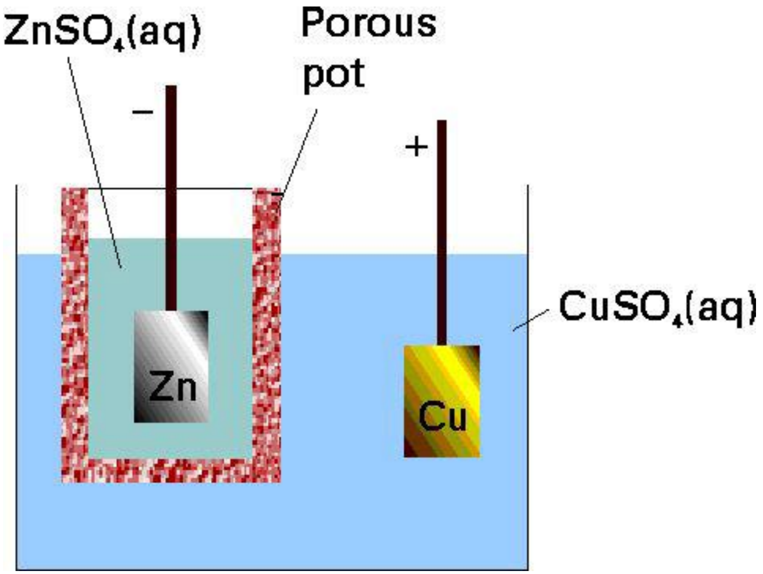
Atkins, Elements of Physical Chemistry, 3rd Ed, Oxford

ARRANGEMENT FOR ELECTROCHEMICAL CELLS



The flow of electrons in the external circuit is from the anode of a galvanic cell, where they have been lost in the oxidation reaction, to the cathode, where they are used in the reduction reaction. Electrical neutrality is preserved in the electrolytes by the flow of cations and anions in opposite directions through the salt bridge.

A Daniell cell consists of copper in contact with copper(II) sulfate solution and zinc in contact with zinc sulfate solution; the two compartments are in contact through the porous pot that contains the zinc sulfate solution.



A salt bridge or porous membrane serves both to keep the solutions apart and to allow the flow of anions in the direction opposite to the flow of electrons in the wire connecting the electrodes.

Atkins, Elements of Physical Chemistry, 3rd Ed, Oxford

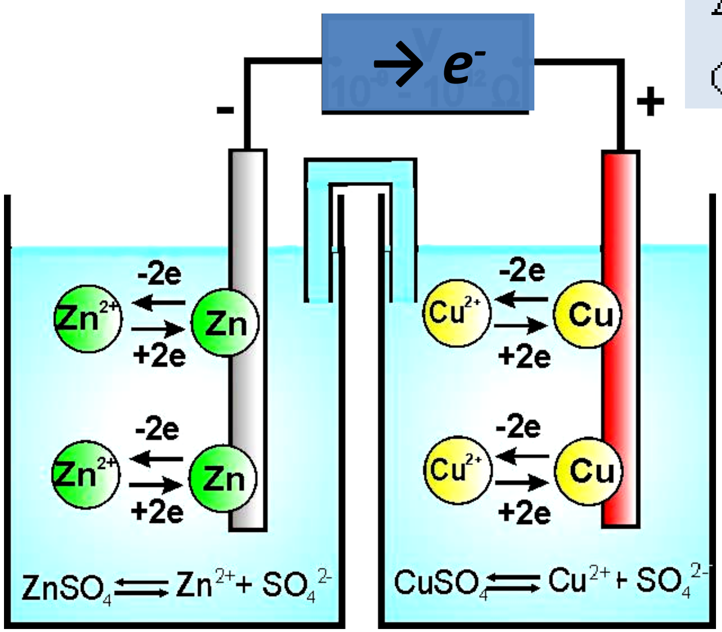
GALVANIC CELLS (ELECTROCHEMICAL CELLS)

$$(-)\ Zn\,|\,Zn^{2+}\ \|\ Cu^{2+}\,|\,Cu\ (+)$$

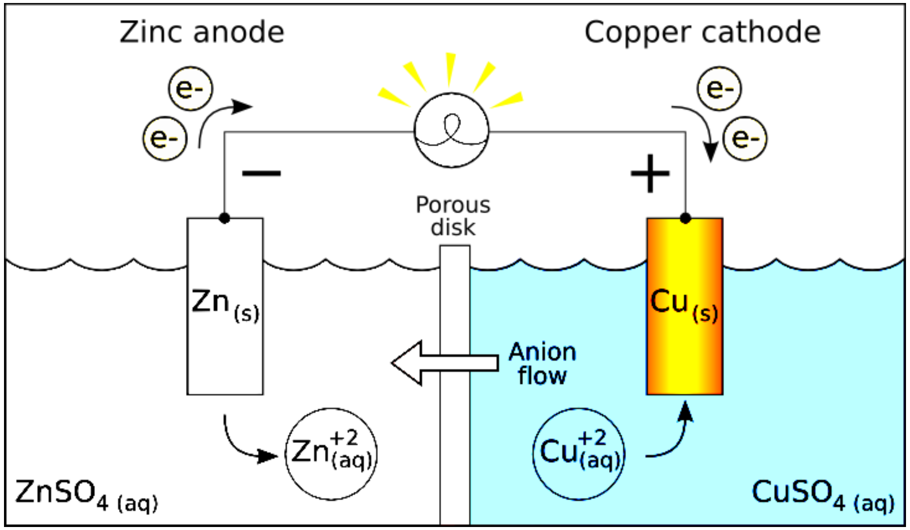
$$\begin{aligned} &Zn \rightleftarrows Zn^{2+} + 2\bar{e}\ \ominus \\ &Cu \rightleftarrows Cu^{2+} + 2\bar{e}\ \oplus \end{aligned}\ \ \bar{e}$$

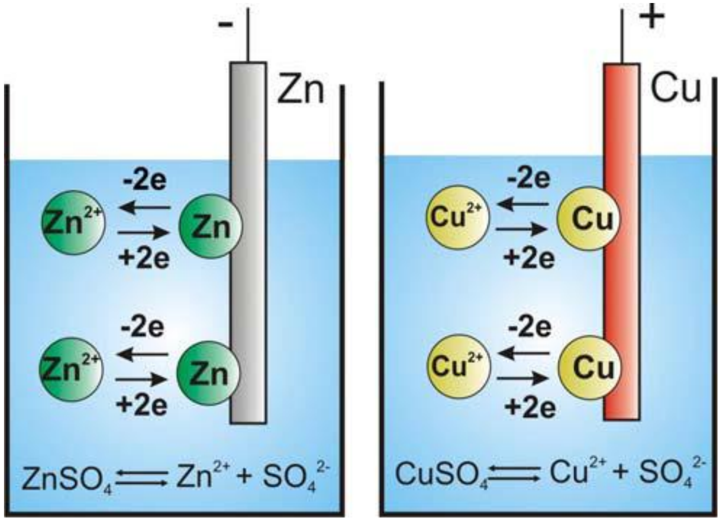
$$(-)Me_{II}\,|\,Me_{II}^{z+}\ \overset{e^-}{\|}\ Me_{I}^{z+}\,|\,Me_{I}\ (+)$$

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



$$(-)\ Zn\,|\,Zn^{2+}\ \vdots\ Cu^{2+}\,|\,Cu\ (+)$$





Open galvanic cell

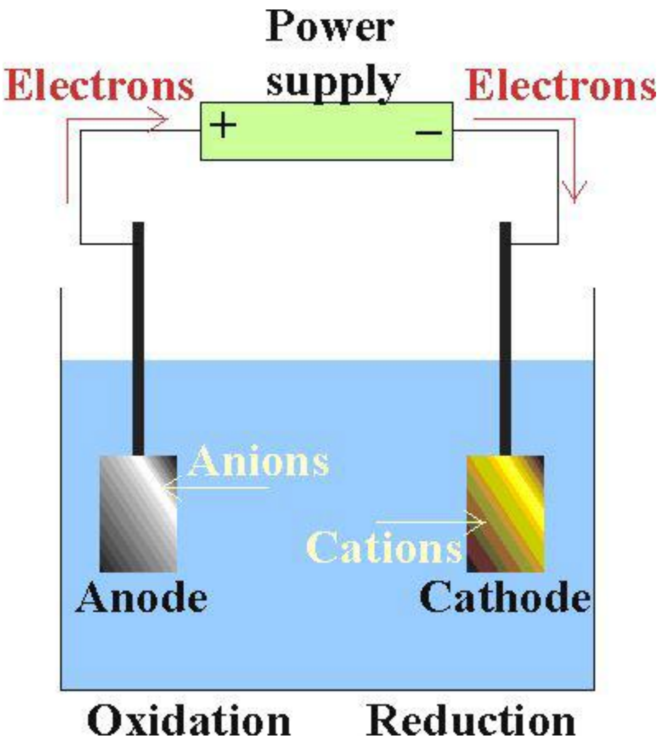
C - 1 mol/dm³ , 298K, E = 0,34V - (-0,76V) = 1,10V

$E^o_{Cu/Cu2+}$ = + 0.34 V; $E^o_{Zn/Zn2+}$ = - 0.76 V

M. Bełtowska-Brzezinska, Wprowadzenie do elektrochemii, UAM, Poznań 2009 (www.wbc.poznan.pl); www//File:Galvanic_cell_labeled.svg

ELECTROLYTIC CELL (ELECTROLYZER). SYSTEM IN WHICH CHEMICAL REACTIONS ARE INDUCED BY EXTERNAL ELECTRICAL ENERGY

electrical energy ⟶ chemical transformation



The flow of electrons and ions in an electrolytic cell:

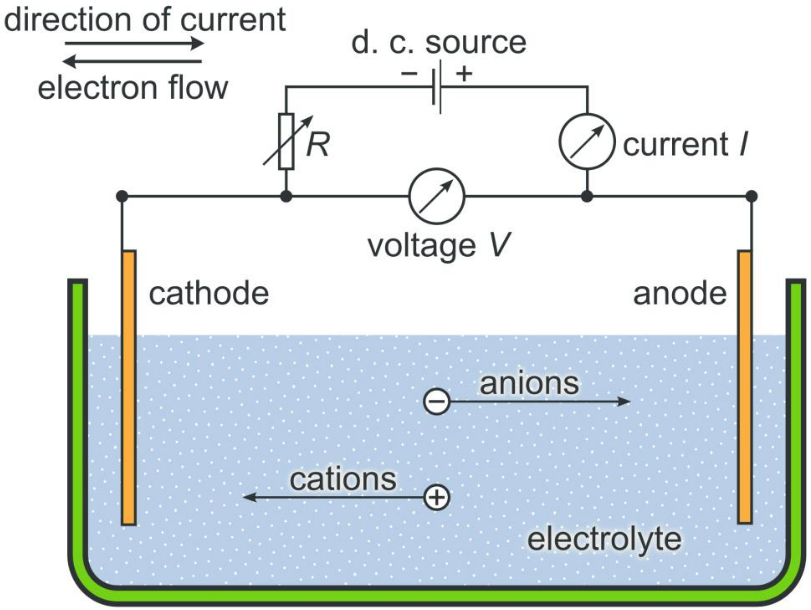
An external supply forces electrons into the cathode, where they are used to bring about a reduction, and withdraws them from the anode, which results in an oxidation reaction at that electrode. Cations migrate towards the negatively charged cathode and anions migrate towards the positively charged anode.

Atkins, Elements of Physical Chemistry, 3rd Ed, Oxford

ELECTROLYSIS

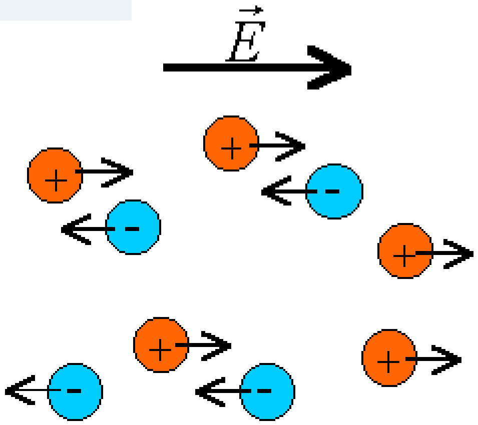
Electrolysis (a forced process) - the totality of phenomena (a number of oxidation – reduction reactions) induced by the flow of electric current through electrolyte solutions.

The energy required to cause the ions to migrate to the electrodes is provided by the external source of electrical potential. Each electrode attracts ions that are of the opposite charge. Positively charged ions (cations) move towards the electron-providing (negative) cathode, whereas negatively charged ions (anions) move towards the positive anode.



Electrolytic cell

$U_r > EMF$



http://www.fizykon.org

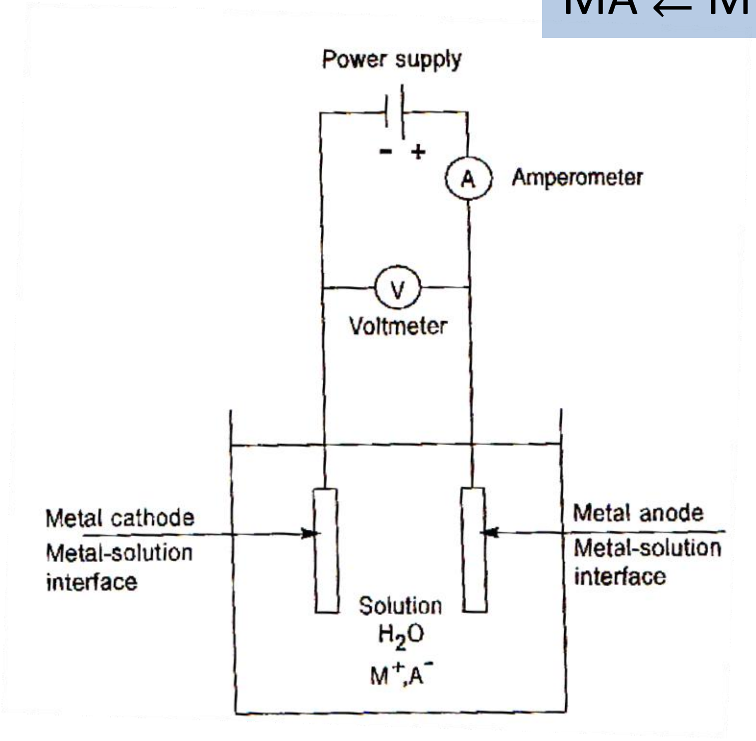
ELECTROLYSIS

At the electrodes, electrons are absorbed or released by the atoms and ions. Those ions that gain or lose electrons to become uncharged atoms separate from the electrolyte.

The formation of uncharged atoms from ions is called discharging

$MA \rightleftarrows M^{z+} + A^{z-}$

$2H_2O \rightleftarrows H_3O^+ + OH^-$



Electrolytic cell for deposition of metal M from an aqueous solution of metal salt MA

Cathode (-):

$M^{z+}_{(aq)} + ze = M^0_{(s)}$

side reaction: $2H^+ + 2e^- \rightarrow H_2\uparrow$

$2H_3O^+ + 2e^- = H_2\uparrow + 2H_2O$ (pH < 7)

$2H_2O + 2e^- = H_2\uparrow + 2OH^-$ (pH ≥ 7)

Soluble anode (+) : $M^0 \rightarrow M^{z+} + ze^-$

Insoluble anode (+):

$2A^{z-} - 2ze^- = A_2\uparrow$

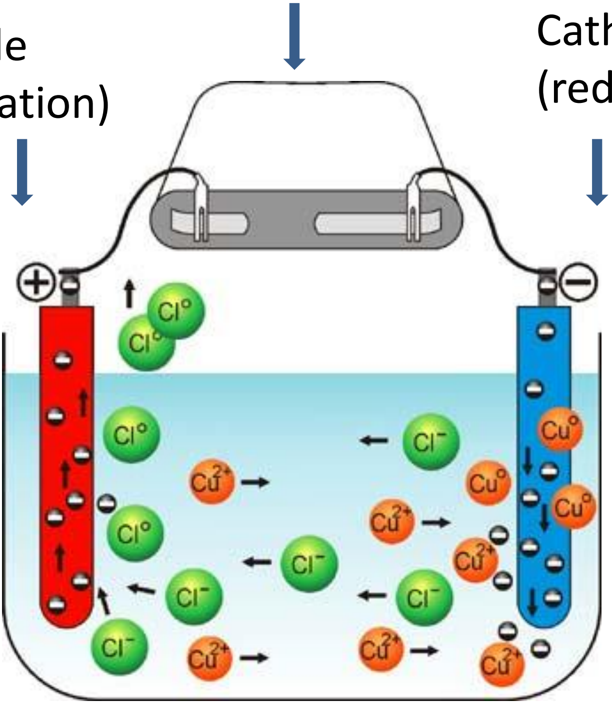
$4OH^- - 4e \rightarrow 2H_2O + O_2\uparrow$

$(H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2\uparrow + 2e^-)$

S^{2-}, J^-, Br^-, Cl^-, fluorine can not be separated

ELECTROLYTIC CELL (ELECTROLYZER). EXAMPLE OF ELECTROLYSIS

Example: electrolysis of an aqueous solution of copper chloride ($CuCl_2$)



Power supply

Anode (oxidation)

Cathode (reduction)

$CuCl_2$ salt in aqueous solution dissociate into ions: **$CuCl_2$ ---> Cu^{2+} + $2Cl^-$**

Cu^{2+} cations migrate to the cathode and they are reduced (discharged) gaining two electrons: **Cathode: Cu^{2+} + 2 e ----> Cu^0**

Cl^- anions are moving in the direction of anode and they are oxidized loosing their electrons: **Anode (Pt): 2 Cl^-- 2 e ----> Cl_2 ↑**

$$K(-) \Rightarrow Cu^{2+} + 2e \rightarrow Cu$$

$$\underline{A(+) \Rightarrow 2Cl^- - 2e \rightarrow Cl_2}$$

$$sum..Cu^{2+} + 2Cl^- \rightarrow Cu + Cl_2$$

Cl^- ions are discharged at the anode in preference to OH^- ions because Cl is below OH in the electrochemical series. The products of electrolysis are thus Cu at the cathode and Cl_2 (and not O_2) at the anode.

total process: **$CuCl_2$ ----> Cu(s) + Cl_2↑**

ELECTROLYTIC CELL (ELECTROLYZER). EXAMPLE OF ELECTROLYSIS

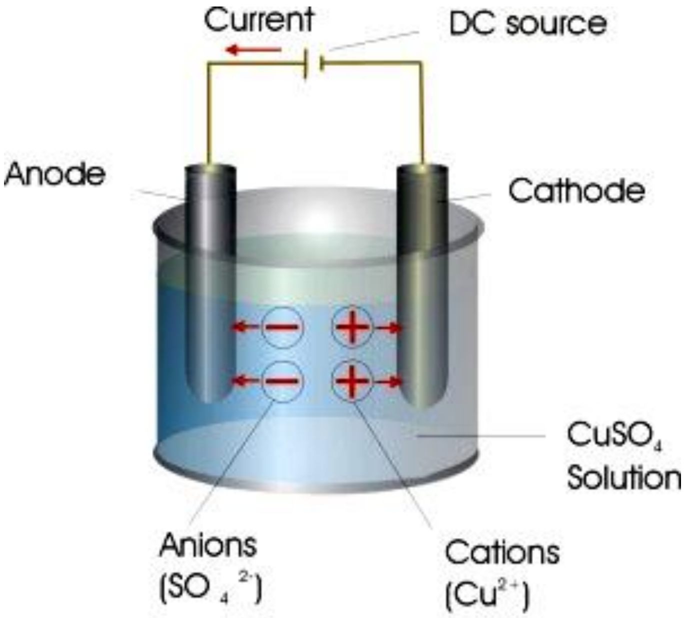
Example: electrolysis of an aqueous solution of copper sulfate ($CuSO_4$)

Following series shows the electrochemical series for cations and anions in the decreasing order of reactivity:

Cations – $K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+} > Mn^{2+} > Zn^{2+} > Fe^{2+} > Ni^{2+} > Sn^{2+} > Pb^{2+} > H^+ > Cu^{2+} > Ag^+$

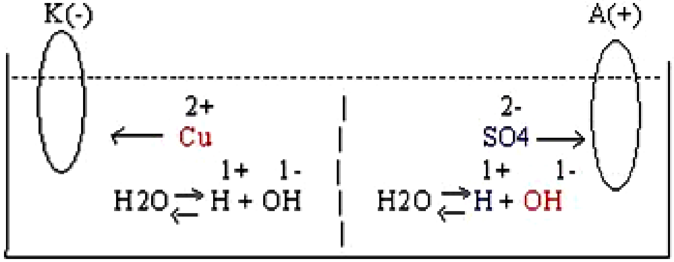
Anions – $SO_4^{2-} > NO^{3-} > CO_3^{2-} > OH^- > Cl^- > Br^- > J^- > S^{2-}$

E^0 Cu/Cu^{2+} = +0,345 V



An Electrolytic Cell

As a rule, the cation or anion which is lower in position in the electrochemical series is discharged first. Further, the anion which does not contain oxygen, is discharged in preference to that which contains oxygen.



K (-): Cu^{2+} + 2 e ----> Cu^0

A (+) Pt: $2OH^-$ - 2e ----> H_2O + ½ O_2↑

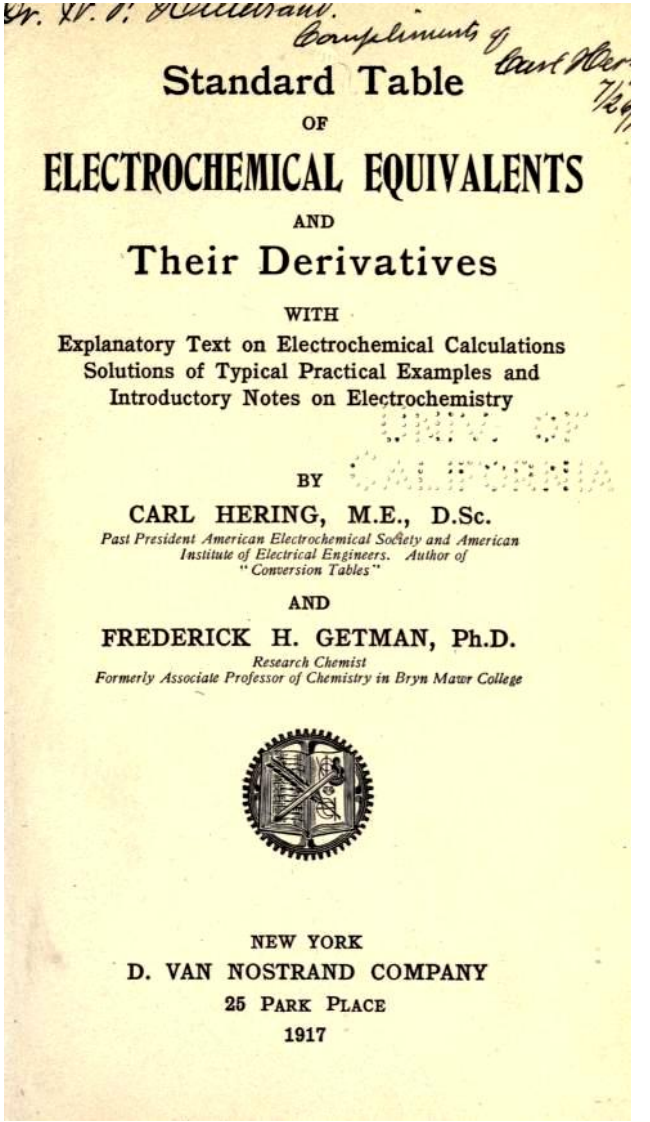
FARADAY’S LAWS OF ELECTROLYSIS, FIRST LAW

Farady’s laws are quantitative relationships based on the electrochemical researches published by Michael Faraday in 1834.

FIRST LAW : The mass of a substance produced by electrolysis is directly proportional to the quantity of electricity passed through the cell.

$$m = kQ = kIt$$

Q = quantity of electricity or charge in coulombs (C),
I = current in amps (A),
t = time (seconds);
k [mg/A·s]– the **electrochemical equivalent**: the quantity of a substance produced by 1 ampere second (1 coulomb), 1 ampere hour (ah) = 3600 coulombs is used as the practical unit in electroplating technology.



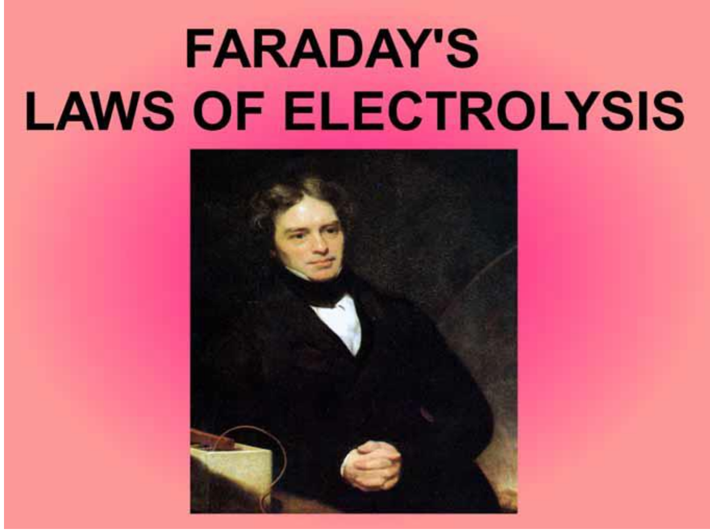
Dr. W. D.
Compliments of
Carl Her
7/2

Standard Table
OF
ELECTROCHEMICAL EQUIVALENTS
AND
Their Derivatives
WITH
Explanatory Text on Electrochemical Calculations
Solutions of Typical Practical Examples and
Introductory Notes on Electrochemistry

BY
CARL HERING, M.E., D.Sc.
Past President American Electrochemical Society and American Institute of Electrical Engineers. Author of "Conversion Tables"
AND
FREDERICK H. GETMAN, Ph.D.
Research Chemist
Formerly Associate Professor of Chemistry in Bryn Mawr College

NEW YORK
D. VAN NOSTRAND COMPANY
25 PARK PLACE
1917

FARADAY’S LAWS OF ELECTROLYSIS
SECOND LAW



The second law states that the masses of different substances deposited or dissolved as a result of the passage of the same quantity of electricity through the electrolyte are proportional to the chemical equivalents *A* of the substances.

$$\frac{m_1}{m_2} = \frac{A_1}{A_2} = \frac{k_1}{k_2}$$

$$\frac{A_{chem}}{k_{el}} = const = F$$

$$k \cdot F = A_{chem}$$

$$Q = \frac{Fmz}{M}$$

$$A_{chem} = \frac{M}{z}$$

$$k = \frac{M}{zF}$$

$$m = k \cdot Q$$

$$F = \frac{M}{k \cdot z}$$

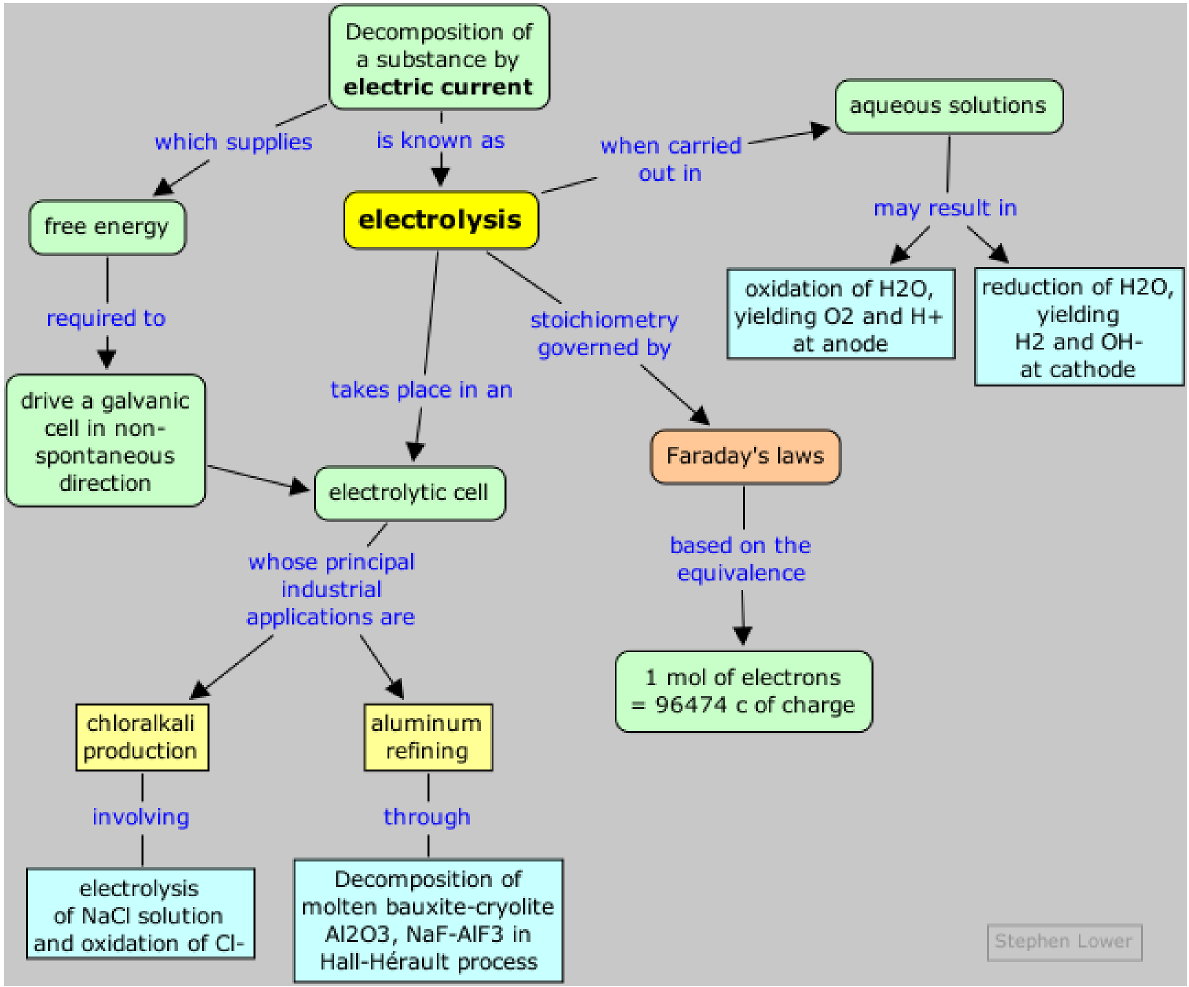
It follows from the second law that the same quantity of electricity, called the Faraday constant *F*, is required for the deposition of the same gram-equivalent weight of different substances.

Faraday's laws can be summarized by $m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$

m is the mass of the substance deposited at an electrode in grams; *Q* is the total electric charge passed; ***F* = 96 485 C mol^{-1}** is the **Faraday constant**; *M* is the molar mass of the substance; *z* is the valency number of ions of the substance (electrons transferred per ion).

ELECTROLYSIS - SUMMARY

During the electrolysis of an aqueous solution of salt on the cathode metals are released (but not all, and only the number of voltage standing for aluminum). When a metal cation is not discharged, the separated hydrogen (originating from the decomposition of water).



Following **factors** determine the **preferential discharge** of the ion at the electrode:

- **The position of the ion in the electrochemical series**
- **Concentration of the ion in the electrolyte**

  If the concentration of a particular ion is high, then this can alter the preferential discharge
- **Nature of the electrode**

  The electrodes (active or inert) used in electrolysis determine the ion preferred for discharge.

Reactive ions (potassium, sodium, calcium, magnesium, aluminium) will **NEVER BE DISCHARGED**
Sulphate and nitrate are **NEVER DISCHARGED** in concentrated/dilute solutions.

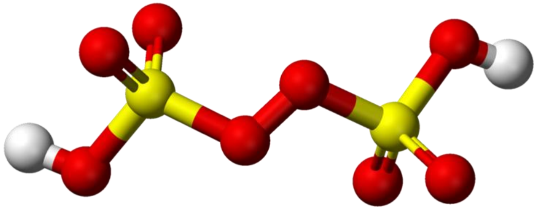
INDUSTRIAL APPLICATIONS

Electrolysis of aqueous solutions

Electrolysis is used in almost all industries mainly: chemical, hydrometallurgy, electronics, aviation, automotive, jewelery and others. Electrolysis is commercially highly important as a stage in the separation of elements from naturally occurring sources such as ores.

Electrolysis processes used in industry can be divided as follows:

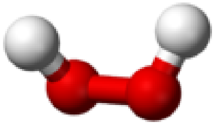
Processes in which there is no deposition of the metal on the cathode:
e.g. production of pure hydrogen by decomposition of water, production of chlorine and sodium hydroxide by the electrolysis of sodium chloride, production of hypochlorite or sodium chlorate (used as a strong bleaching or oxidizing agents), oxidation of sulfuric acid to the corresponding peroxy compounds, which decomposition leads to a hydrogen peroxide, various processes of reduction and oxidation etc.



$H_2S_2O_8$

peroxydisulfuric acid

$$H_2S_2O_8 + 2H_2O \rightarrow H_2O_2 + 2H_2SO_4$$



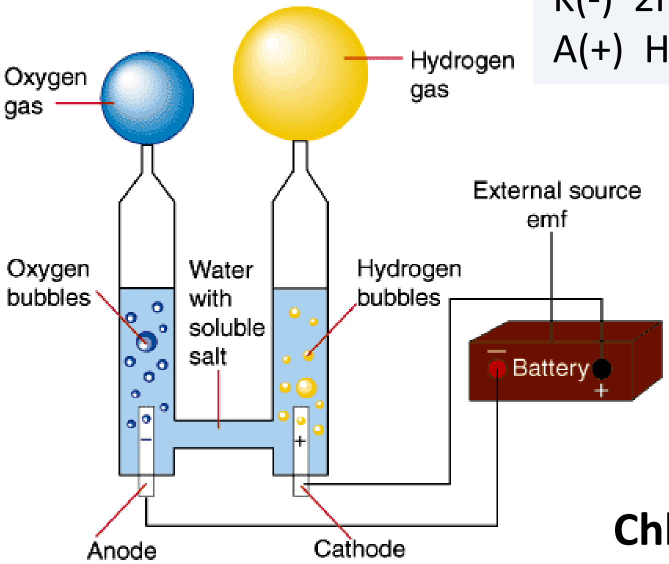
H_2O_2

hydrogen peroxide

Anodic oxidation of sulphuric acid at the platinum electrodes

PROCESSES IN WHICH THERE IS NO DEPOSITION OF THE METAL ON THE CATHODE

Setup for the electrolysis of water



K(-) $2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-$
A(+) $H_2O \longrightarrow 2H^+ + ½O_2\uparrow + 2e.$

$E > -1.23$ V

$2H_2 + O_2 \rightarrow 2H_2O$

Chlor-alkali cell room produced by electrolysis of concentrated seawater

$K(-) \Rightarrow 2H_2O + 2e \rightarrow H_2 + 2OH^-$

$A(+) \Rightarrow 2Cl^- - 2e \rightarrow Cl_2$

$2NaCl + 2H_2O \rightarrow 2Na^+ + 2OH^- + Cl_2 + H_2$

Chlorate cell room

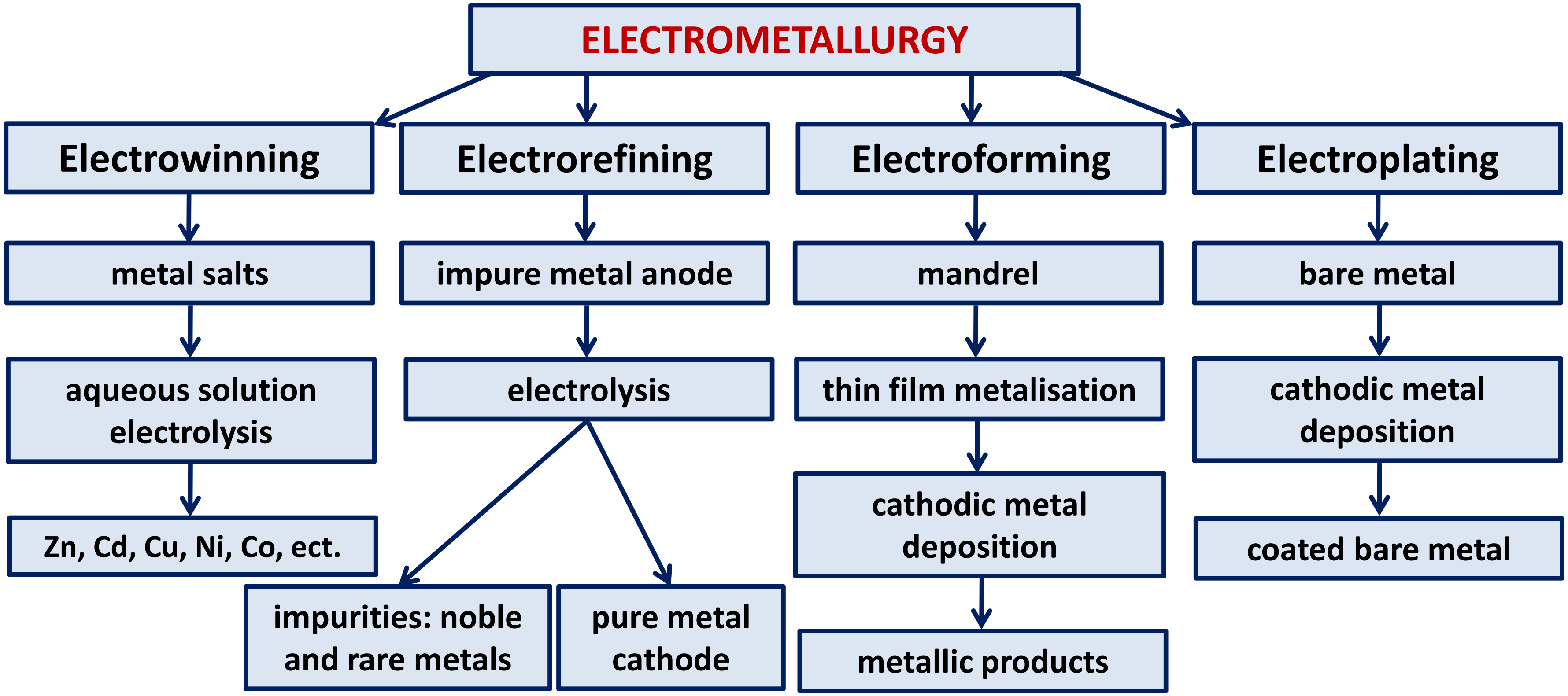
K(-) $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$
A(+) $2Cl^- \rightarrow Cl_{2\,(aq)} + 2e^-$

$Cl_{2\,(aq)} + H_2O \rightarrow HClO + H^+ + Cl^-$
$HClO - H_2O \rightarrow H^+ + ClO^-$
$Na^+ + ClO^- \rightarrow NaOCl$

A(+) $12HClO + 6H_2O \rightarrow 3O_2\uparrow + 8Cl^- + 4ClO_3^- + 24H^+ + 12e^-$

(http://electrochem.cwru.edu/encycl/)
http://www.sparknotes.com/chemistry/electrochemistry/electrolytic

PROCESSES DESIGNED TO THE DEPOSITION OF THE METALS ON THE CATHODE -ELECTROMETALLURGY


ELECTROMETALLURGY

Electrowinning
- metal salts
- aqueous solution electrolysis
- Zn, Cd, Cu, Ni, Co, ect.

Electrorefining
- impure metal anode
- electrolysis
- impurities: noble and rare metals
- pure metal cathode

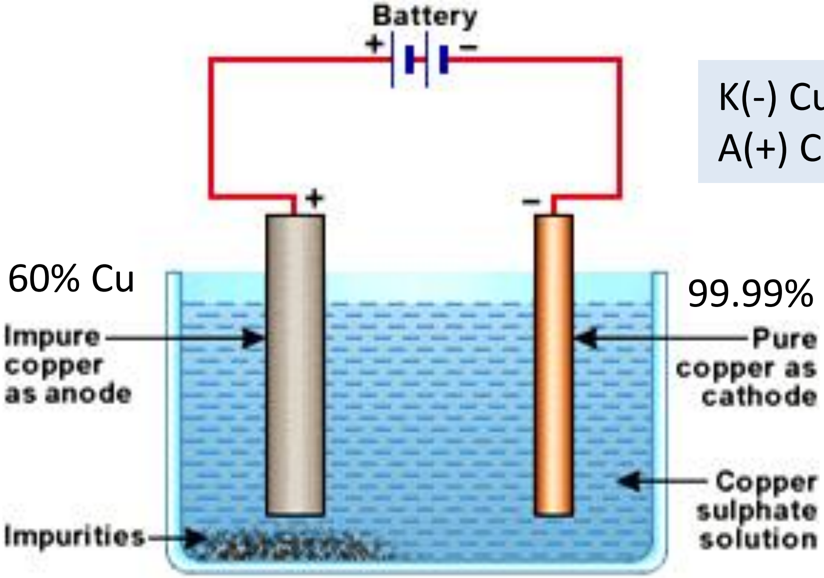
Electroforming
- mandrel
- thin film metalisation
- cathodic metal deposition
- metallic products

Electroplating
- bare metal
- cathodic metal deposition
- coated bare metal

Nasser Kanani, Electroplating-Basic Principles, Processes and Practice Elsevier, 2006

PROCESSES DESIGNED TO THE DEPOSITION OF THE METALS ON THE CATHODE REFINING (Industrial purifications)

e.g. **refining** of metallurgical copper (used as an anode) to the pure electrolytic copper (deposited on the cathode)



60% Cu

99.99% Cu

K(-) $Cu^{2+} + 2e \longrightarrow Cu^0$
A(+) $Cu^0 \longrightarrow Cu^{2+} + 2e$

Experimental setup for the electrolytic refining of copper

Copper Refining Cells

The Xstrata copper electrorefining tankhouse

KGHM
POLSKA MIEDŹ S.A.

PROCESSES DESIGNED TO THE DEPOSITION OF THE METALS ON THE CATHODE
ELECTROWINNING (Extraction of metals from ores)

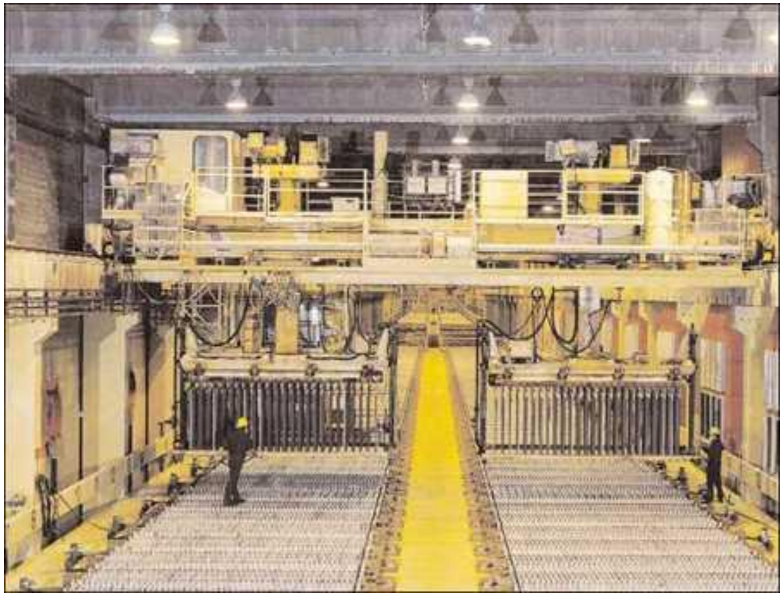
electrowinning (extraction of metals starting from their ores e.g. hydrometallurgical production of zinc etc.). Today over 90% zinc is produced hydrometallurgically in electrolytic plants.

Lead Electrowinning Anodes

$Pb(+)\ 2H_2O \longrightarrow 4H^+ + O_2 + 4e$

$Al(-)\ Zn^{2+} + 2e \longrightarrow Zn^0$

$E \approx -3.3\text{-}3.5$ volts

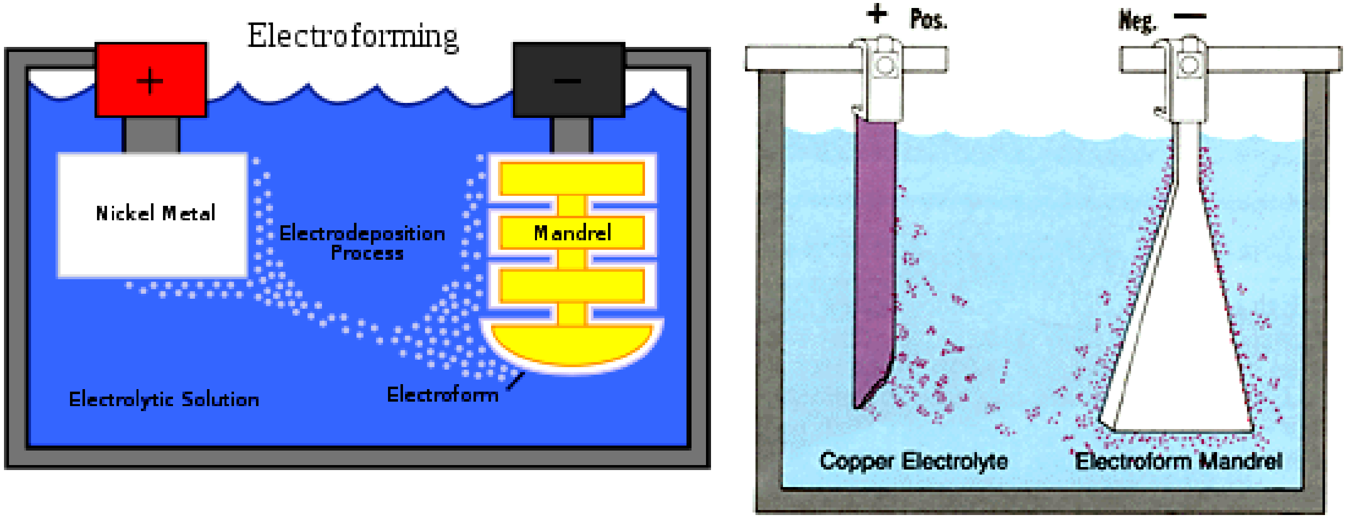


Zinc electrowinning at the Teck Cominco zinc refinery in Trail, BC, Canada

Electrowinning cells for recovery of zinc

PROCESSES DESIGNED TO THE DEPOSITION OF THE METALS ON THE CATHODE: ELECTROFORMING

Electroforming in most cases is metal built-up over a non-metallic surface, it can be quite thick and it can be separated from the mandrel or work piece as a stand alone object. This process differs from electroplating in that the plating is much thicker and can exist as a self-supporting structure when the mandrel is removed. Some of the common uses for electroforming are jewelry, mold making and reproduction of parts.



Experimental setup for the elctroforming of nickel and copper

PROCESSES DESIGNED TO THE DEPOSITION OF THE METAL ON THE CATHODE: ELECTROPLATING (ELECTRODEPOSITION, ELECTROCHEMICAL DEPOSITION)

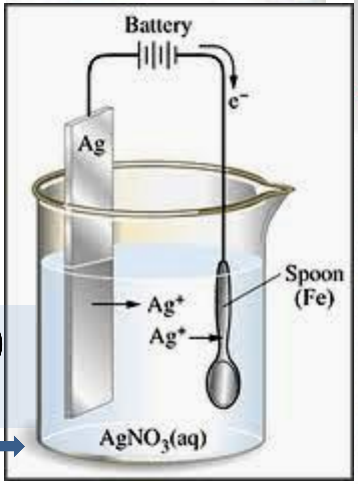
Electroplating is a technology related to surface engineering. An electric current passing through the solution causes objects at the cathode or work piece to be coated by the metal in the solution.

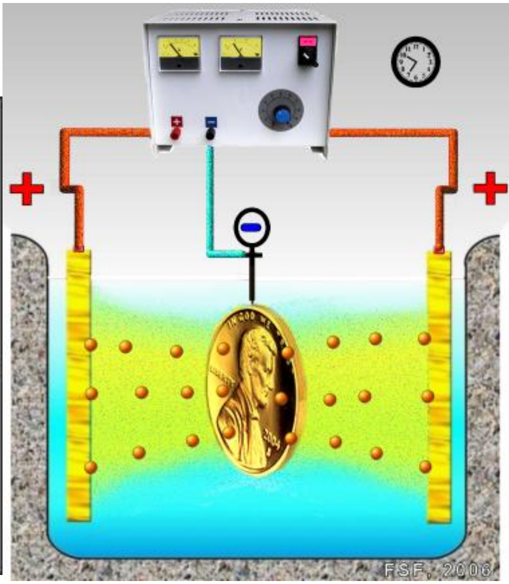
In the electroplating processes, coatings may be formed either from pure metals, alloys of several metals, alloys of metals and non-metals, multilayers or composite coatings. Surface layers, depending on their intended use, comply with the functions: **protective, decorative, protective + decorative and technical**.

Electroplating (one of surface engineering techniques) is now used in many industries e.g.: electrical industry, automotive, aviation, electronics, jewelry, biomedical engineering.

In general, to electroplate, we need to make the cathode the object for plating. The anode is then made of the metal we wish to plate with and the electrolyte needs to be a solution of a salt of this metal.

A(+): Ag (s) -> Ag$^+$ (aq) + e$^-$ (Silver dissolves from the anode)
K(-) : Ag$^+$ (aq) +e$^-$ -> Ag (s) (Silver deposits on the object)





PROCESSES DESIGNED TO THE DEPOSITION OF THE METAL ON THE CATHODE: ELECTROPLATING (ELECTRODEPOSITION, ELECTROCHEMICAL DEPOSITION)

TYPES OF GALVANIC (ELECTROPLATED) COATINGS

Articles are electroplated to alter their appearance; to provide a protective coating; to give the article special surface properties; to give the article engineering or mechanical properties.

Protective coatings **-** used primarily for protection of the basis metal, usually iron and steel (e.g. Zn). To form a thin protective coating of a metal on the surface of another which is likely to corrode.

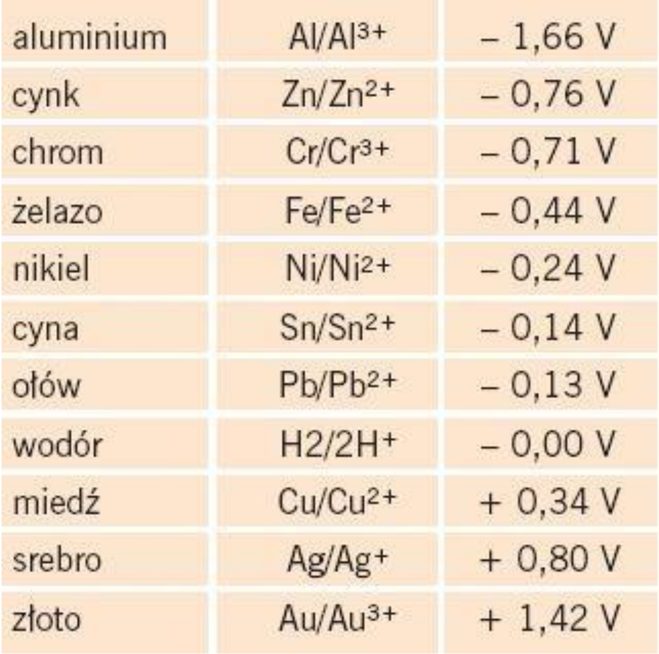
Decorative coatings - applied to improve the surface appearance (color, gloss, smoothness)

Decorative protective coatings, used primarily for adding attractive appearance to some protective qualities e.g. Ni on steel, Cu-Ni-Cr on steel.

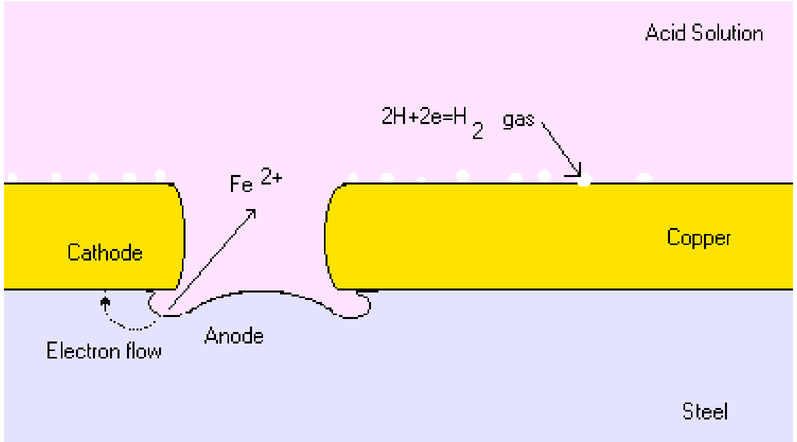
Engineering (functional) coatings - used for specific properties imparted to the surface, such as solderability, wear resistance, reflectivity, conductivity, and many others.

PROTECTIVE COATINGS – CORROSION RESISTANT COATINGS

Cathodic coatings. An example of a corrosion cell is provided by an imperfect coating of copper on steel immersed in dilute sulphuric acid. The current generated passes from the **copper to the steel** by the path of lowest resistance and returns to the copper through the solution by the passage of ions. The steel, which has the greatest negative potential, dissolves and is called the anode; whilst the copper is called the cathode. (e.g. **Ni, Cu, Au, Ag**)

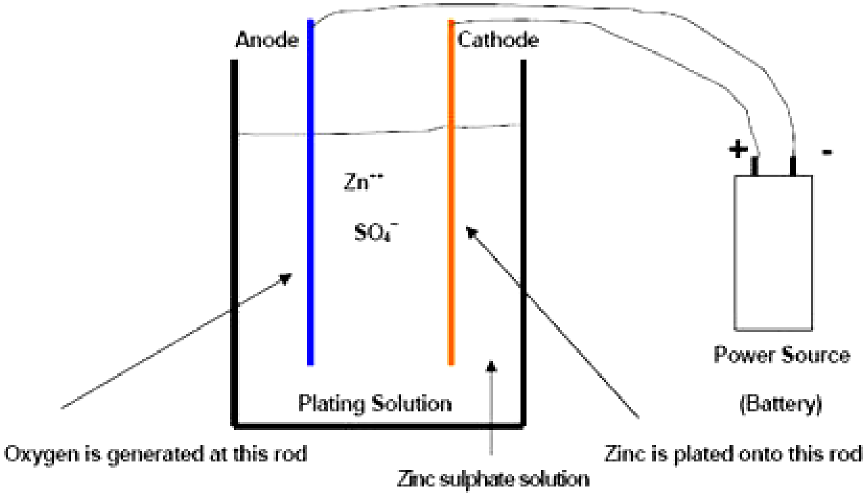


aluminium	Al/Al^{3+}	– 1,66 V
cynk	Zn/Zn^{2+}	– 0,76 V
chrom	Cr/Cr^{3+}	– 0,71 V
żelazo	Fe/Fe^{2+}	– 0,44 V
nikiel	Ni/Ni^{2+}	– 0,24 V
cyna	Sn/Sn^{2+}	– 0,14 V
ołów	Pb/Pb^{2+}	– 0,13 V
wodór	$H2/2H^{+}$	– 0,00 V
miedź	Cu/Cu^{2+}	+ 0,34 V
srebro	Ag/Ag^{+}	+ 0,80 V
złoto	Au/Au^{3+}	+ 1,42 V



Anodic coatings for the protection of iron and steel substrates are almost entirely limited to **zinc** and its alloys. Where coatings anodic to the substrate are applied, the corrosion protection is referred to as cathodic protection or sacrificial protection. The substrate is made to be the cathode and the coating the sacrificial corroding anode.

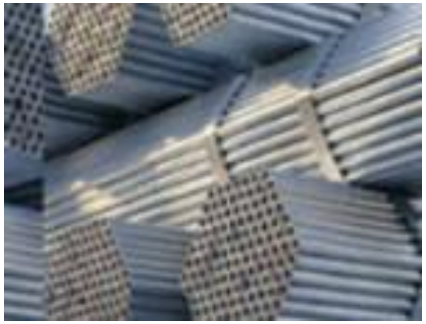
ELECTROPLATING (ELECTRODEPOSITION): PROTECTIVE COATINGS
ZINC PLATED STEEL SHEETS – CORROSION RESISTANT COATINGS



The schema of the electroplating cell

http://www.keytometals.com

The steel sheet electroplating process utilizes the same basic principle as that for conventional decorative finish electroplating. However, the steel sheet process differs in that the electroplated coating is applied by passing the strip at high speeds through a series of plating cells, building the coating thickness by a small amount each time the strip passes through an individual cell.



Modern Continuous Electroplating Line

ELECTROPLATING (ELECTRODEPOSITION): DECORATIVE COATINGS
DECORATIVE CHROMIUM PLATING

Chrome plating is a very popular finish for many decorative applications, especially for the automotive and building industries in which there are many decorative trims and components. Stainless steel is electroplated first with nickel and then with a very thin layer of the more expensive but more attractive metal chromium.

Appearance	Hardness, HV
Matte	640
Milky	830
Slightly Milky	990
Bright	1000
Slightly Frosty	1005
Frosty (smooth)	1020
Frosty (rough)	1060
Burnt	1165

Decorative chrome plating line

ELECTROPLATING (ELECTRODEPOSITION): TECHNICAL COATINGS
HARD CHROMIUM PLATING

Hard chromium plating is produced by electrodeposition in a solution of chromic acid. It is also known as industrial, functional or engineering chromium plating and is very different from decorative chromium plating.

Hard chrome plating line

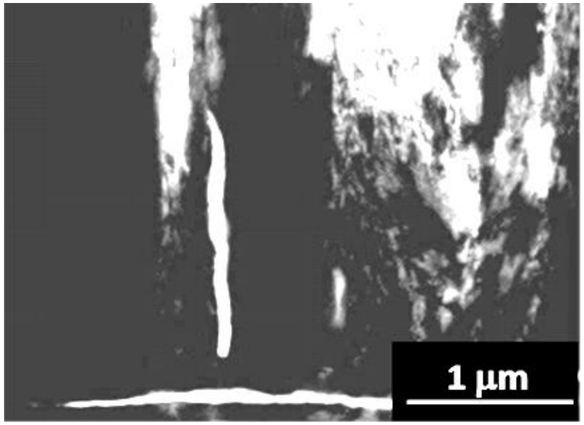
Industrial **hard chrome plating** is applied on bearing surfaces, seal areas

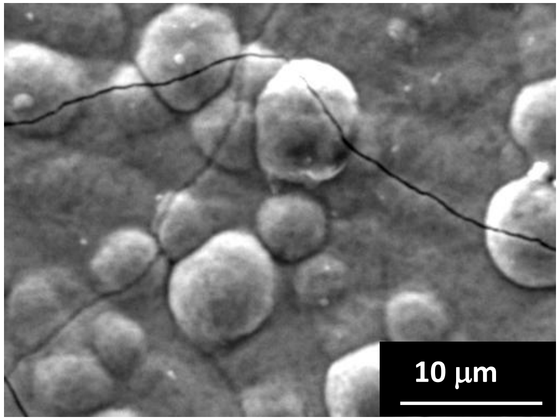
Hard chromium plating solution

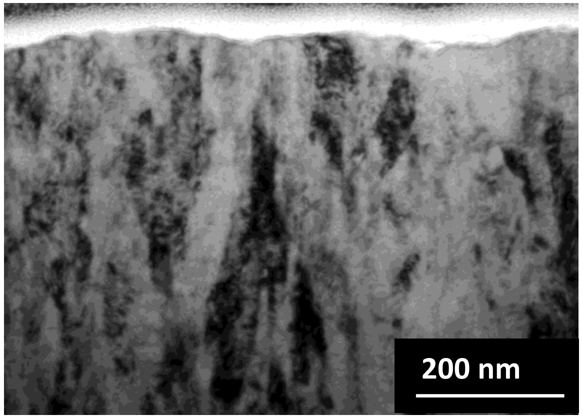
Hard chromium deposits are intended primarily to increase service life of functional parts by increasing their resistance to wear, abrasion, heat and corrosion.

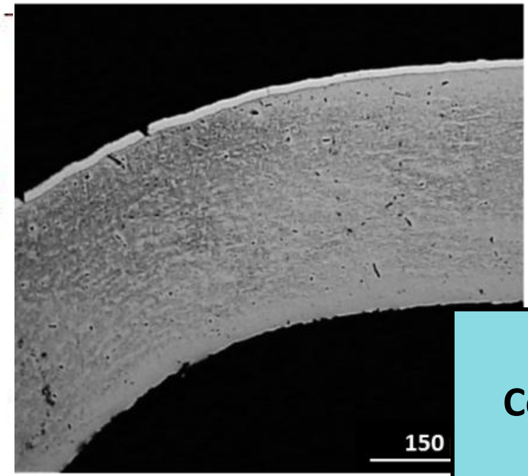
Typical chromed parts would be: automotive valve stems, piston rings, shock rods, Mac Pherson struts, the bores of diesel and aircraft engine cylinders, and hydraulic shafts.

ELECTROPLATING (ELECTRODEPOSITION): TECHNICAL COATINGS
HARD CHROMIUM PLATING









Coating	H_{IT} GPa	E_{IT} GPa	$W_v \cdot 10^{-6}$ mm^3/Nm	L_C [N]
Ni-W	7,72	192	2,16	>30
Ni-W/Al_2O_3	8,50	193	2,25	>30
Cr	9,78	219	3,43	8

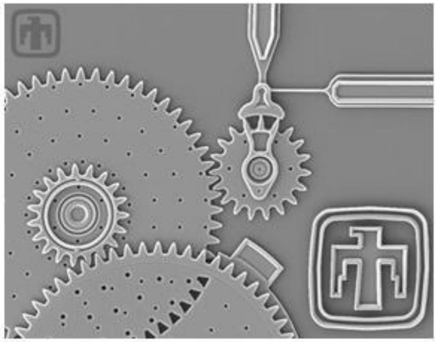
Hard chromium electrodeposited coatings (IMIM PAN)

MODERN ELECTROPLATING TECHNOLOGY

In addition to the traditional use, modern plating technology is highly advanced, and has developed to cover a wide range of applications, e.g. for surface finishing, plating technology can offer novel processes to fabricate high performance films or fine microstructural bodies in the microelectronics industry. (MicroElectroMechanical Systems (MEMS), data storage, to fabricate thin films of compound semiconductors and nanoscale multilayers in micro-patterns etc.). Size of MEMS systems and elements – about 0.02 – 1 mm and 0.001 – 0.1 mm, respectively.

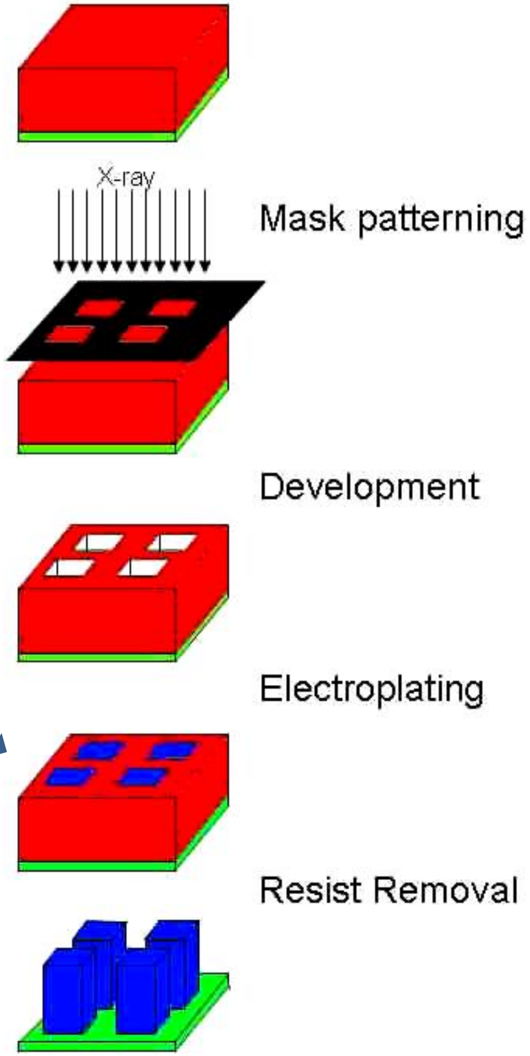
Through mask electrodeposition.
In the electroplating step, nickel, copper, (Ni-Fe) or gold is plated upward from the metalized substrate into the voids left by the removed photoresist.

LIGA is a German acronym for ***Li**thographie, **G**alvanoformung, **A**bformung* (Lithography, Electroplating, and Molding) that describes a fabrication technology used to create high-aspect-ratio microstructures.



Microransmission (gear) Sandia National Laboratories

Schematic process flow LIGA



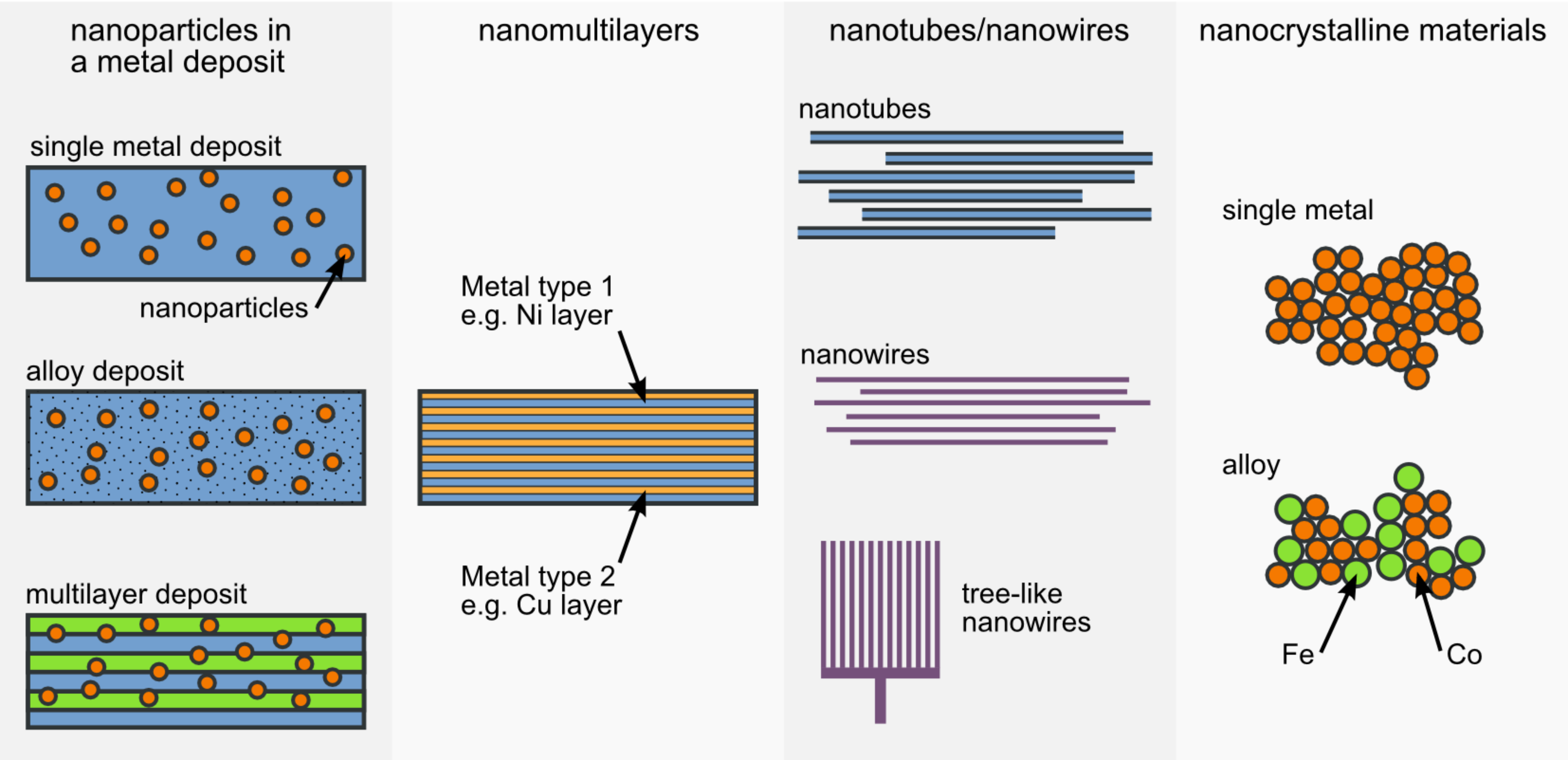
http://www.lboro.ac.uk

MODERN ELECTROPLATING TECHNOLOGY - IN NANOTECHNOLOGIES

Nanostructured materials produced by the electrodeposition techniques

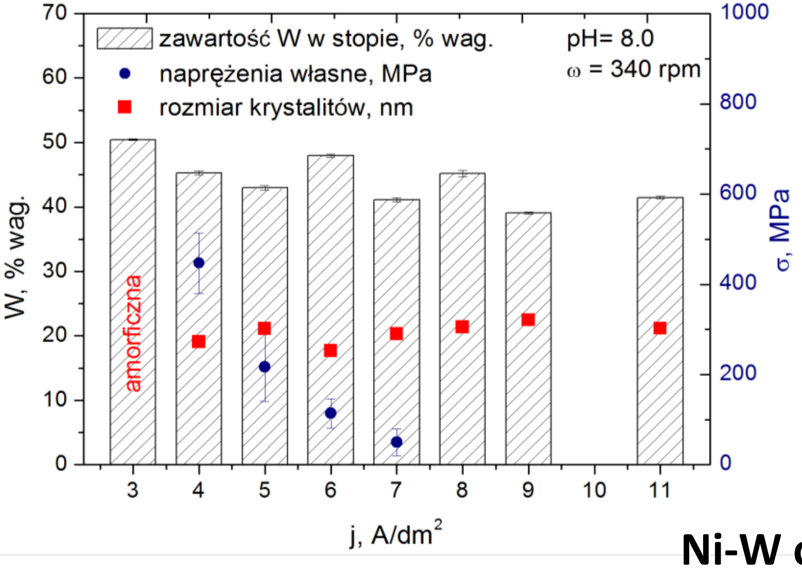
Types of nanostructure materials

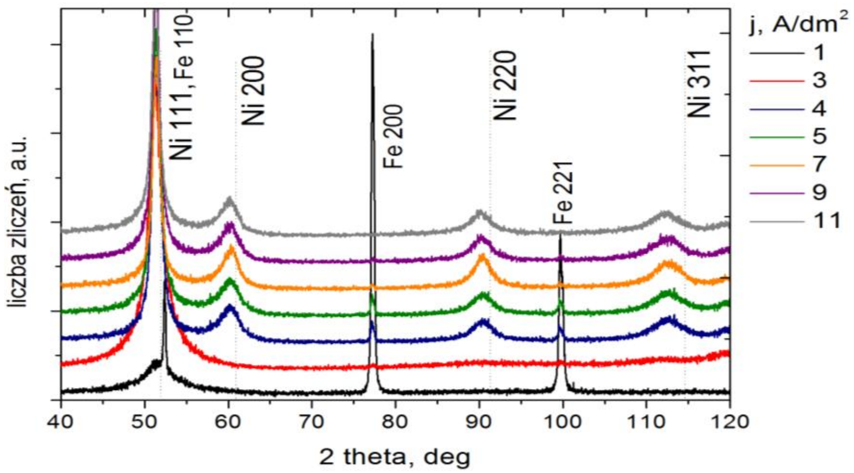
1 nano= 10^{-9} m



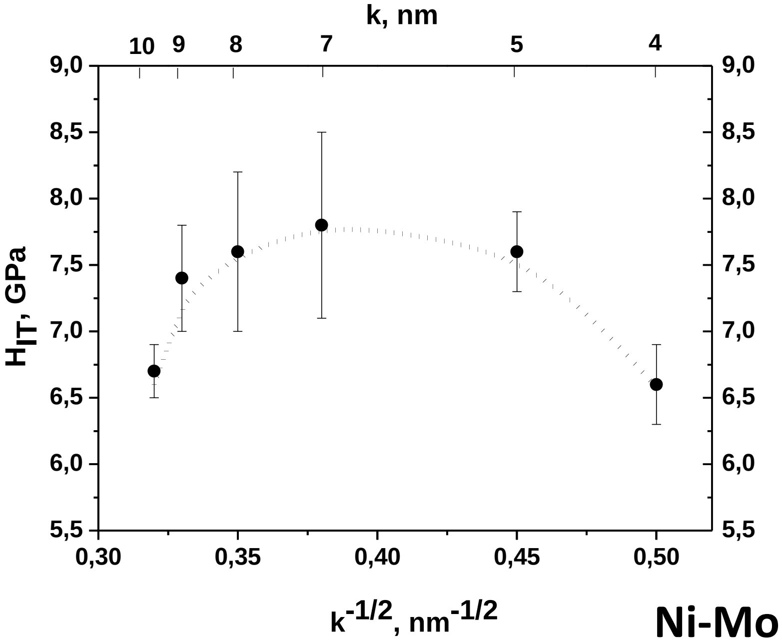
C.T.J. Low, R.G.A. Wills, F.C. Walsh, Electrodeposition of composite coatings containing nanoparticles in a metal deposit

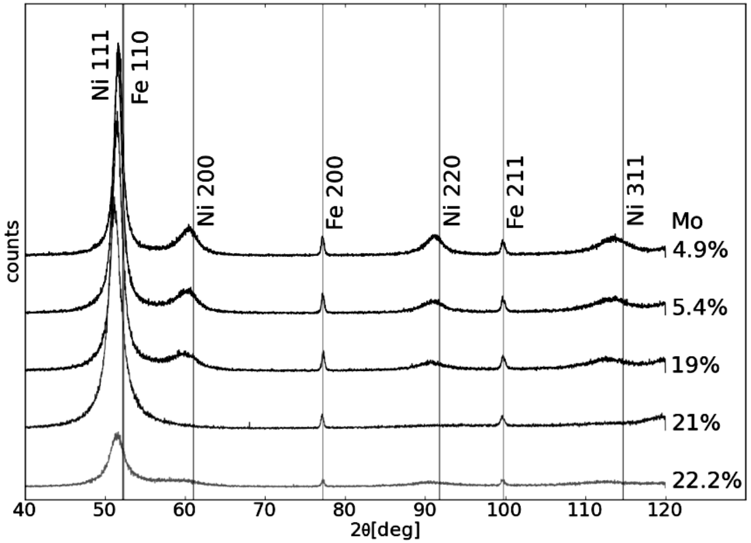
NANOCRYSTALLINE ELECTRODEPOSITED COATINGS - EXAMPLES





Ni-W coatings (IMIM PAN)

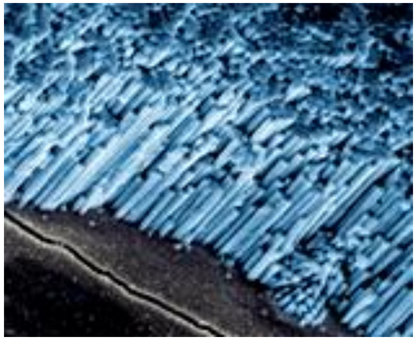




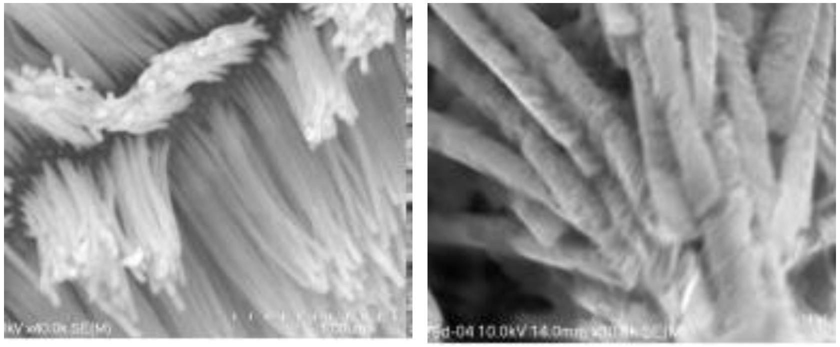
Ni-Mo coatings (IMIM PAN)

MODERN ELECTROPLATING TECHNOLOGY - IN NANOTECHNOLOGIES

Electrodeposition becomes a viable process for nanofabrication, important in the tailoring of nanosized structural features

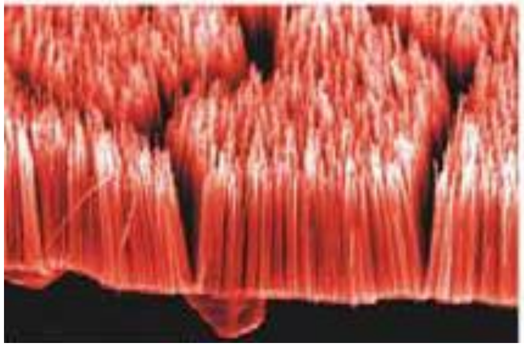


Ni-W nanowires

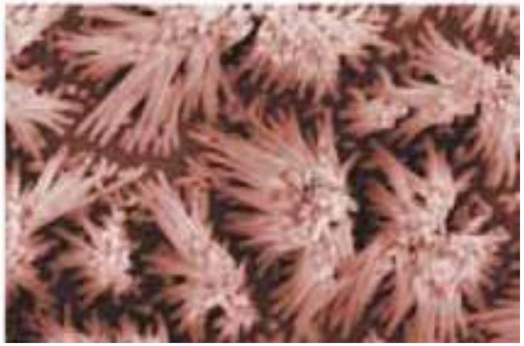


Ag nanowires

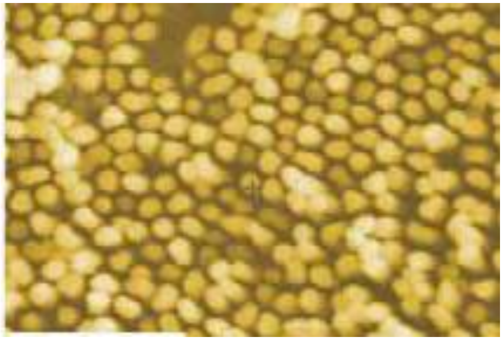
Sb nanowires



Cu nanowires



Sn nanowires



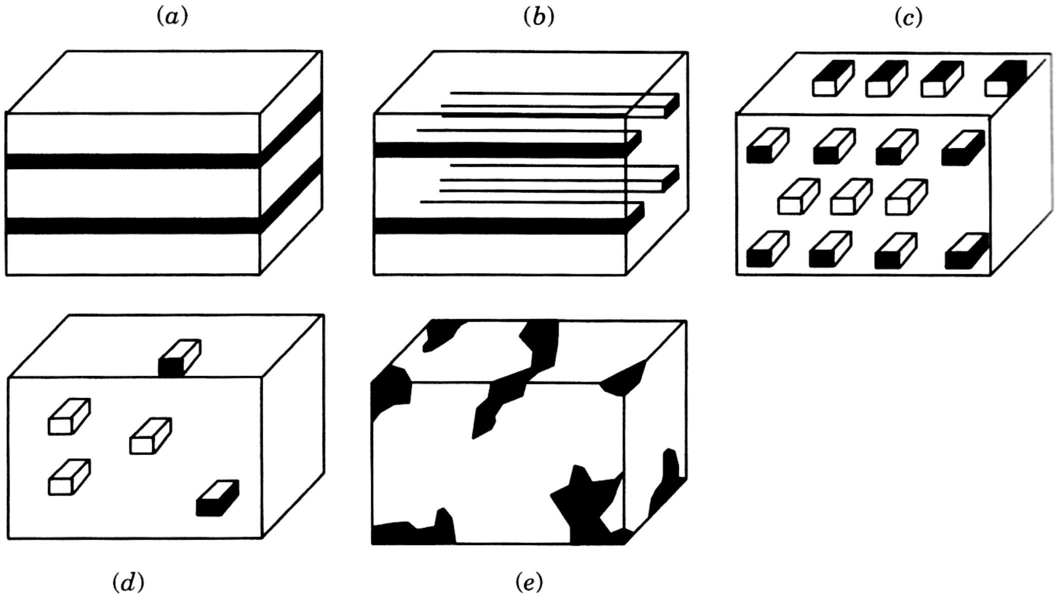
Au nanowires

http://www.chemia.uj.edu.pl

Poster at Nanotechnologia PL, by Agnieszka Brzózka See On-line Journal of Nanotechnologia PL

MODERN ELECTROPLATING TECHNOLOGY

Nanostructural materials are divided into three main types: one-dimensional structures (known as multilayers) made of alternate thin layers of different composition, two-dimensional structures (wire-type elements suspended within a three-dimensional matrix), and three-dimensional constructs made of a distribution of fine particles suspended within a matrix (in either periodic or random fashion) or an aggregate of two or more phases with a nanometric grain size.



(*a*) Quantum wells, (*b*) quantum wires, (*c*) ordered arrays of quantum boxes, (*d*) random quantum dots, and (*e*) aggregate of nanometer-sized grains.

A RAPID PROGRESS REFLECTS THE POTENTIAL FOR THE ELECTROPLATING METHOD TO BECOME ONE OF TODAY LEADING-EDGE TECHNOLOGIES

ELECTROPLATING (ELECTRODEPOSITION, ELECTROCHEMICAL DEPOSITION)

ADVANTAGES

ELECTRODEPOSITION TECHNOLOGY

- LOW PROCESSING TEMPERATURE
- COST-EFFECTIVE (ECONOMIC)
- SIMPLICITY AND LOW COST EQUIPMENT
- EASE AUTOMATING
- HIGH RATE OF DEPOSITION
- CONTINUOUS DEPOSITION
- POSSIBILITY OF DEPOSITION ON LARGE, IRREGULAR SURFACE AREAS
- STRICTLY DEFINED COATINGS THICKNESS
- ASSURES PRECISE THE PROCESS CONTROL BY ADJUSTING SEVERAL PARAMETERS
- HIGH PURITY DEPOSITED METAL

DISADVANTAGES

It requires electrical contact to the substrate when immersed in the liquid bath. In any process, the surface of the substrate must have an electrically conducting coating before the deposition can be done.

ELECTROPLATING VARIABLES

TYPE OF METALS (PURE METAL, ALLOY)

BATH PARAMETERS

- Solution composition and concentration
- Type of metallic salts (effect of anion type)
- Type and concentration of complexing agents
- Solution pH and pH buffer
- Additives (brightener, leveling agent, stress reducer, supporting electrolyte)

OPERATING PARAMETERS

- Substrate material (metal, non-metal)
- Pre-treatment of substrate materials (deoxidation, degreasing, washing, drying)
- Current density: *(Direct current (DC); Pulsed direct current (PDC); Pulsed reverse current (PRC); Potentiostatic (P); Pulsed potentiostatic (PP)*
- Overpotential
- Agitation (static, stirrer, bubbling, ultrasonic, vibration etc.)
- Plating temperature

OTHER: Shape of electrolyzer, type of anode materials (soluble, non-soluble)

STRUCTURES OF ELECTRODEPOSITED COATINGS

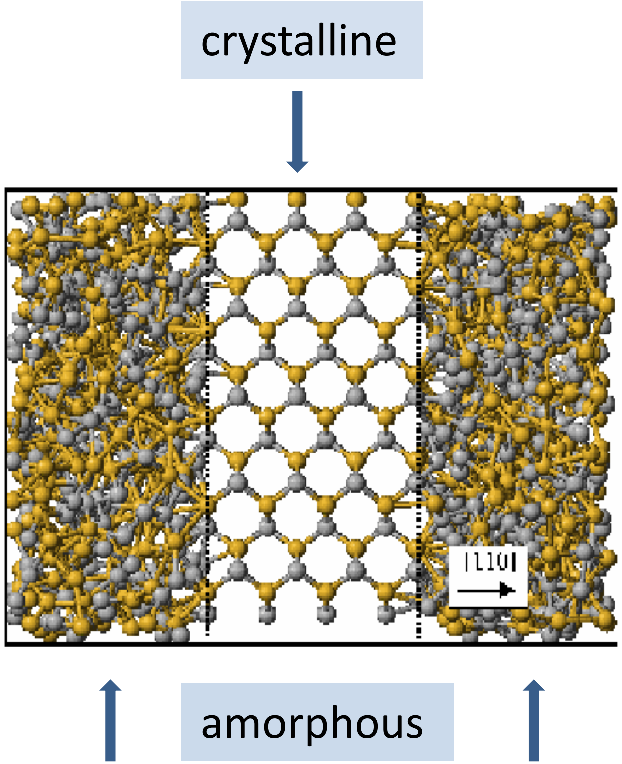
In the electroplating processes, coatings may be formed either from pure metals, alloys of several metals, alloys of metals and non-metals, multilayers or composite coatings.

In most cases, the metallic deposit thus obtained is crystalline; hence, this proces is called **electrocrystallization**.

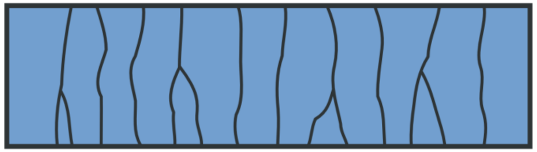
During electrocrystallization of alloys, as in crystallization from a melt, the components can crystallize out separately or solid solution and intermediate phases can be formed. An important difference is that the electrolitically crystallized alloys are normally **not present in thermodynamic equilibrium**. Hence, characteristic differences occur as compared to the phase diagram, and the composition of the individual phases often deviates greatly from the phase diagram.

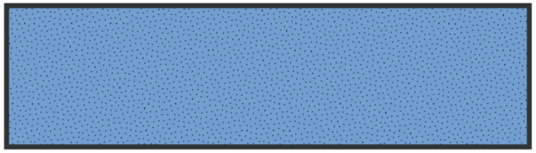
SCHEME OF MICROSTRUCTURES OF ELECTRODEPOSITED COATINGS

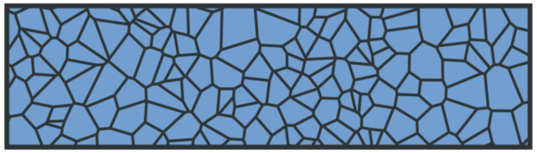
Different microstructures of electrodeposited coatings are observed: **single phase** microstructures, including **columnar**, **fine grained** and **dendritc** deposits. Besides these, plating can yield **amorphous** materials, **multiphase alloys**, composition **modulated alloys** or **metal matrix composites**.

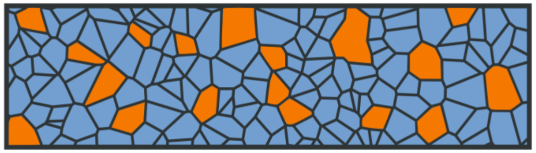


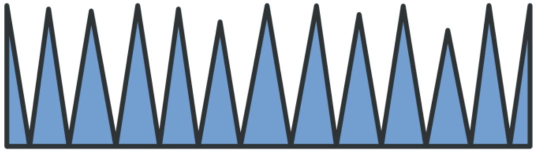
Crystalline layer between amorphous layers

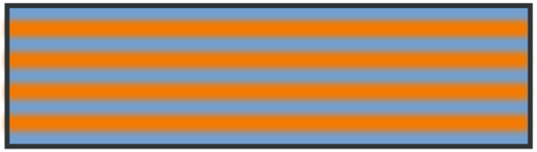

columnar

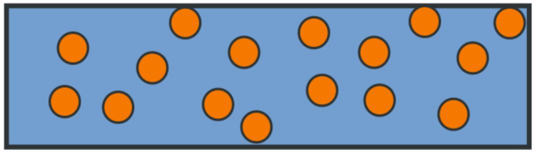

amorphous


equiaxed small grain


multiphase

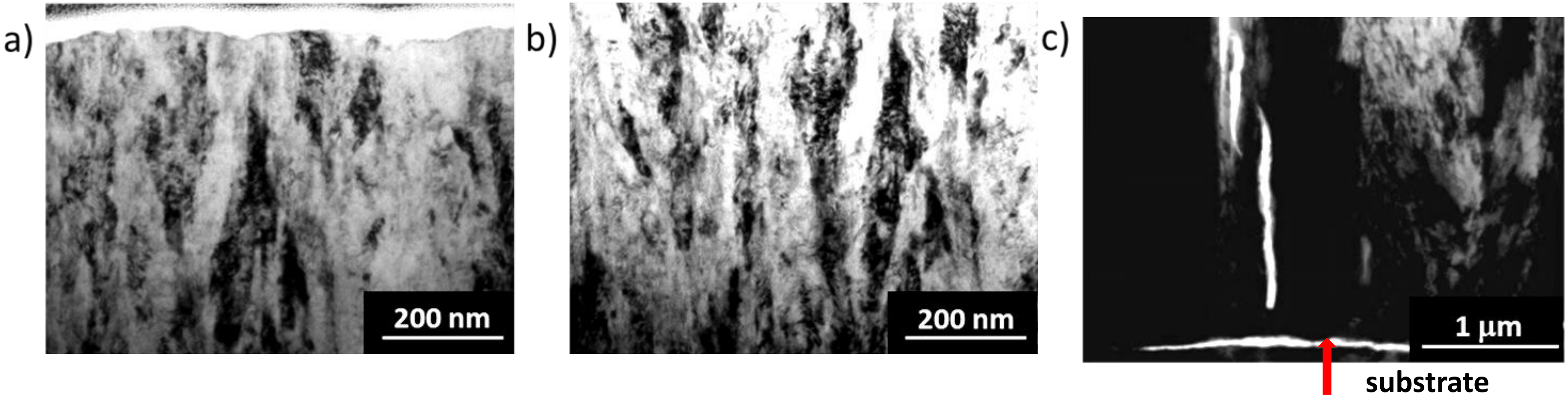

dendritic


composition modulated

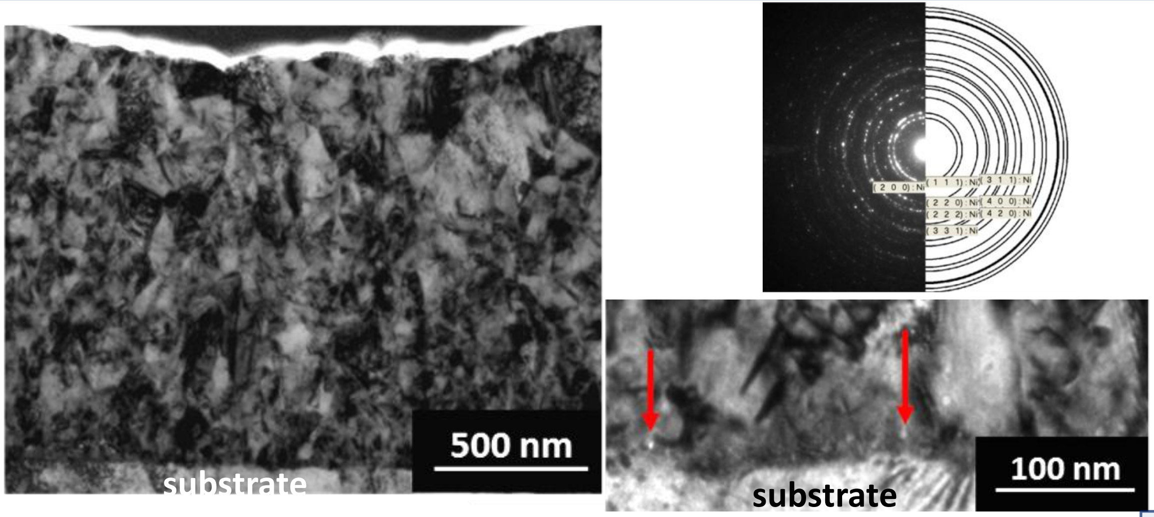

metal matrix composite

D. Landolt, Electrochimica Acta. Vol 39 (1994) 1075-1090
L.A. Dobrzański, IMIiB, Gliwice 2006

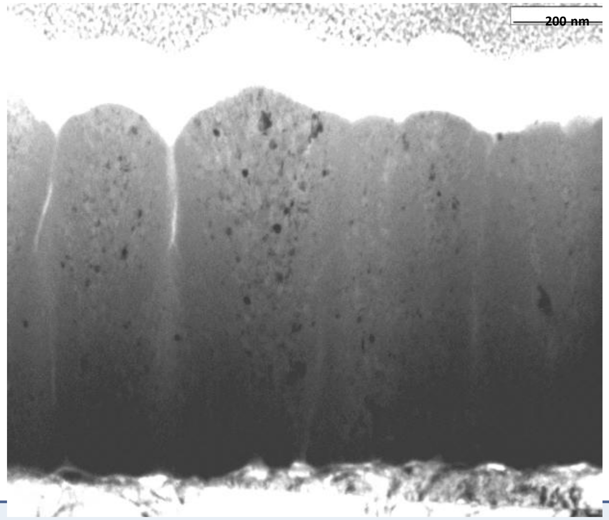
MICROSTRUCTURES OF ELECTRODEPOSITED COATINGS - COLUMNAR



TEM image of the microstructure of the Cr coating cross section (deposited electrochemically): the surface (a), the middle layer (b), at the substrate (c) (IMIM PAN).

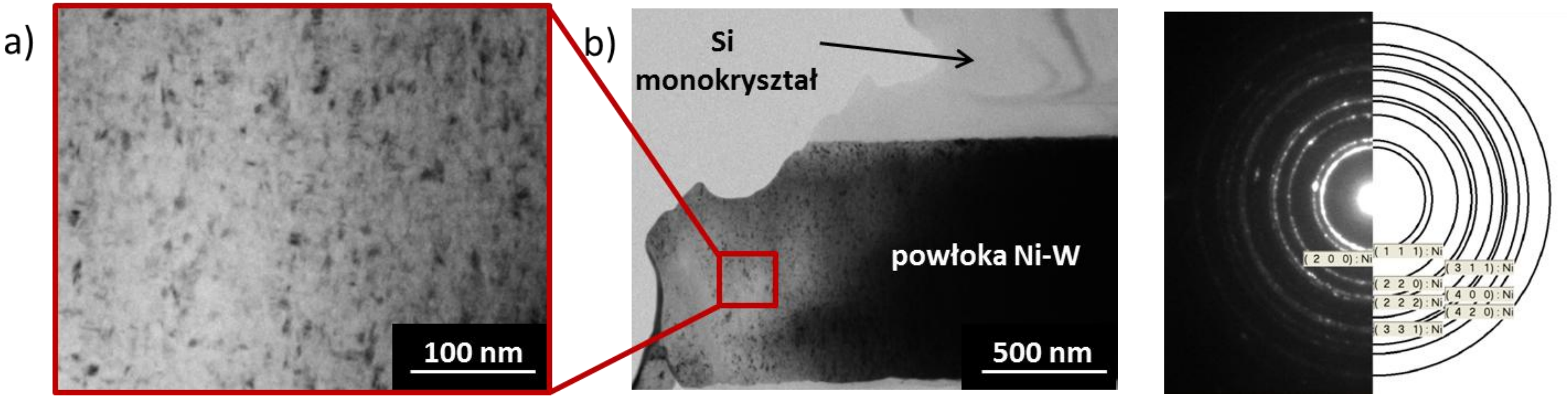


TEM image (BF) of the cross section microstructure of electrodeposited Ni coating and at the steel substrate (higher magnification) (IMIM PAN)

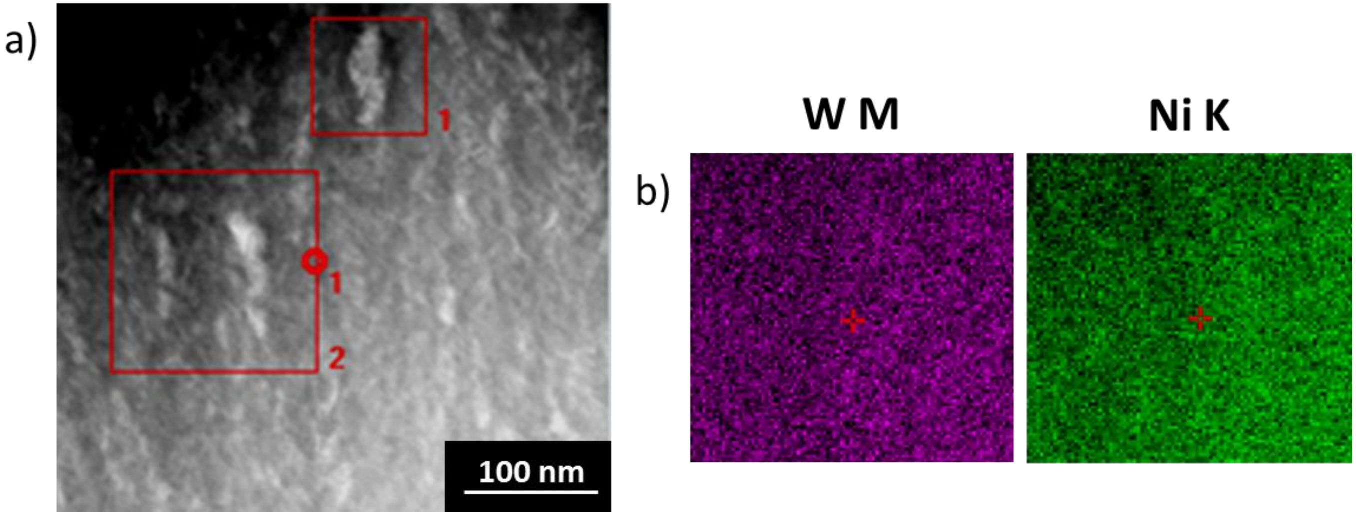


TEM image of the cross section of pseudocolumnar microstructure of amorphous-nanocrystalline Ni-Mo coating (IMIM PAN)

MICROSTRUCTURES OF ELECTRODEPOSITED COATINGS - EQUIAXED SMALL GRAIN



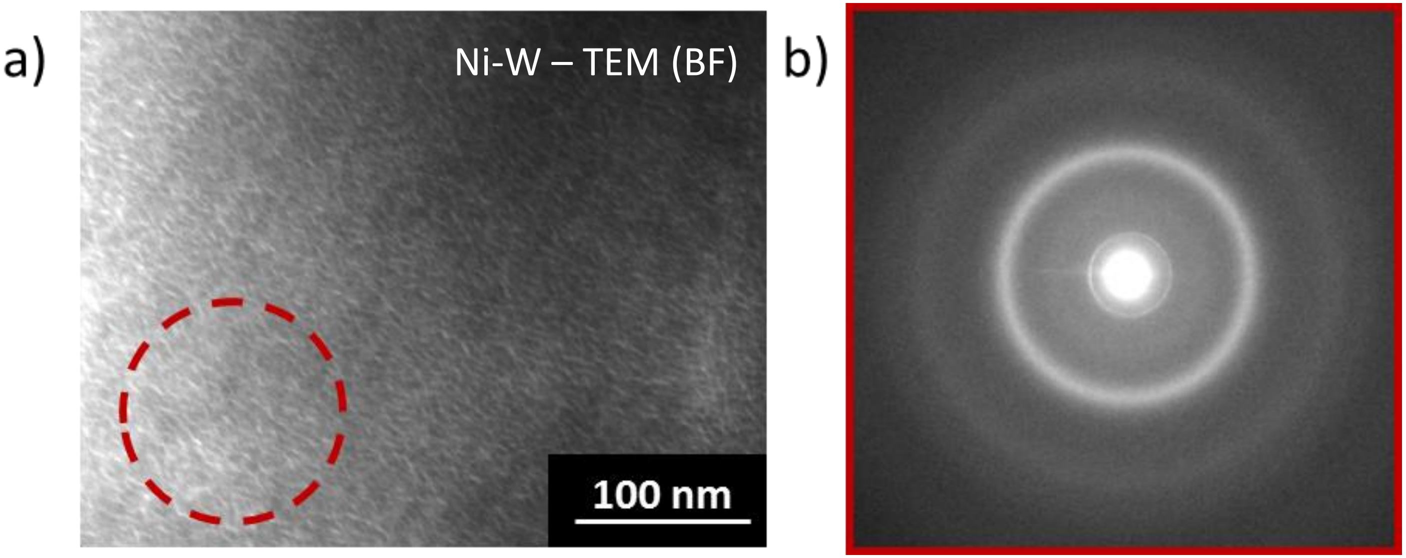
TEM image (BF) of the microstructure of the metallic Ni-W film cross section (48.5% wt. (23.1% at.) W) at high magnification (a), the cross-section of the coating and the materials used for the preparation at low magnification (b) (IMIM PAN).



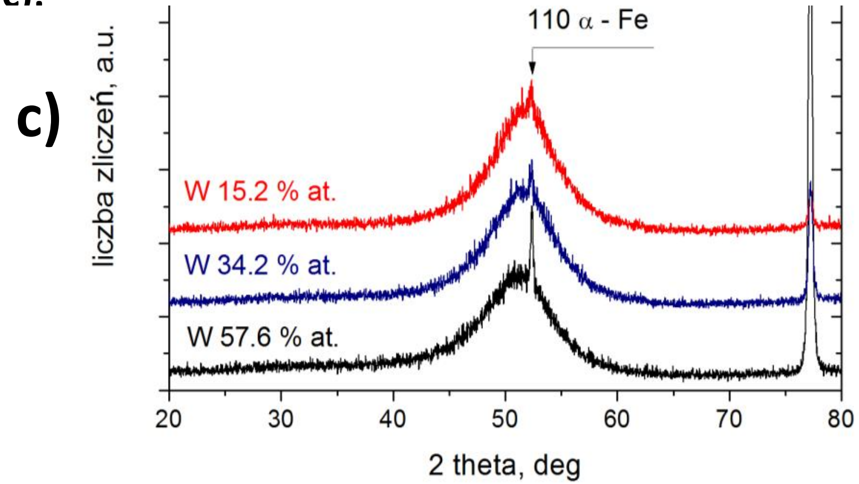
TEM image (STEM) of the microstructure of Ni-W (43.0% wt. (19.4% at.) W (a), a local analysis of the chemical composition from the 2 zones – map of the elements distribution (b) (IMIM PAN).

MICROSTRUCTURES OF ELECTRODEPOSITED COATINGS - AMORPHOUS

Samples prepared at IMMS PAS, Krakow



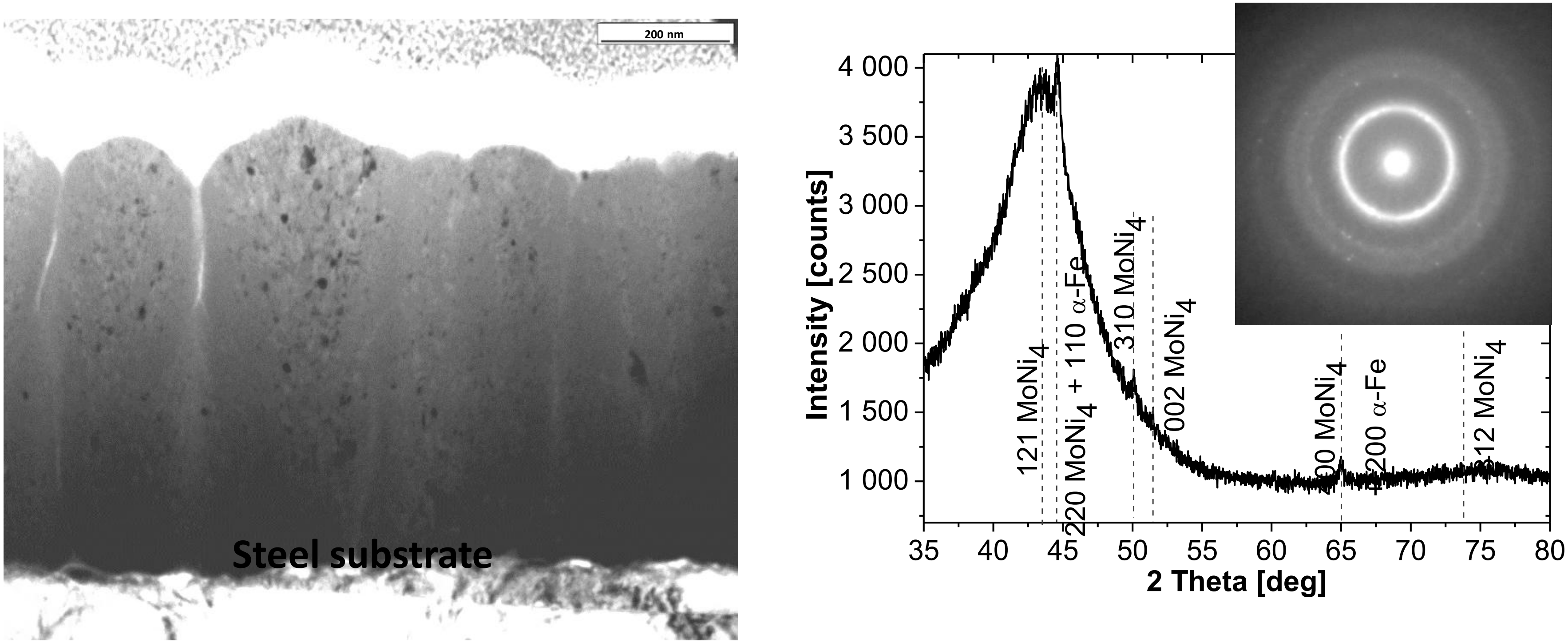
TEM image (BF) of microstructure of Ni-W coating (81.0% wt. (57.6% at.) W) (a, b) and electron diffraction (SAED) of the selected area of the sample (IMIM PAN) and a corresponding X-ray diffraction pattern (c):



MICROSTRUCTURES OF ELECTRODEPOSITED COATINGS – AMORPHOUS WITH EMBEDDED NANOCRYSTALLITES

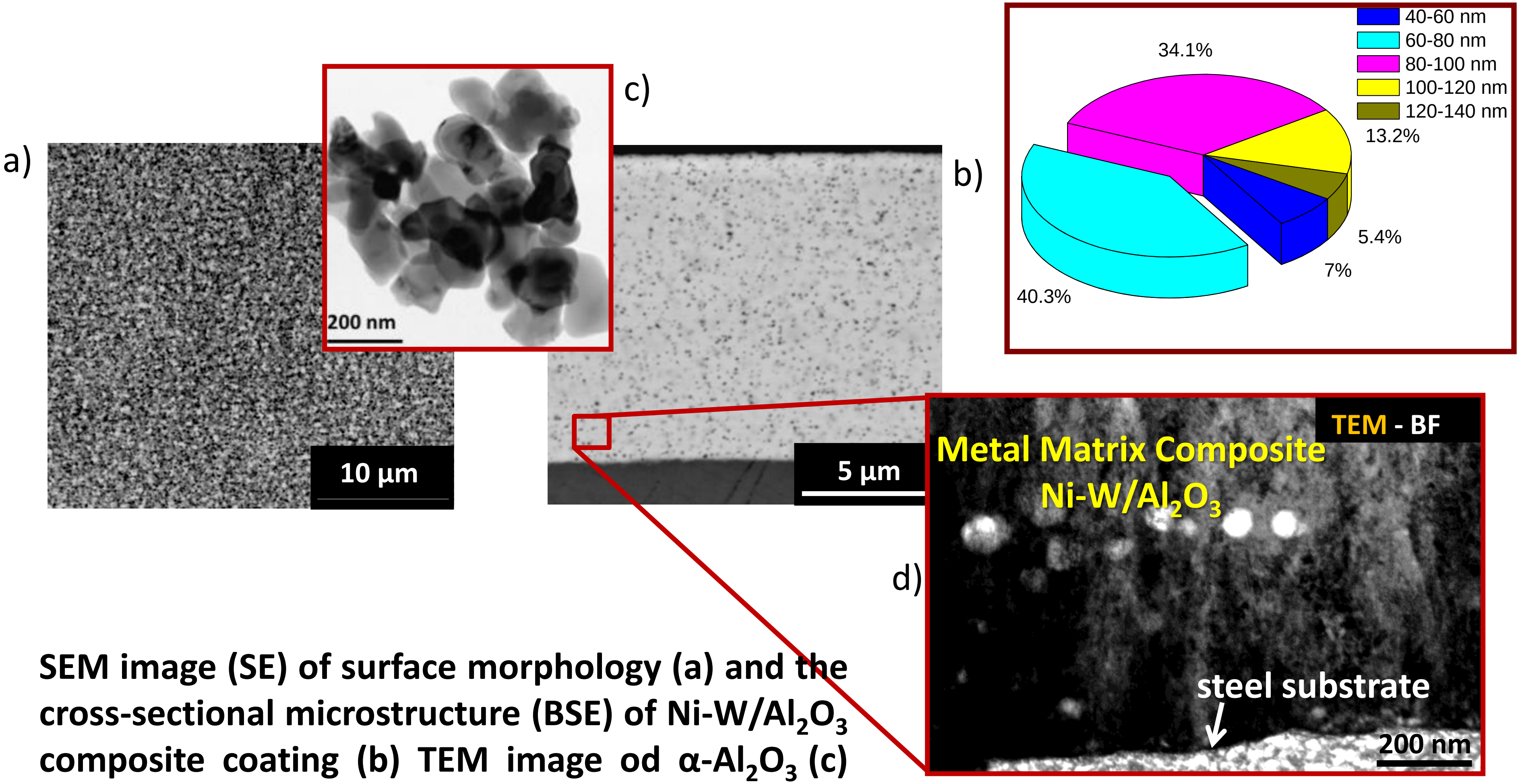
The microstructure of these materials consists of nanosized particles embedded in an amorphous matrix.

The Ni–Mo coatings are characterised by amorphous microstructure with randomly distributed nanocrystallites of the intermetallic compound $MoNi_4$, about 5–30 nm in size.



TEM cross-section images of typical as-deposited Ni–Mo coating (40 wt.% Mo) and XRD (CuKα) and TEM diffraction patterns (IMIM PAN).

STRUCTURES OF ELECTRODEPOSITED COATINGS - NANOCOMPOSITE COATINGS (METAL MATRIX COMPOSITES)



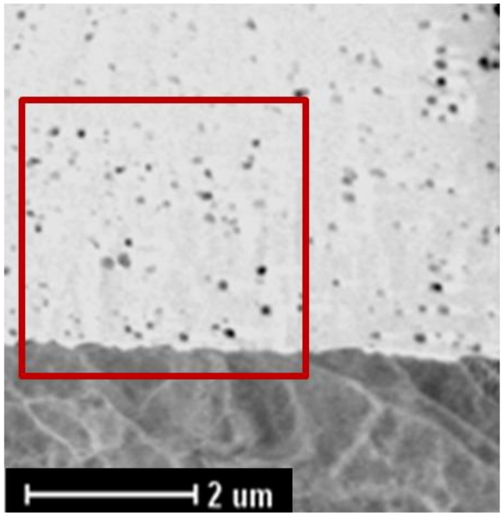
SEM image (SE) of surface morphology (a) and the cross-sectional microstructure (BSE) of Ni-W/Al_2O_3 composite coating (b) TEM image od α-Al_2O_3 (c) TEM image (BF) of the microstructure of the composite coating (FIB lamella) (d) (IMIM PAN).

Metal Matrix Composite
Ni-W/Al_2O_3

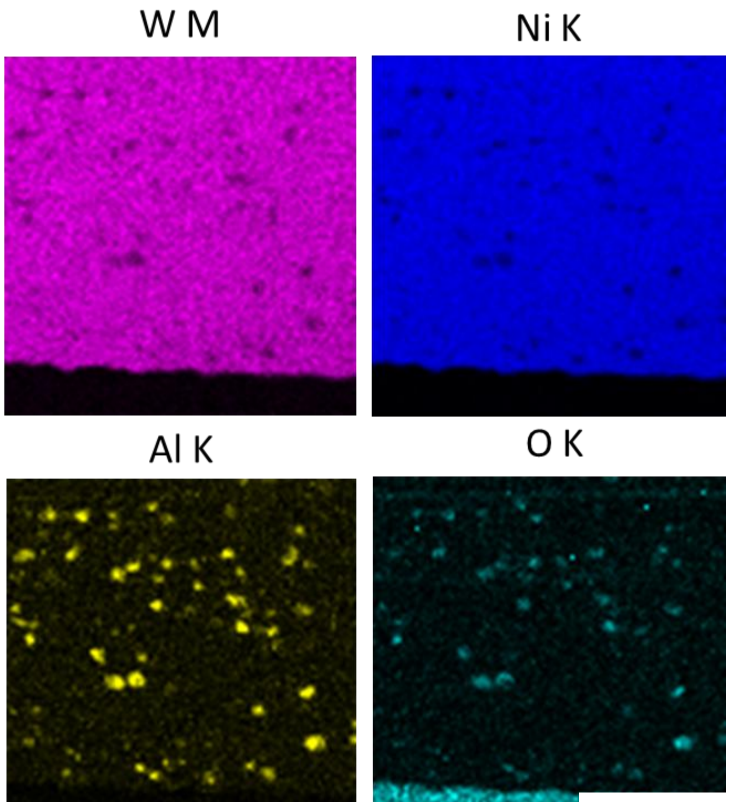
STRUCTURES OF ELECTRODEPOSITED COATINGS, NANOCOMPOSITE COATINGS (METAL MATRIX COMPOSITES)

Metal Matrix Composite
Ni-W/Al_2O_3

a)

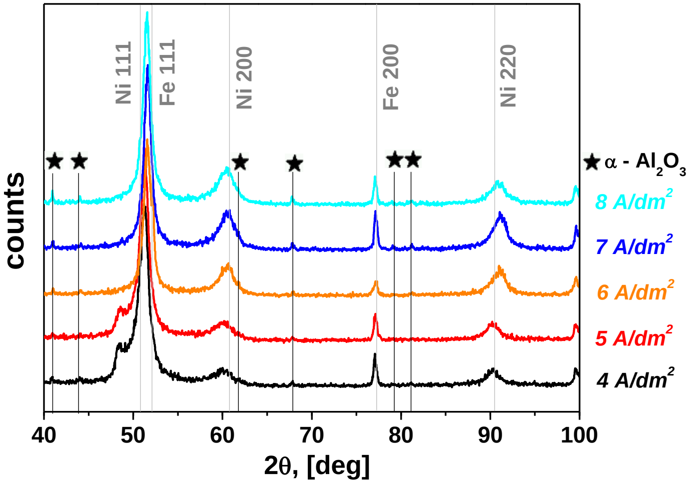


b)

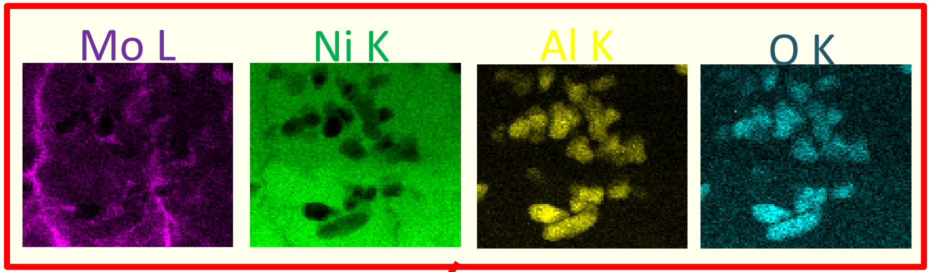


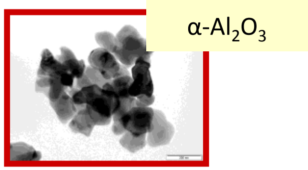
TEM image (STEM) of microstructure of electrodeposited Ni-W/Al_2O_3 coating (FIB lamella) (40.0 wt.%, 57.5% wt. Ni, 2.5% wt. Al_2O_3) (a), EDX local chemical analysis of the selected area (map of the distribution of elements) (b) (IMIM PAN).

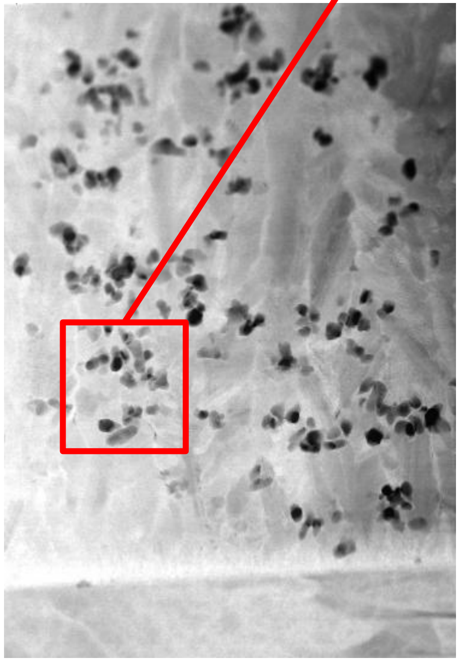
XRD patterns of Ni-W/Al_2O_3 composites deposited at different current densities.

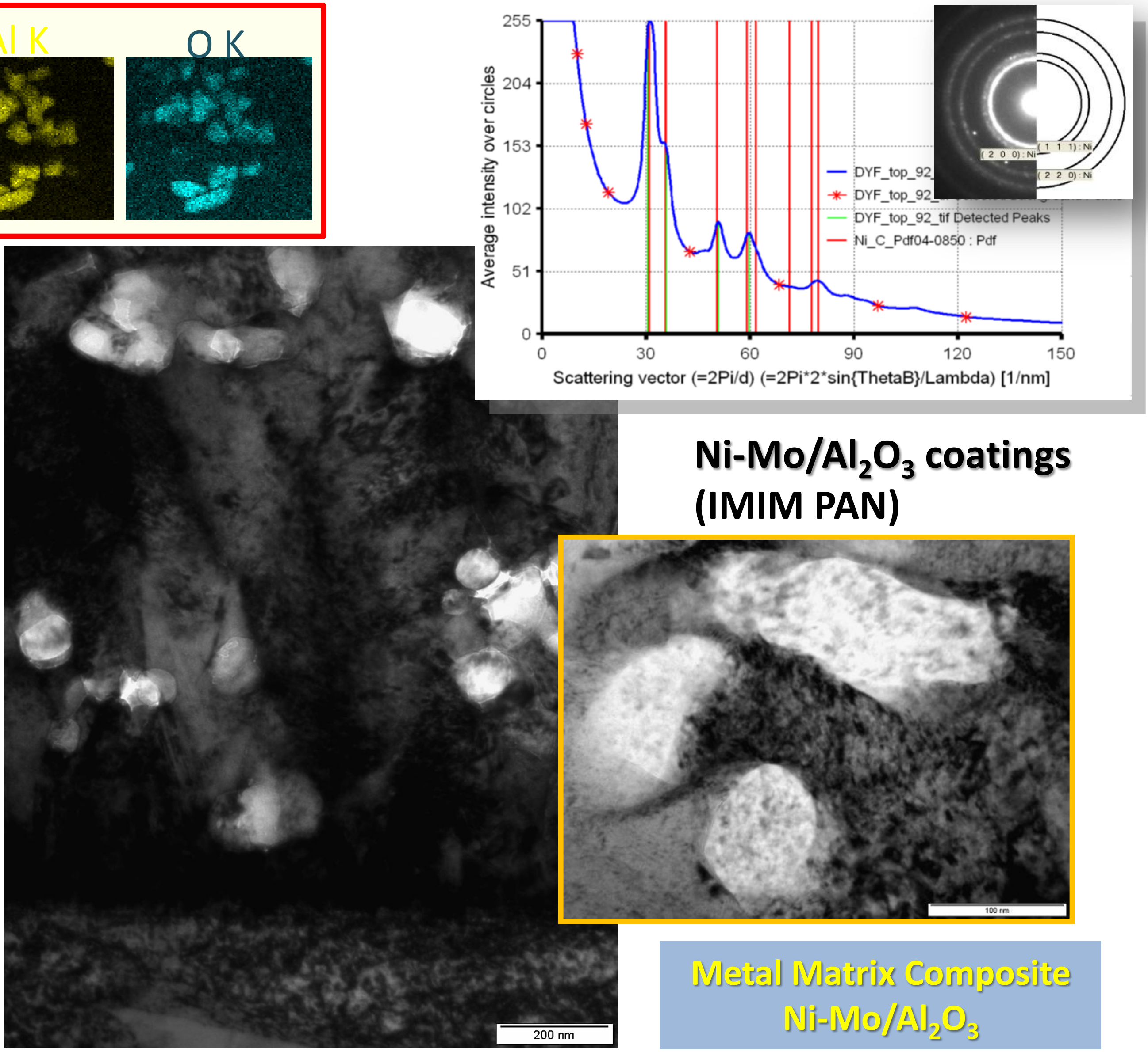


STRUCTURES OF ELECTRODEPOSITED COATINGS, NANOCOMPOSITE COATINGS (METAL MATRIX COMPOSITES)





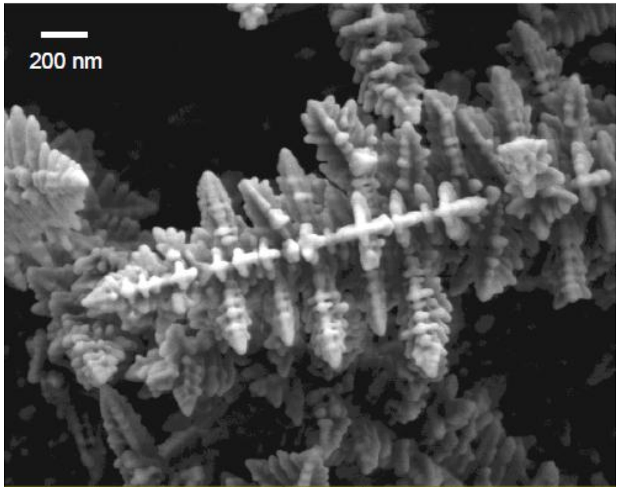




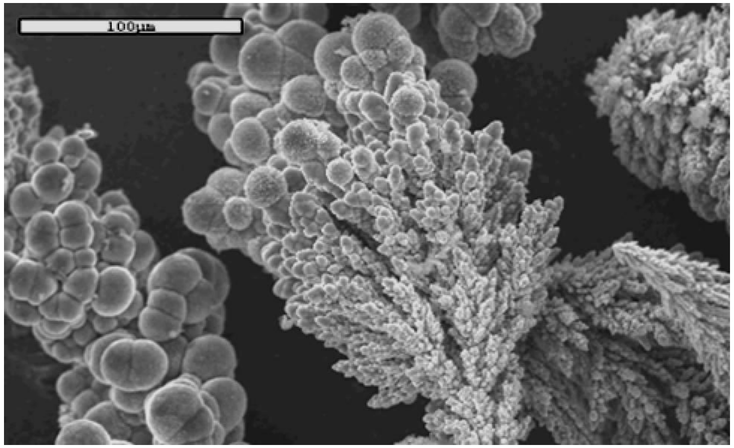
Ni-Mo/Al_2O_3 coatings (IMIM PAN)

Metal Matrix Composite Ni-Mo/Al_2O_3

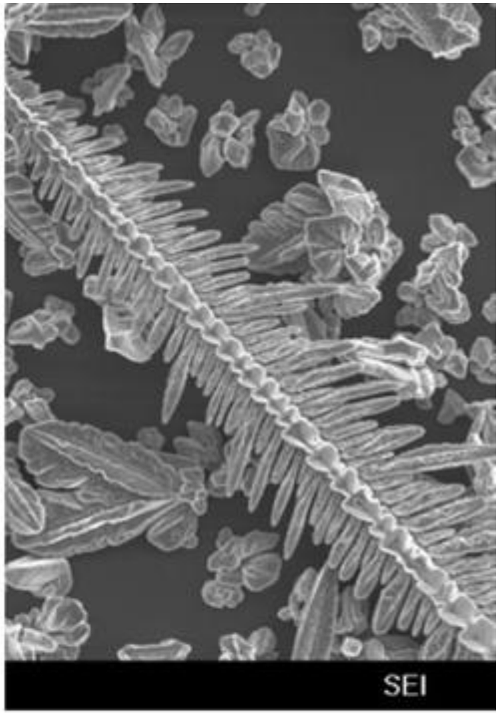
STRUCTURES OF ELECTRODEPOSITED COATINGS – DENDRITIC DEPOSITS



SEM image of electrodeposited Au



SEM image showing Al–Mg dendrites



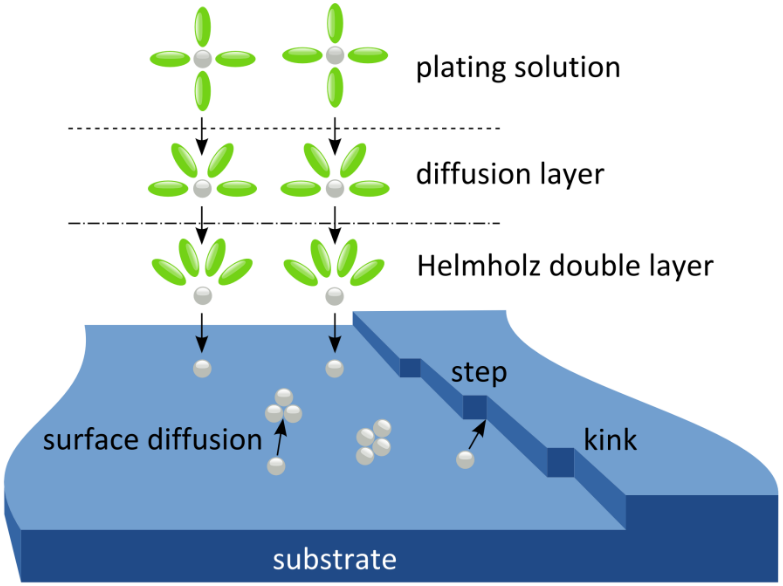
Morphology of electrodeposited Cu

Metals 2011, 1, 3-15; doi:10.3390/met1010003

J. Phys. Chem. C, 2009, 113 (23), pp 10097–10102; DOI: 10.1021/jp8095456
Supplementary Material (ESI) for Chemical Communications

STAGES OF ELECTRODEPOSITION PROCESS

Electrodeposition is a **multistep** process. The hydrated metal ion present in the electrolyte arrives at the cathode under the influence of the imposed electrical field as well as by diffusion and convection. At the cathode it enters the diffusion layer, where the loosely bound H_2O molecules are aligned by the field. The metal ion then passes through the diffuse part of the double layer and enters the external layer of the fixed double layer, where it is dehydrated, and then undergo electroreduction. Discharging ions leads to the formation of neutral ad-adions or ad-atoms. **Electrocrystallization** is the last stage of electrodeposition process, in which the phase of a new material is formed by diffusion of adatoms (or adions) at the cathode surface to create nucleation sites and growth to form the crystalline structure.

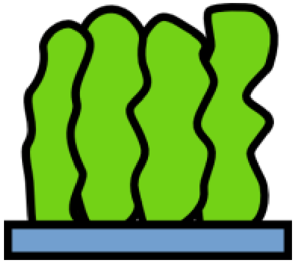


Stages of electrodeposition process

MAIN GROWTH TYPES IN ELECTROCRYSTALLIZATION (FISCHER'S CLASSIFICATION)

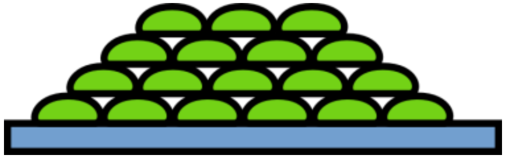
The growth type of the different metals during electrocrystallization depends on the kind of metal and on electrolyte composition and operating parameters. Combination and transition forms often occurs, thus making it difficult to distinguish the various growth types.

Field-orientated isolation type (FI) – the growth of single (isolated) crystals on the cathode, often show dendritic branching, not form continuous coating



Basis-orientated reproduction type (BR) – a tendency for the orientation of the surface crystallites of the substrate to affect the orientation of electrocrystallized metals; an orientation of the crystallites in the coating is parallel to that of the crystallites in the substrate metal, metal coatings crystallize with a relatively small number of nuclei and relatively large crystallites are formed

Field-orientated texture type (FT) – a large number of elongated crystals perpendicular to the substrate, forming a coherent deposit

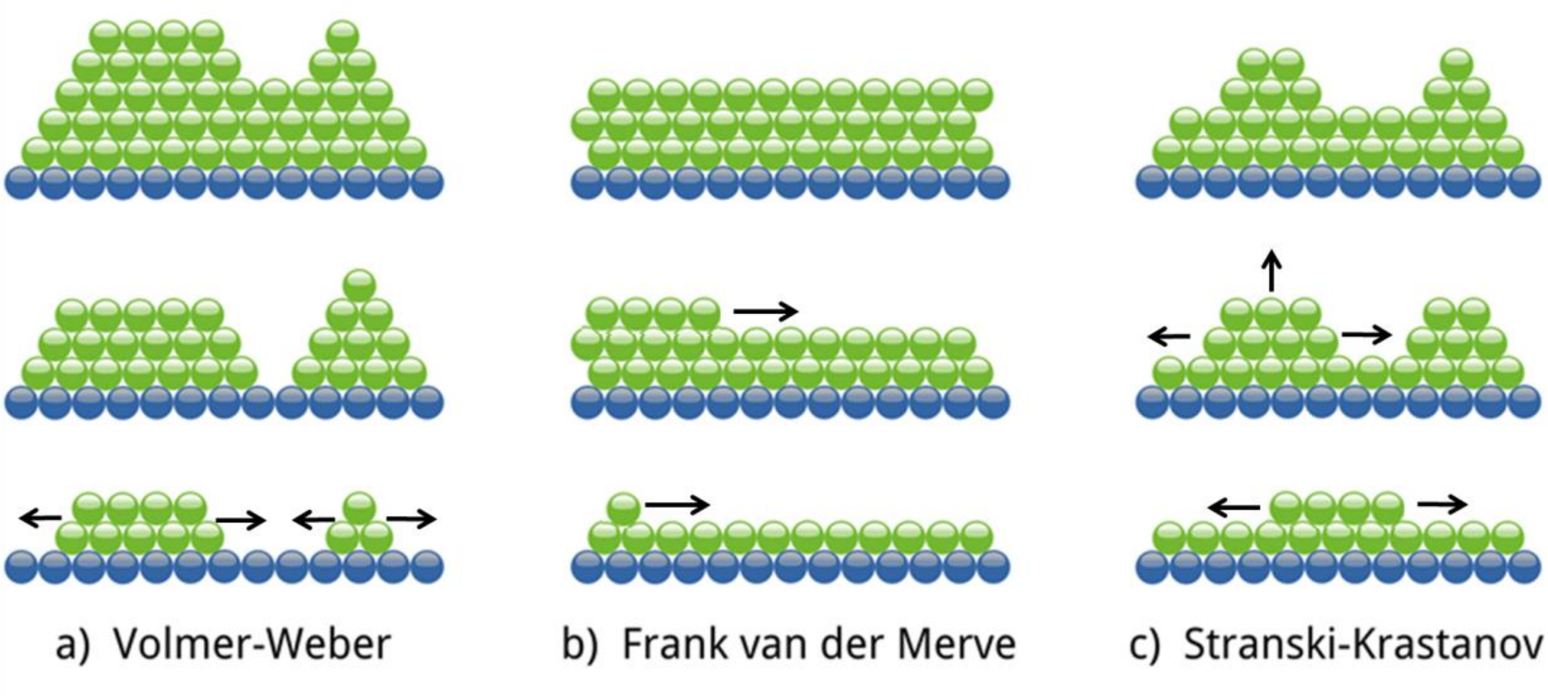


Unorientated dispersion type (UD) - a large number of small crystals, forming a coherent deposit

ELECTROCRYSTALLIZATION STAGE

The early stages of electrocrystallization process can be described by three growth modes: Volmer-Weber (VW), Frank-van der Merve (FM) and Stranski-Krastanov (SK) mechanisms.

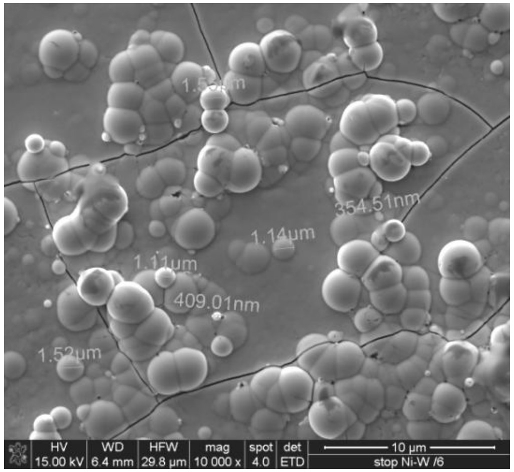
Nature of the substrate and the coating of the metal or alloy decide which mechanism will give the best description of the electrocrystallization process.

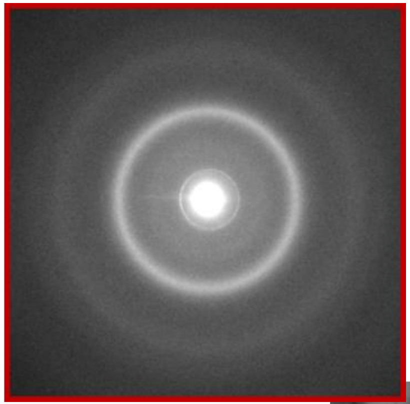


Three modes for describing the initial stages of thin film growth

MORPHOLOGY OF ELECTRODEPOSITED LAYERS

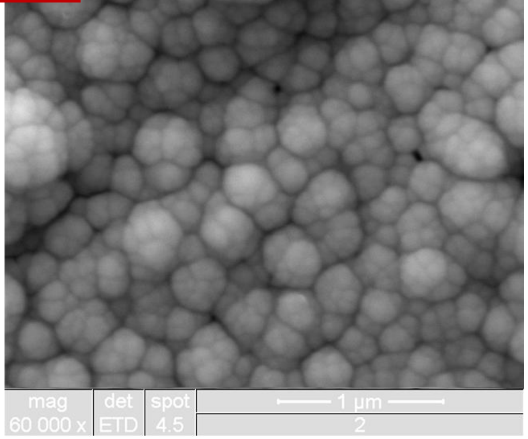
Under real conditions, the morphology of electrodeposits are mainly determined by the shape of the initial growth layers. Depending on the film thickness, surface roughness profile can be distinguished related to the profile of the substrate and to the conditions of electrodeposition process. Like, as crystallographic orientation of the substrate, also some inequalities of its surface (scratches, cracks) are reflected in the surface morphology of electrodeposits. Characteristic of the morphology of electrodeposited material is the „island" structure. The size, number and location of each islands are related to the process of film electrocrystallization. **Often, „islands" are considered as crystallites or grains, what is completely untrue.**

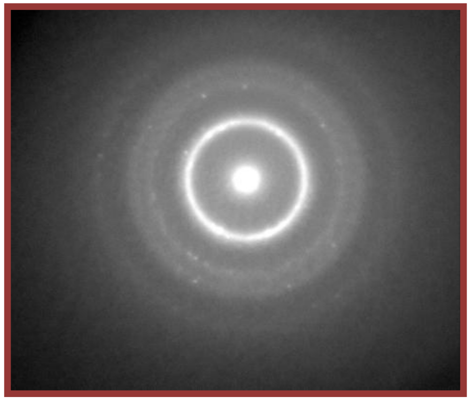




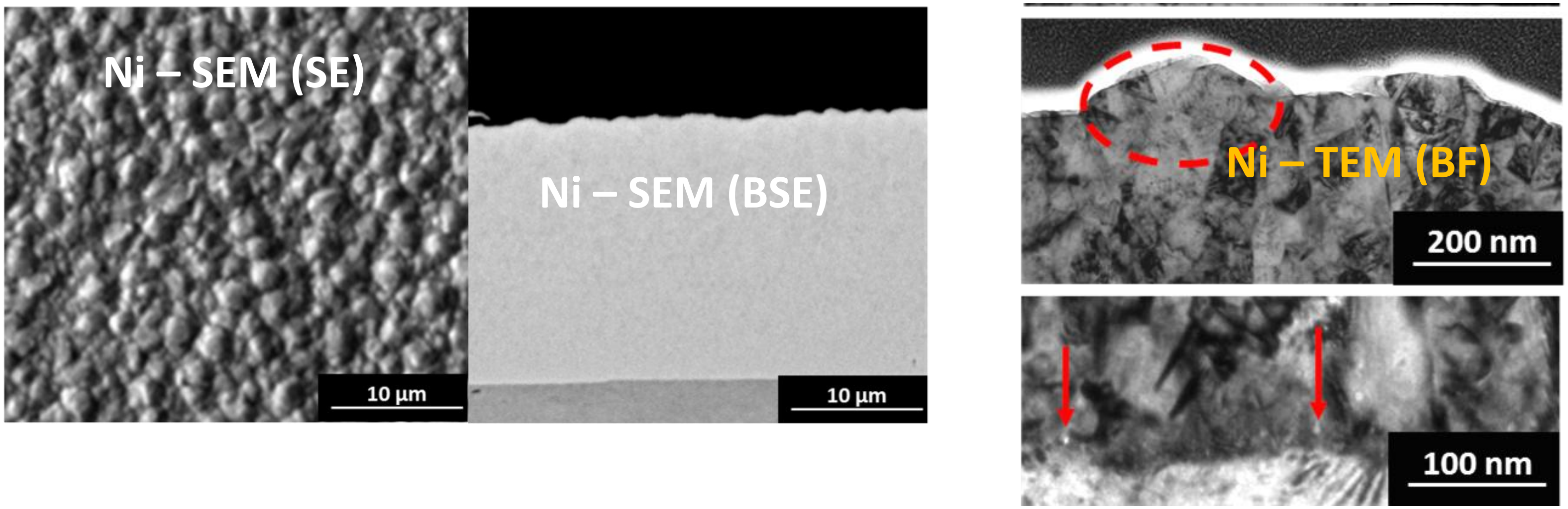
Surface morphology (SEM) of amorphous metallic Ni-W layer and corresponding diffraction pattern (TEM) (IMIM PAN)

Surface morphology (SEM) of amorphous - nanocrystalline Ni-Mo layer and corresponding diffraction pattern (TEM) (IMIM PAN)

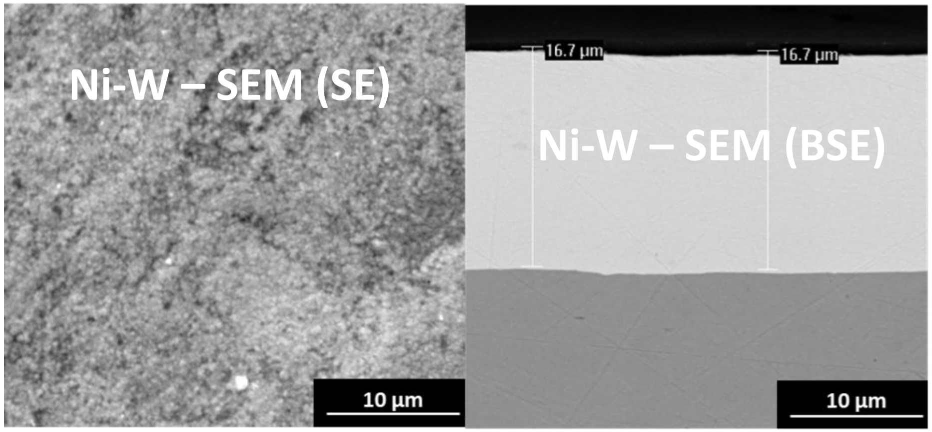




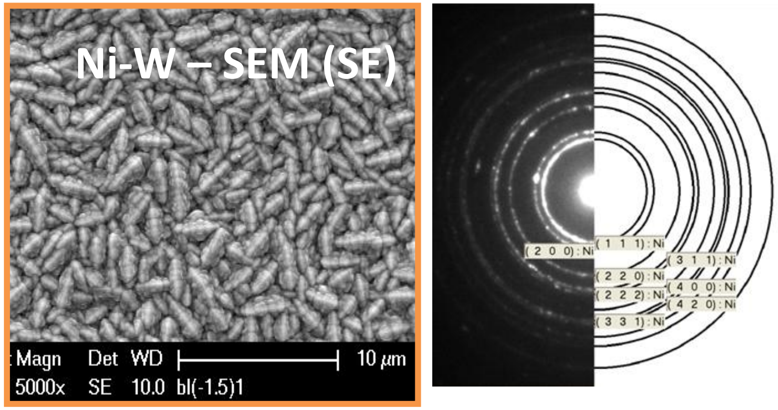
MORPHOLOGY OF ELECTRODEPOSITED COATINGS



SEM image of surface (SE) and cross section (BSE) of metallic nickel layer and corresponding TEM image (IMIM PAN)



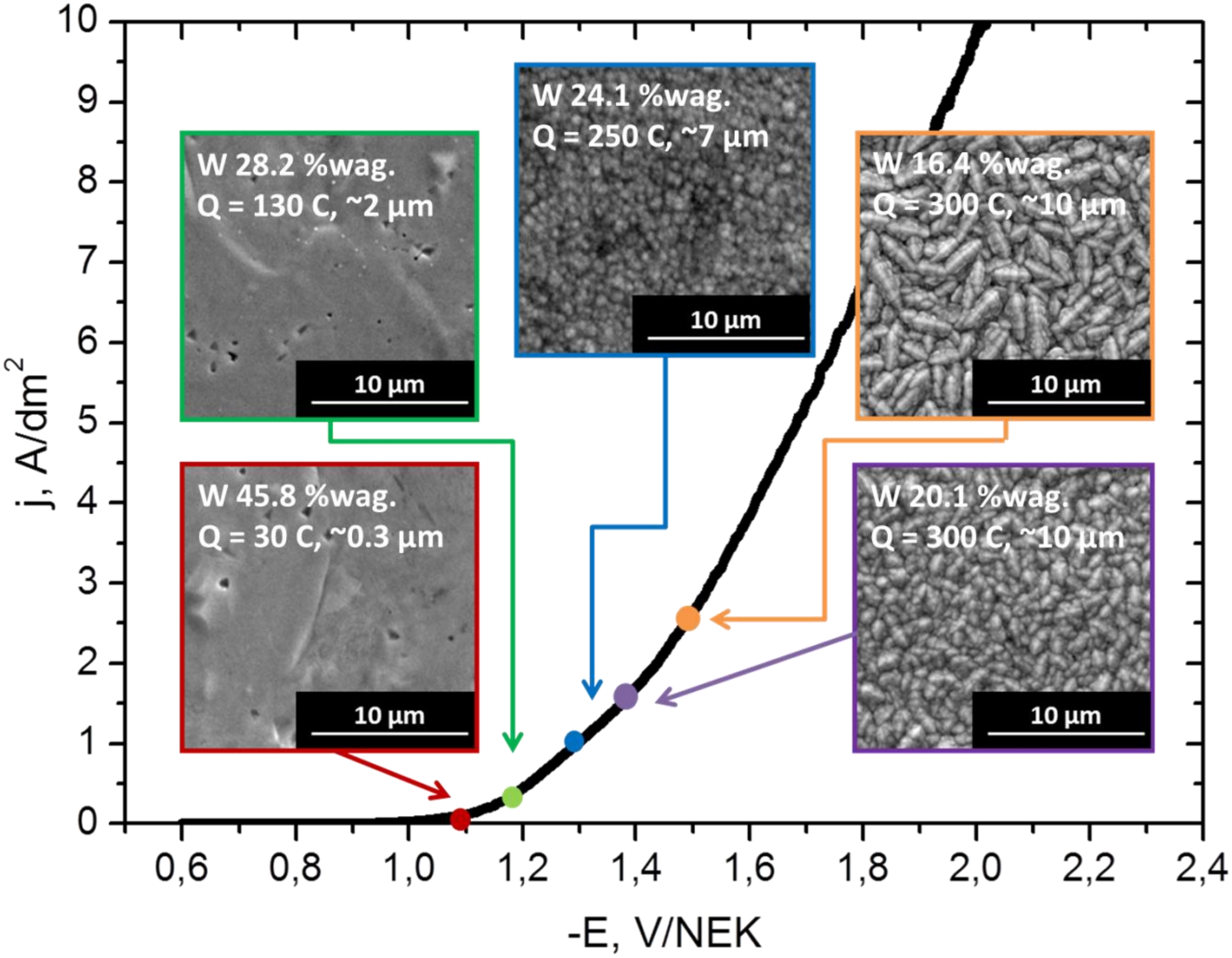
SEM image of surface (SE) and cross section (BSE) of metallic Ni-W coatings (IMIM PAN)



Surface morphology (SEM) of nanocrystalline metallic Ni-W layer and corresponding diffraction pattern (TEM) (IMIM PAN)

MORPHOLOGY OF ELECTRODEPOSITED COATINGS

Cathode potential (or current density) strongly influence the surface morphology of electrodeposited coatings

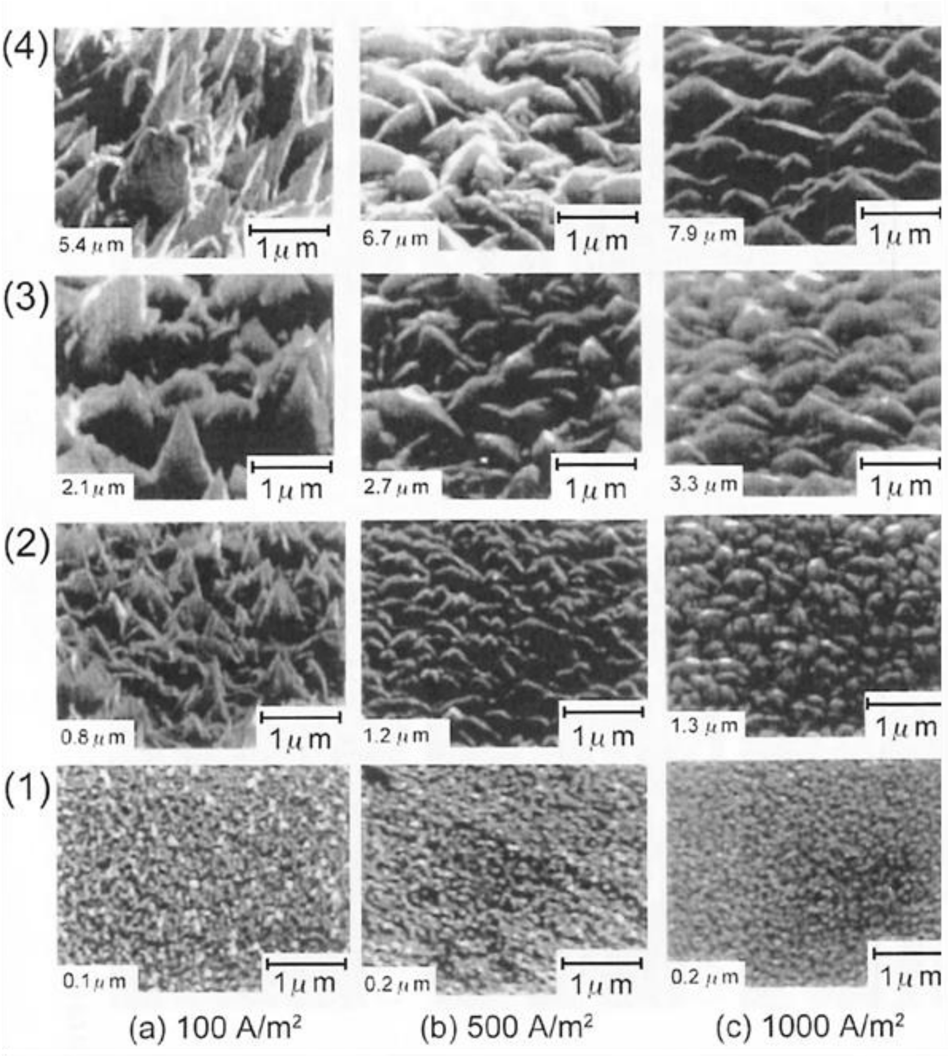


Surface morphology SEM (SE) of the Ni-W coatings electrodeposited at different cathode potential along the polarization curve (IMIM PAN).

MORPHOLOGY OF ELECTRODEPOSITED COATINGS

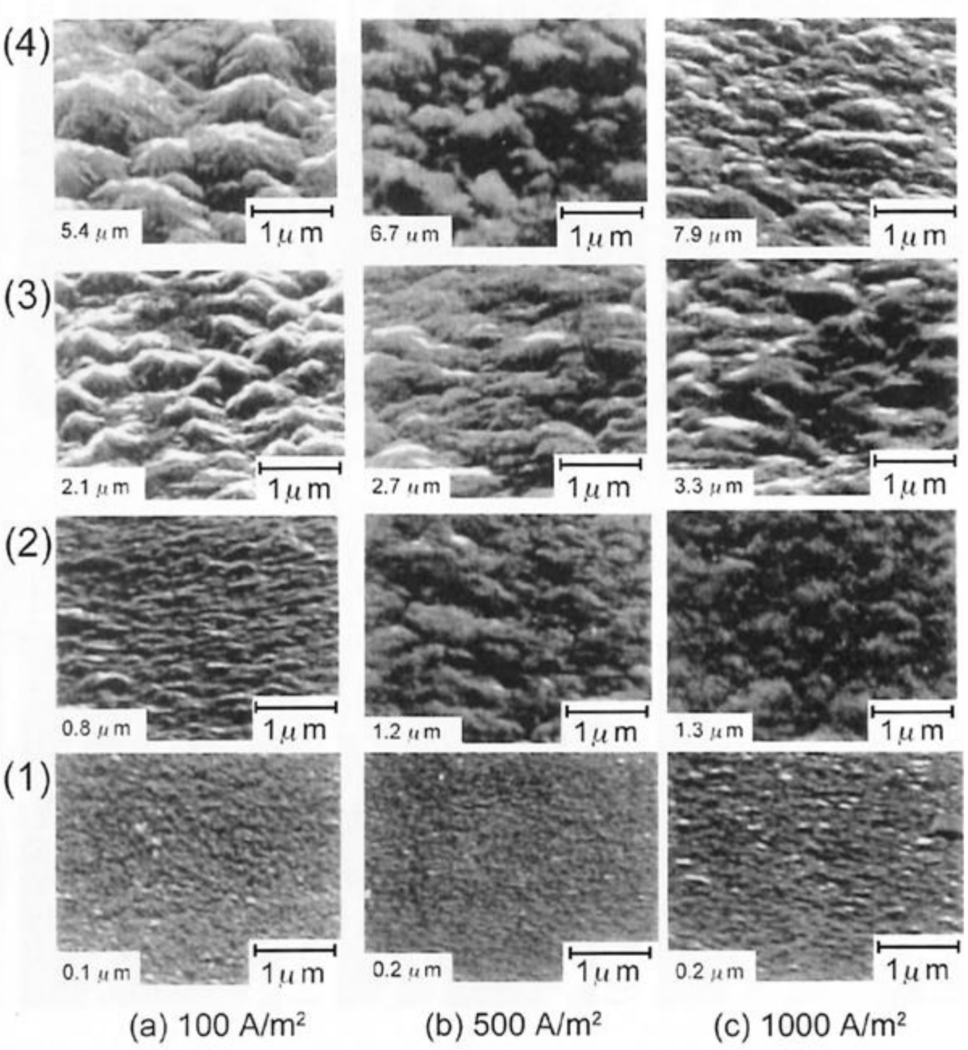
Morphology of nickel coatings in relation to type of plating bath (salts of basic metal)

Chloride electrolytic solution



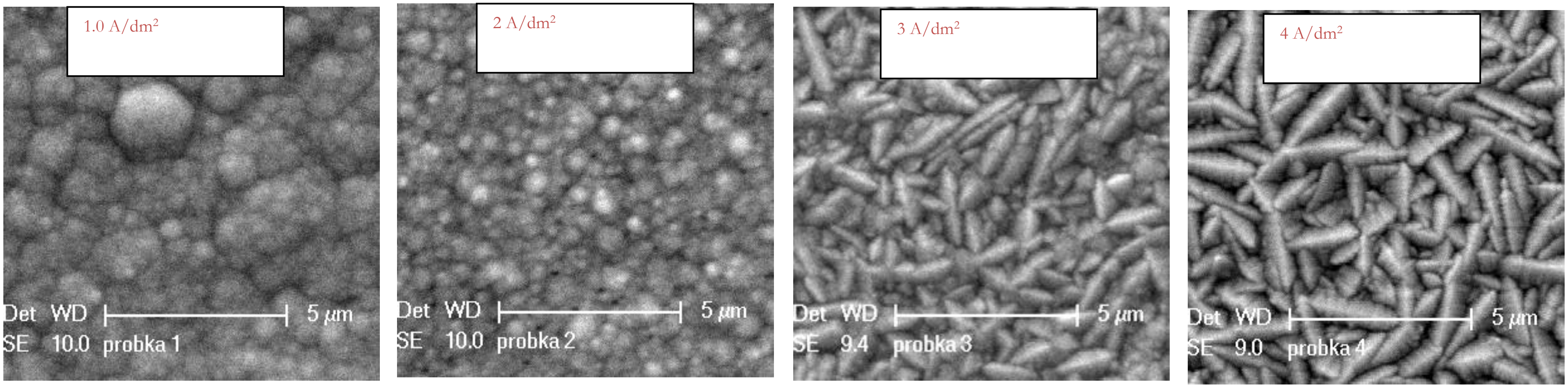
(a) 100 A/m^2 (b) 500 A/m^2 (c) 1000 A/m^2

Sulphate electrolytic solution



(a) 100 A/m^2 (b) 500 A/m^2 (c) 1000 A/m^2

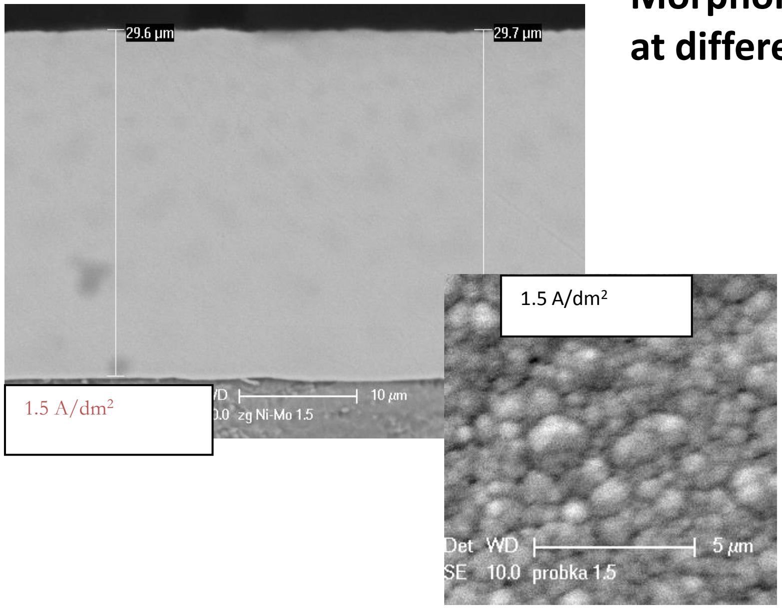
MORPHOLOGY OF ELECTRODEPOSITED COATINGS


1.0 A/dm^2

2 A/dm^2

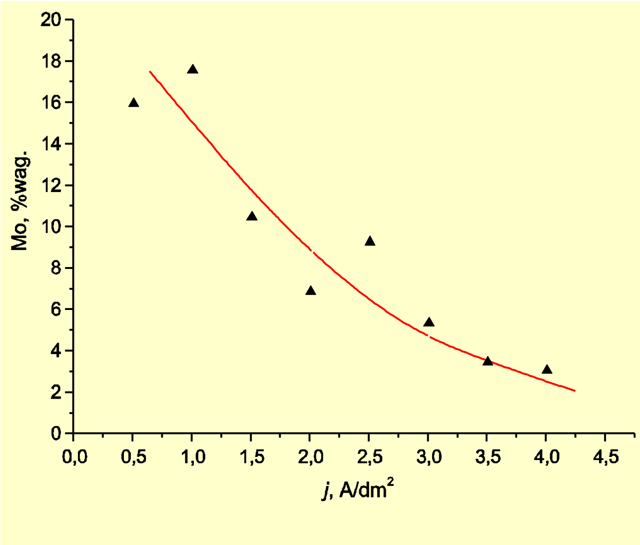
3 A/dm^2

4 A/dm^2


1.5 A/dm^2

1.5 A/dm^2

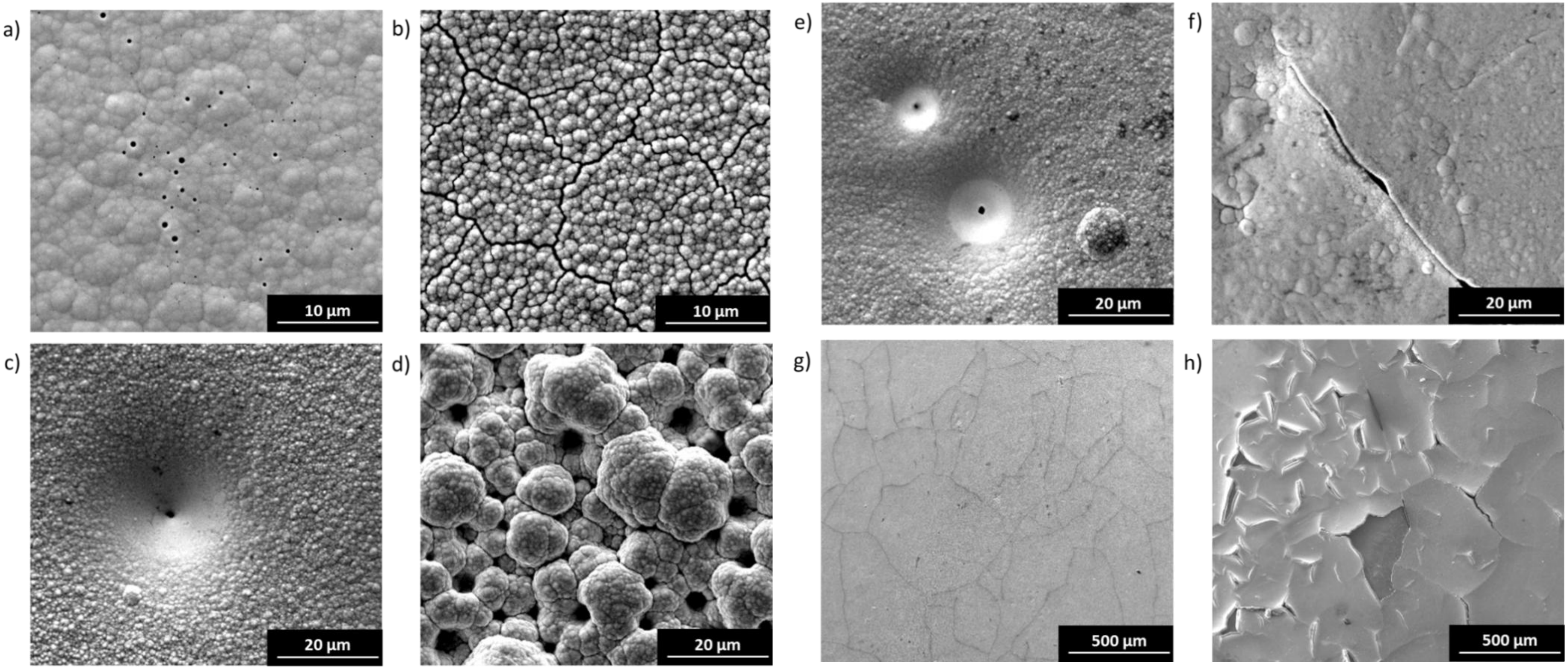
Morphology of Ni-Mo coatings electrodeposited at different current density (IMIM PAN)



Mo content in function of current density

MORPHOLOGY OF ELECTRODEPOSITED COATINGS

Surface defects: small pores, porosity, micro-cracks, fractures etc.



SEM image of surface morphology of Ni-W coatings deposited in different conditions (IMIM PAN)

ELECTROPLATING - PROPERTIES RELATIONSHIPS

Plating conditions

- Bath composition (kinds of metal salt, concentration)
- pH, kinds of anion, addition, reduction,
- Overvoltage, current density, pulse,
- Agitation, temperature, electrode, etc.

↓

Reaction in solution

- Ion, aqua-ion,
- Complex ion,
- Dissociation, diffusion,
- Reaction velocity, etc.

↓

Reaction on electrode

- Electronic double layer,
- Diffusion layer
- Adhesion
- Discharge, etc.

↓

Composition

- Pure metal
- Alloy
- Imputity

↓

Crystallographic structure

- Crystal (phase, crystal size, orientation, stress, etc.)
- Amorphous (uniformity)

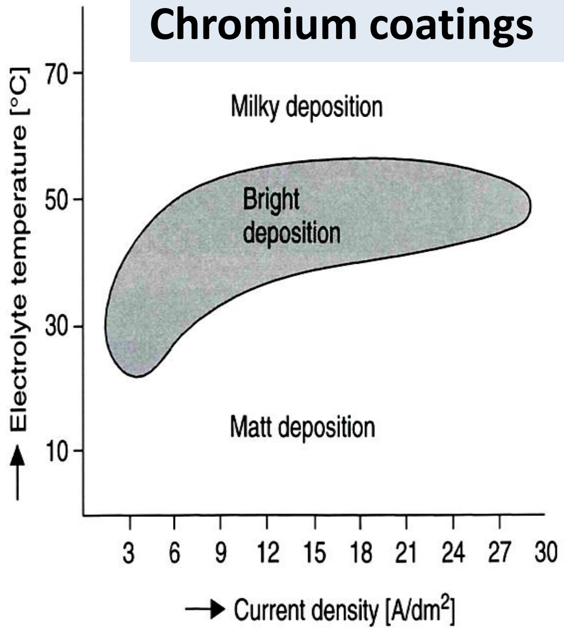
↓

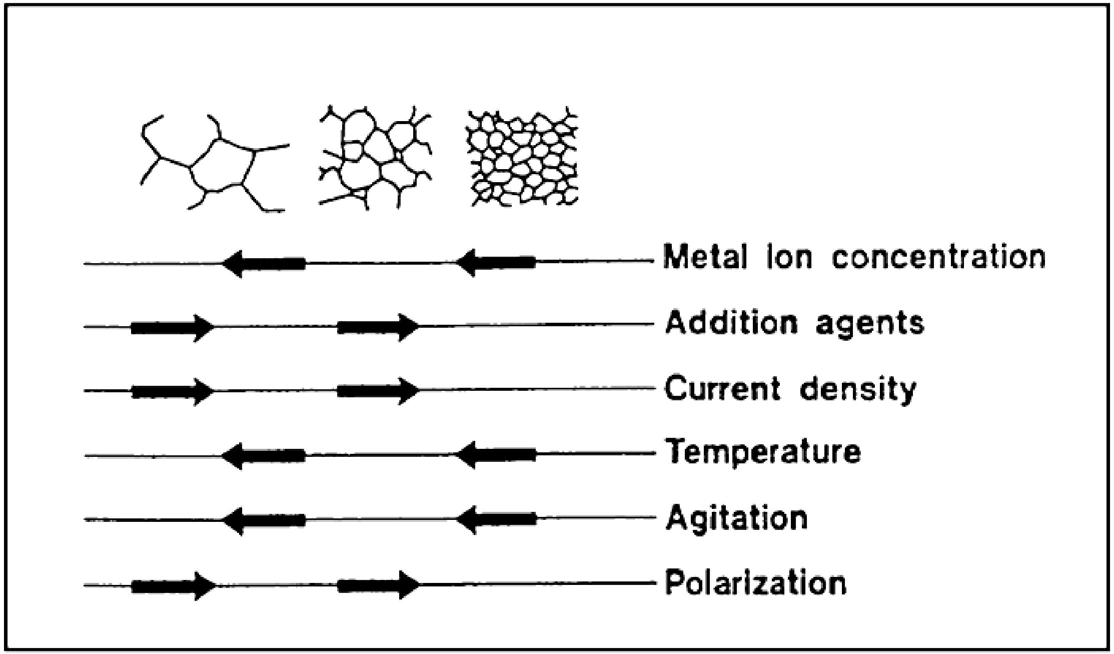
Physical properties

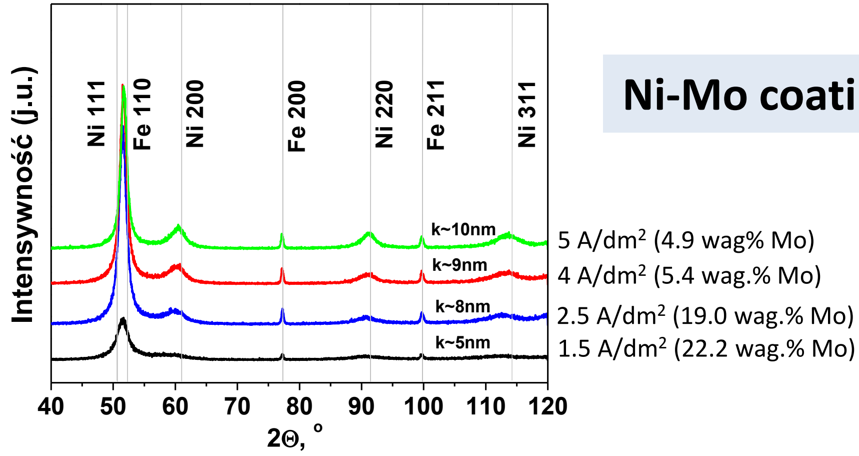
- Physical properties (electrical, magnetic, etc.)
- Chemical properties (anti-corrosion, catalytic, etc.)
- Mechanical properties (hardness, plasticity, tensile strength, etc.)

RELATION OF STRUCTURE OF ELECTRODEPOSITS TO OPERATING CONDITIONS

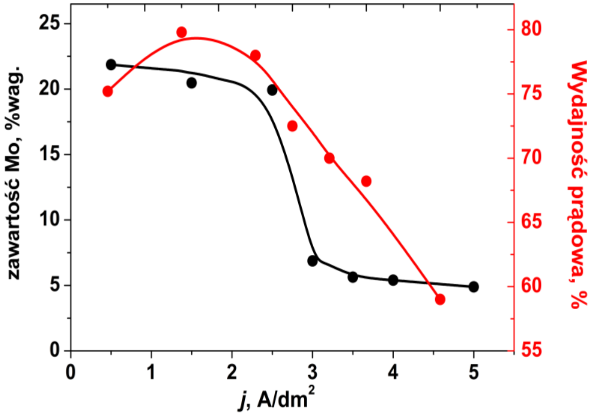
Chromium coatings







Ni-Mo coatings, IMIM



PROPERTIES OF ELECTRODEPOSITED COATINGS

Electrodeposition process have been systematically developed in terms of properties of the coatings required. In this way either pure metal or alloy coatings of virtually any composition can be produced. The properties of such metallic coatings are often different from those of the corresponding massive metal or alloy due to the microscopic or sub-microscopic structure of such metal layer. The Vickers microhardness value is one of the simplest ways of demonstrating such differences.

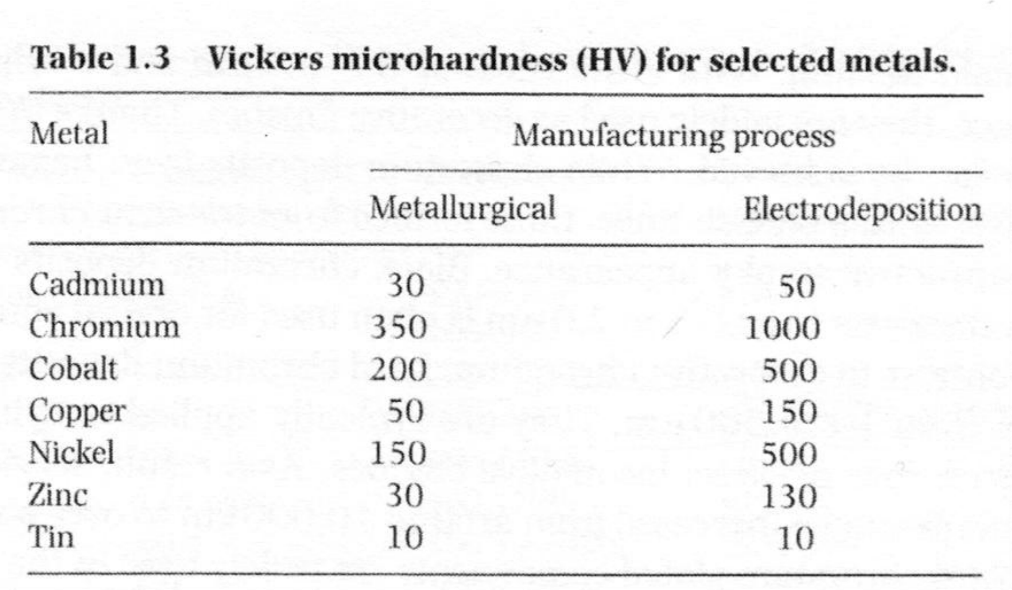


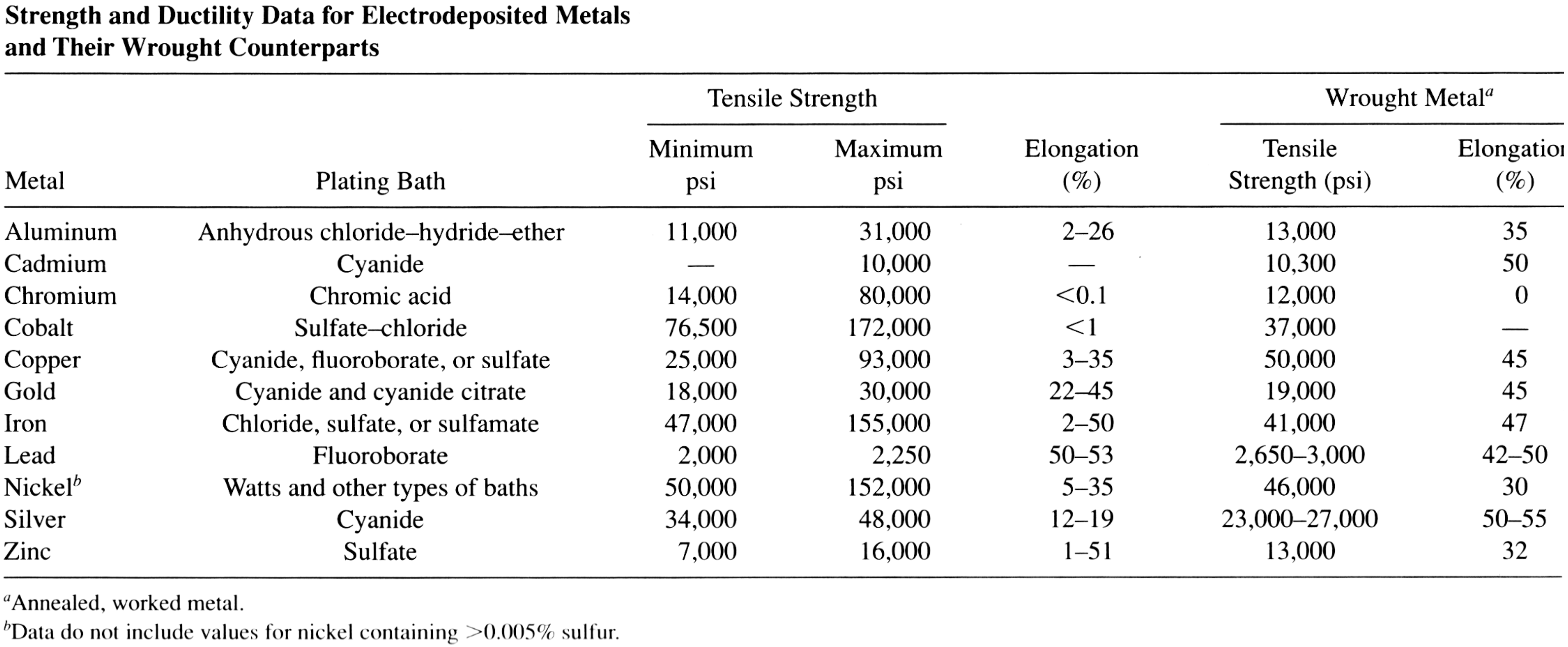
Table 1.3 Vickers microhardness (HV) for selected metals.

Metal	Manufacturing process	
	Metallurgical	Electrodeposition
Cadmium	30	50
Chromium	350	1000
Cobalt	200	500
Copper	50	150
Nickel	150	500
Zinc	30	130
Tin	10	10

Electrodeposited metal coatings usually are uniformly harder than their counterparts prepared by metallurgical methods

PROPERTIES OF ELECTRODEPOSITED COATINGS

Electrodeposited coatings of metals, alloys and composites are characterized by different grain size, texture and phase structure and often superior physicochemical and mechanical properties than the metal layers produced by other techniques.



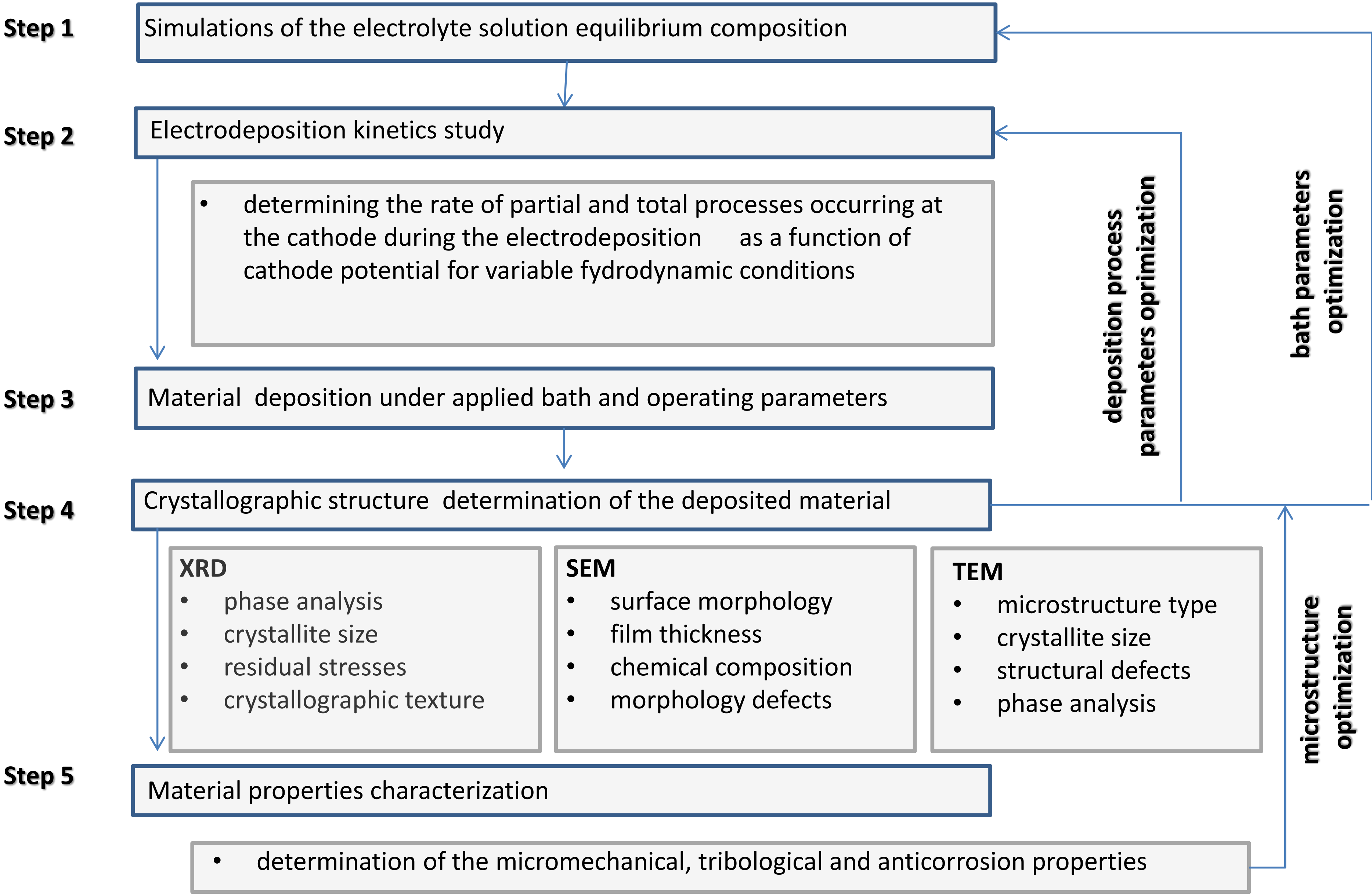
Strength and Ductility Data for Electrodeposited Metals and Their Wrought Counterparts

		Tensile Strength			Wrought Metal[a]	
Metal	Plating Bath	Minimum psi	Maximum psi	Elongation (%)	Tensile Strength (psi)	Elongatio (%)
Aluminum	Anhydrous chloride–hydride–ether	11,000	31,000	2–26	13,000	35
Cadmium	Cyanide	—	10,000	—	10,300	50
Chromium	Chromic acid	14,000	80,000	<0.1	12,000	0
Cobalt	Sulfate–chloride	76,500	172,000	<1	37,000	—
Copper	Cyanide, fluoroborate, or sulfate	25,000	93,000	3–35	50,000	45
Gold	Cyanide and cyanide citrate	18,000	30,000	22–45	19,000	45
Iron	Chloride, sulfate, or sulfamate	47,000	155,000	2–50	41,000	47
Lead	Fluoroborate	2,000	2,250	50–53	2,650–3,000	42–50
Nickel[b]	Watts and other types of baths	50,000	152,000	5–35	46,000	30
Silver	Cyanide	34,000	48,000	12–19	23,000–27,000	50–55
Zinc	Sulfate	7,000	16,000	1–51	13,000	32

[a] Annealed, worked metal.

[b] Data do not include values for nickel containing >0.005% sulfur.

DESIGNING AND MANUFACTURING A NEW MATERIAL (IMIM PAN)



Step 1

Simulations of the electrolyte solution equilibrium composition

Step 2

Electrodeposition kinetics study

- determining the rate of partial and total processes occurring at the cathode during the electrodeposition as a function of cathode potential for variable fydrodynamic conditions

Step 3

Material deposition under applied bath and operating parameters

Step 4

Crystallographic structure determination of the deposited material

XRD
- phase analysis
- crystallite size
- residual stresses
- crystallographic texture

SEM
- surface morphology
- film thickness
- chemical composition
- morphology defects

TEM
- microstructure type
- crystallite size
- structural defects
- phase analysis

Step 5

Material properties characterization

- determination of the micromechanical, tribological and anticorrosion properties