ATOMIC LAYER DEPOSITION: UNA STRATEGIA INNOVATIVA PER LA PROTEZIONE DEI MATERIALI METALLICI

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Giornata di Studio «Pietro Pedeferri», Milano - 30 Novembre 2018

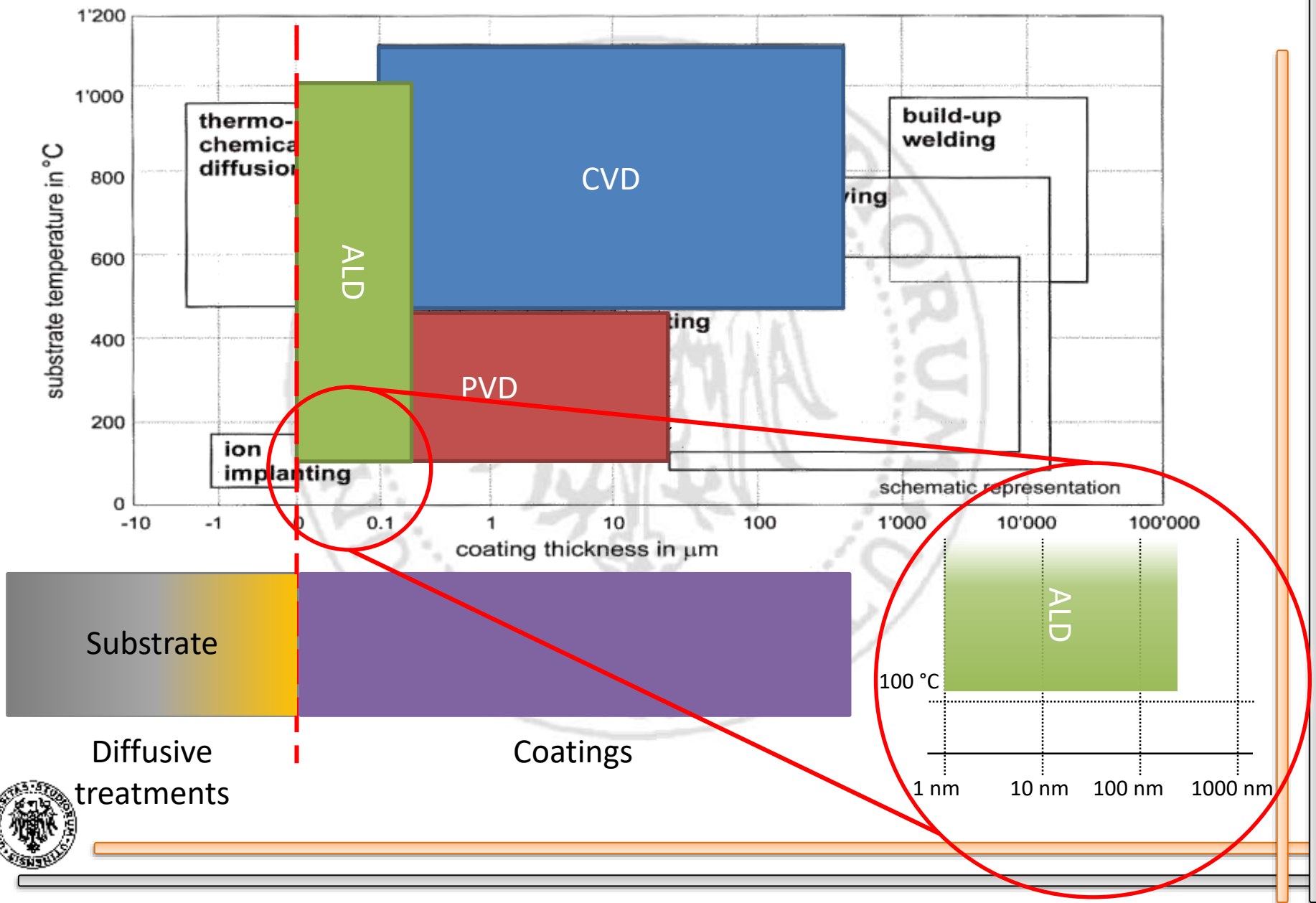
History of Atomic Layer Deposition

Invented 1977 by Dr. Suntola to solve challenge in thin film electroluminecent display production

- Molecular Layering (Kol'tsov, 1960)
- ALD (Suntola & Antson, 1977)
- LASER-ALD (Aoyagi et al.1986)
- Electro-Chemical ALD (ECALE, Gregory et al.1991)
- Plasma-Enhanced ALD (PEALE Niinistö & Leskela, 1993)
- Liquid-Phase ALD (LPALE Nicolau, 1995)
- Photo-Assisted ALD (Photo-ALE Lee et al., 2004)
- Modulated Ion Induced ALD (MIIALE Chiang and Leeser, 2008)

Using Laser and Plasma Enhanced ALD it is possible to deposit more dense layers at lower temperatures, with increased deposition rates and with chemical compositions that cannot be obtained by conventional ALD, like Ta_2O_5. These techniques are the most promising for corrosion protection related applications.

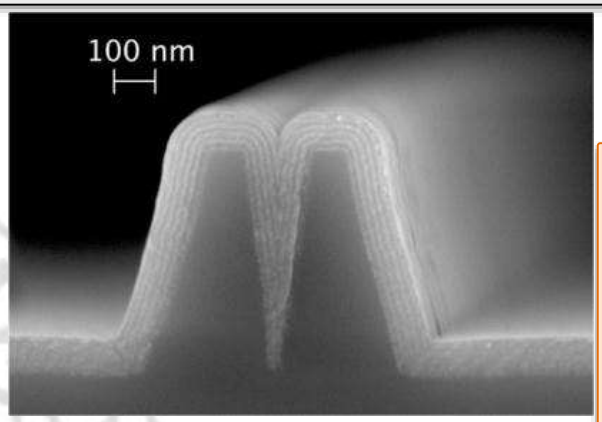
Characteristics of ALD technique

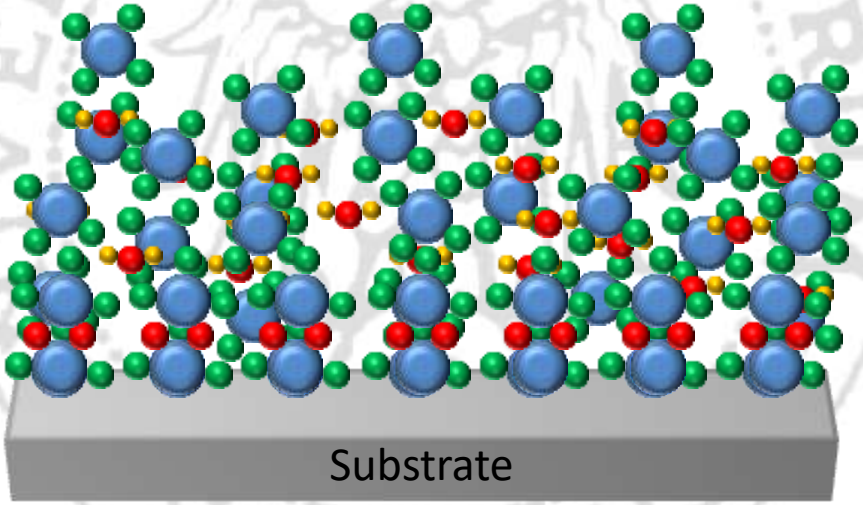


Atomic Layer Deposition

$TiCl_4$

H_2O





Pressure of vacuum typically 1 hPa, temperature (50 to 500° C)

Precursors are dosed as vapor pulses to N_2 carrier gas flowing through the system

Chemicals react (chemisorbtion) only at the surface

Surface controlled, self-limiting growth => conformal, pinhole-free film

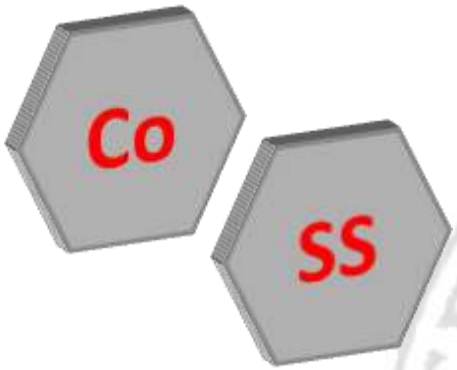
WHAT THE ADVANTAGES OF THIS DEPOSTION TECHNIQUE?

- Self-limited deposition technique - precise dosing not required;
- Covalent bonding - excellent adhesion;
- Multi-layers in one process;
- Conformal – almost pinholes free;
- Can be used to coat any substrate geometry;
- Almost substrate independent;
- Can be used to deposit a wide array of materials;
- Can deposit materials at low temperatures.

Uses of ALD

- Microelectronics;
- Solar panels;
- Anti-stick, low friction films;
- Protection of precious metals against tarnishing;
- Diffusion barriers at high temperature;
- Optical lens coatings;

- Corrosion protection?



Increased corrosion protection

Co-Cr alloys and stainless steels are naturally protected against corrosion thanks to the formation of a Cr_2O_3 protective layer on their surface.

Nevertheless, aggressive environments such as biological medias, sea water and concentrated acids may cause severe corrosion over time.

Can these alloys be further protected against corrosion by the application of a specific coating obtained by ALD?

Reactive alloys

Magnesium and aluminum alloys are easily subjected to corrosion, due to their high reactivity with different medias in a wide range of pH conditions.

Aluminum and magnesium corrosion often leads to reduction of mechanical properties and failures of components.

Can these alloys be coated by ALD to protect them against corrosion thus improving their expected service life?

Sample preparation

Composition of the layers

1) **$TiCl_4$** + **H_2O** **@ 120 °C = TiO_2**

0.6 Å / cycle

2) **TMA** + **H_2O** **@ 120 °C or 300 °C = Al_2O_3**

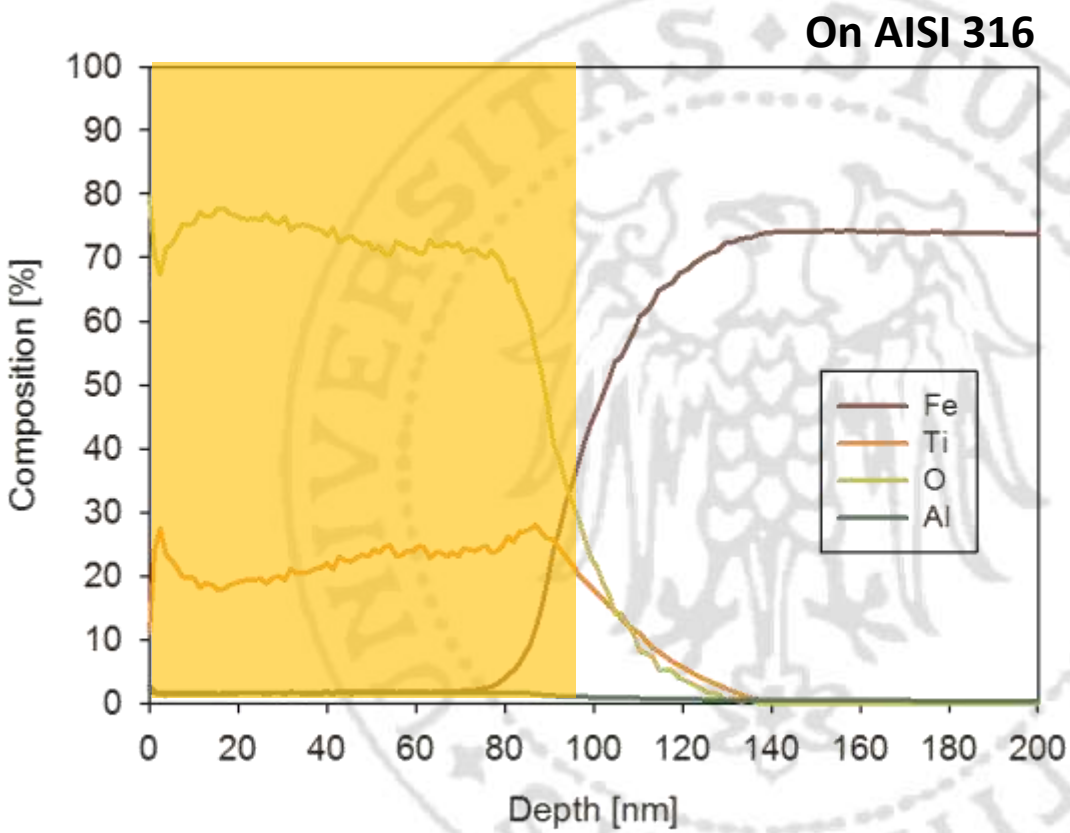
About 1 Å / cycle

3) **TMA** + **NH_3** **@ 300 °C = AlN**

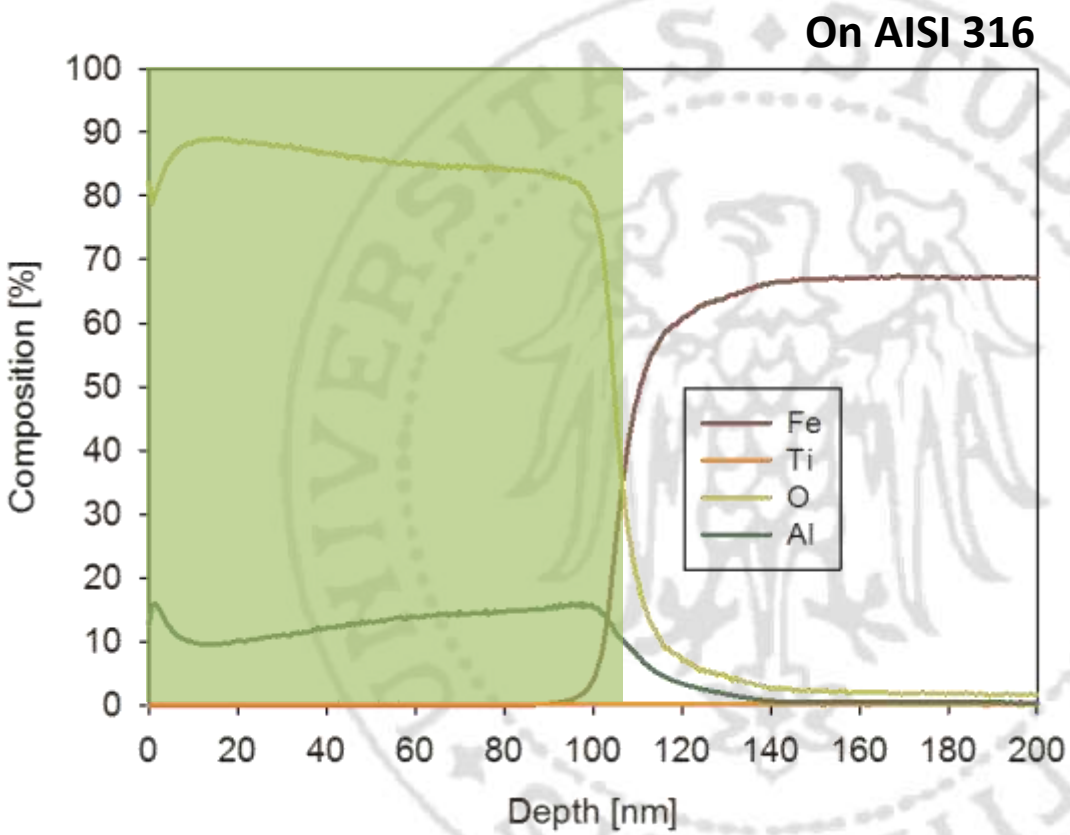
1.5 – 3.2 Å / cycle

Obtained using Beneq (Espoo, Finland) reactors

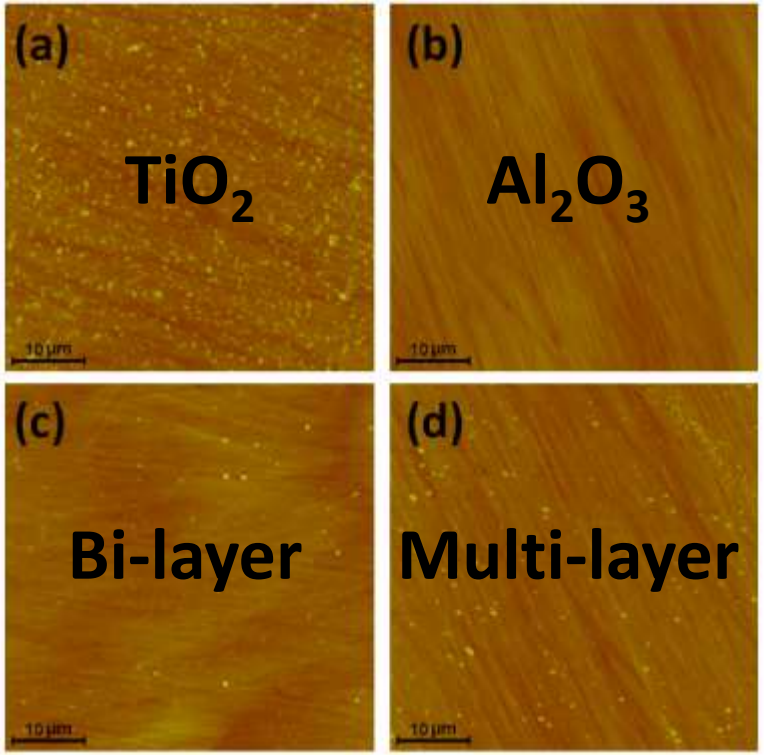
GDOES graph of a 100 nm TiO2 coating

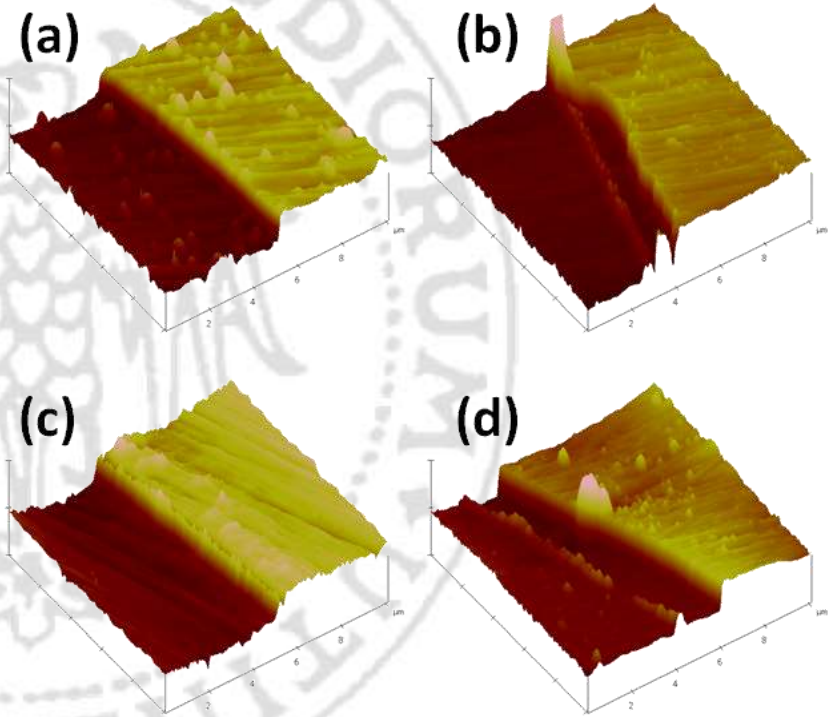


GDOES graph of a 100 nm Al2O3 coating



AFM

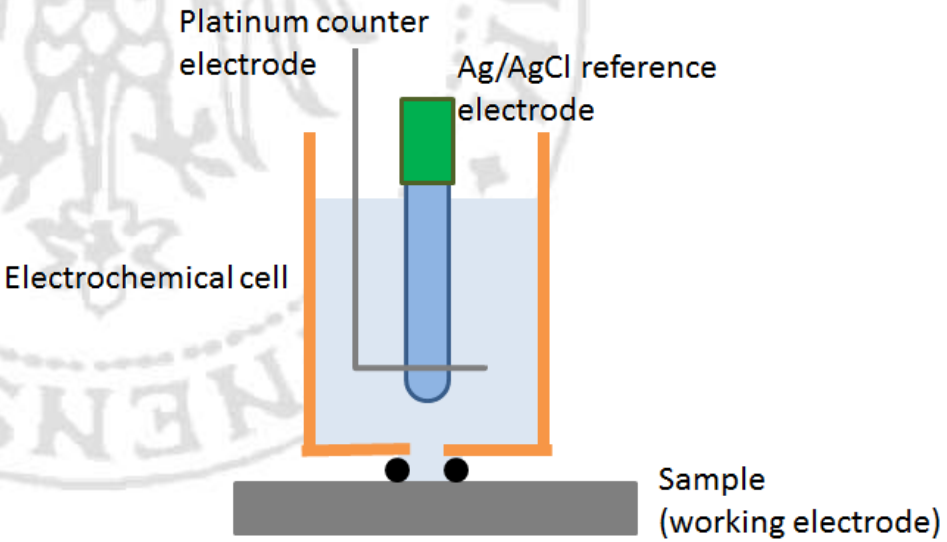

(a)
TiO_2
10 µm
(b)
Al_2O_3
10 µm
(c)
Bi-layer
10 µm
(d)
Multi-layer
10 µm


(a)
(b)
(c)
(d)

Short term corrosion behavior: Potentiodynamic Polarization

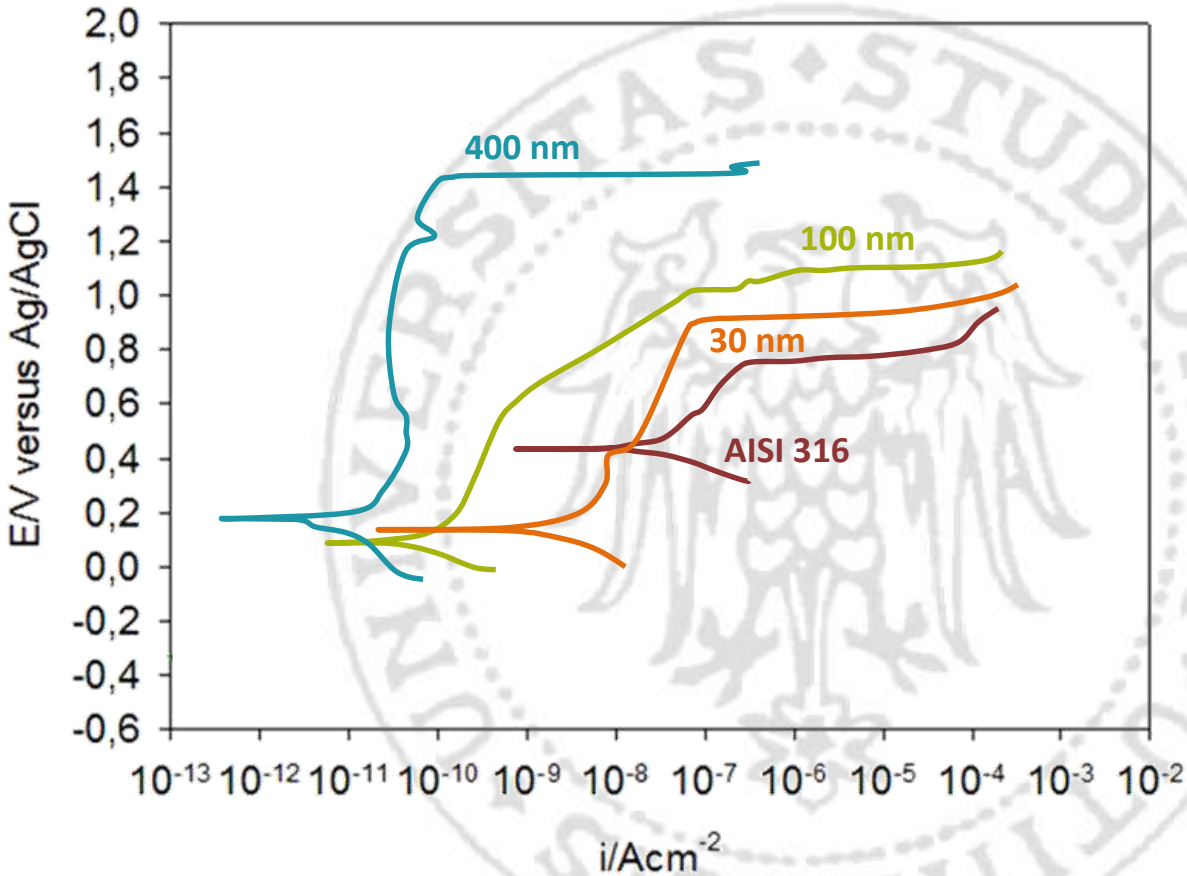
Potentiodynamic Polarizations

- 3 electrodes configuration;
- Ag/AgCl reference electrode;
- Pt (99.95%) counter electrode;
- Area: 10 mm diameter;
- Scan rate: 0.2 mV/s;
- Measuring OCP before test: 5 min;
- Solution: several aggressive electrolytes.



Increased corrosion protection

Stainless Steel - Effect of thickness

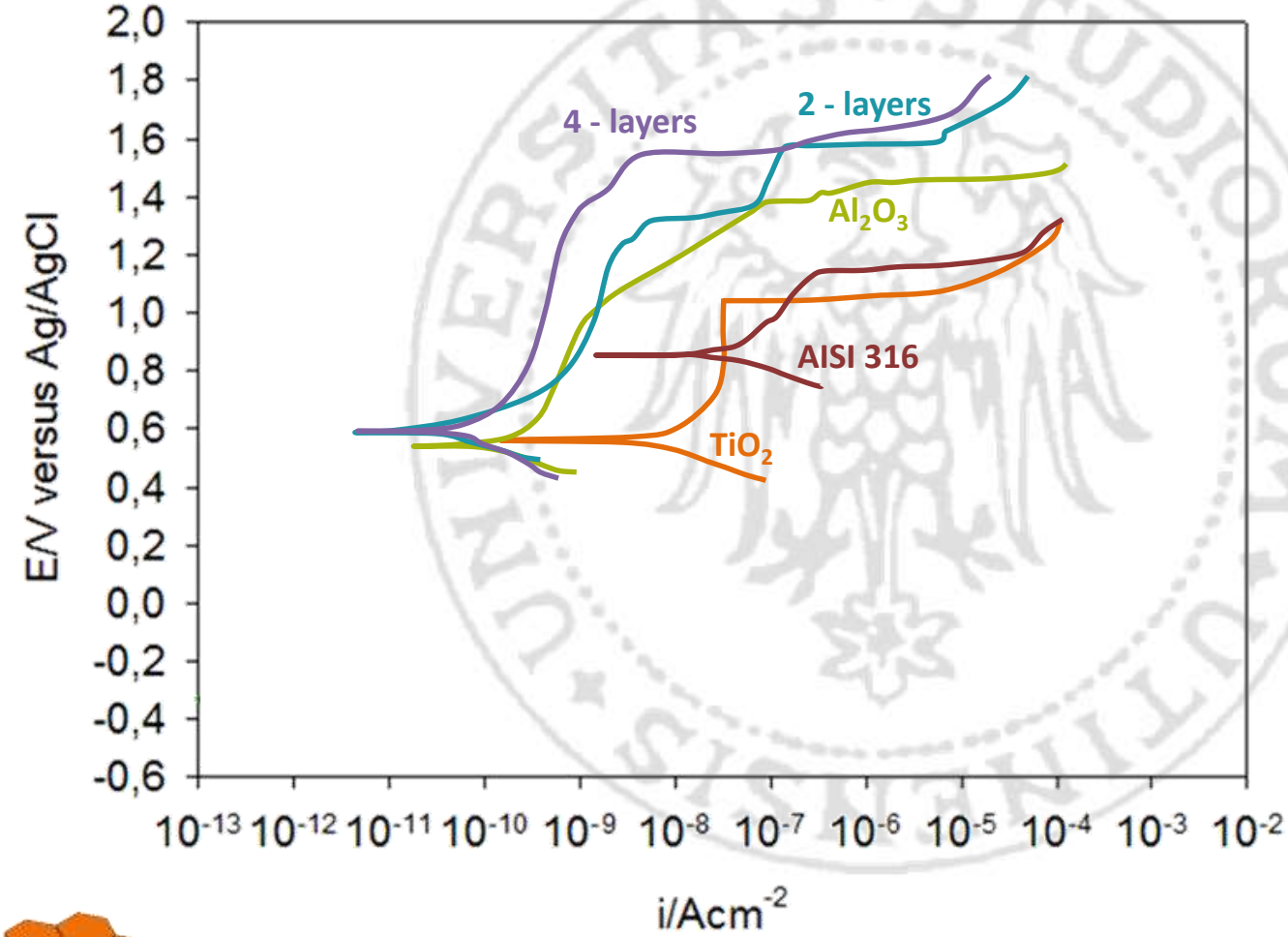


Al_2O_3 Coatings

Electrolyte

9 g/l NaCl

Stainless Steel - Effect of multilayer structures

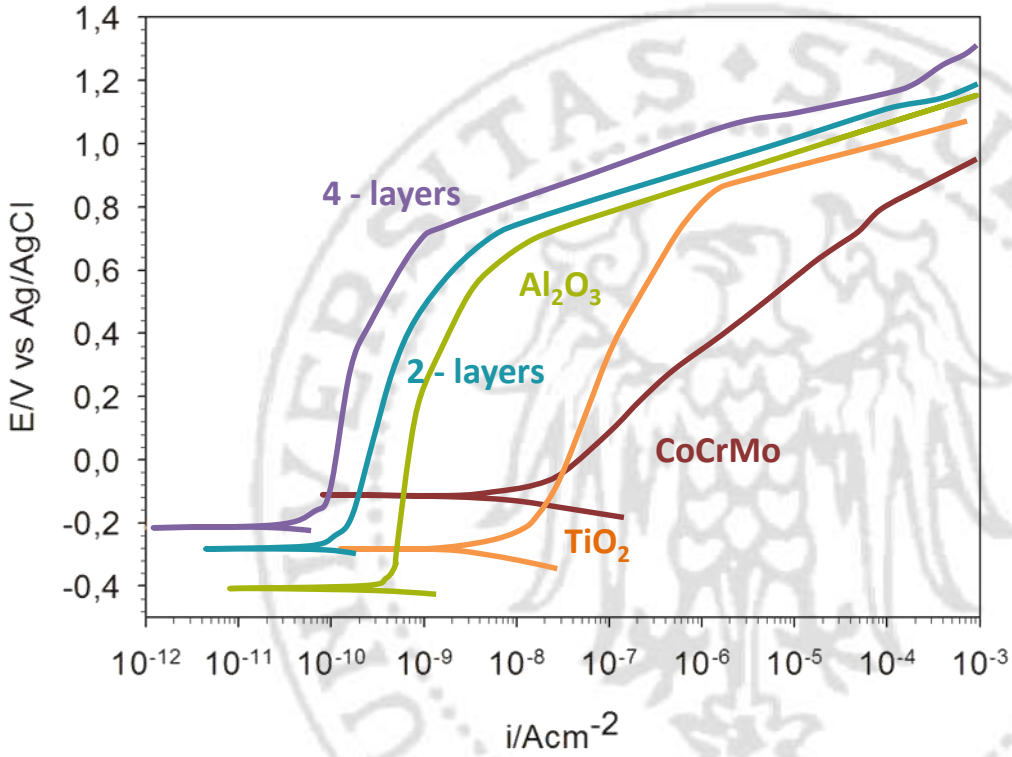


100 nm total thickness

Electrolyte

9 g/l NaCl

Cobalt alloys - Effect of multilayer structures



100 nm total thickness

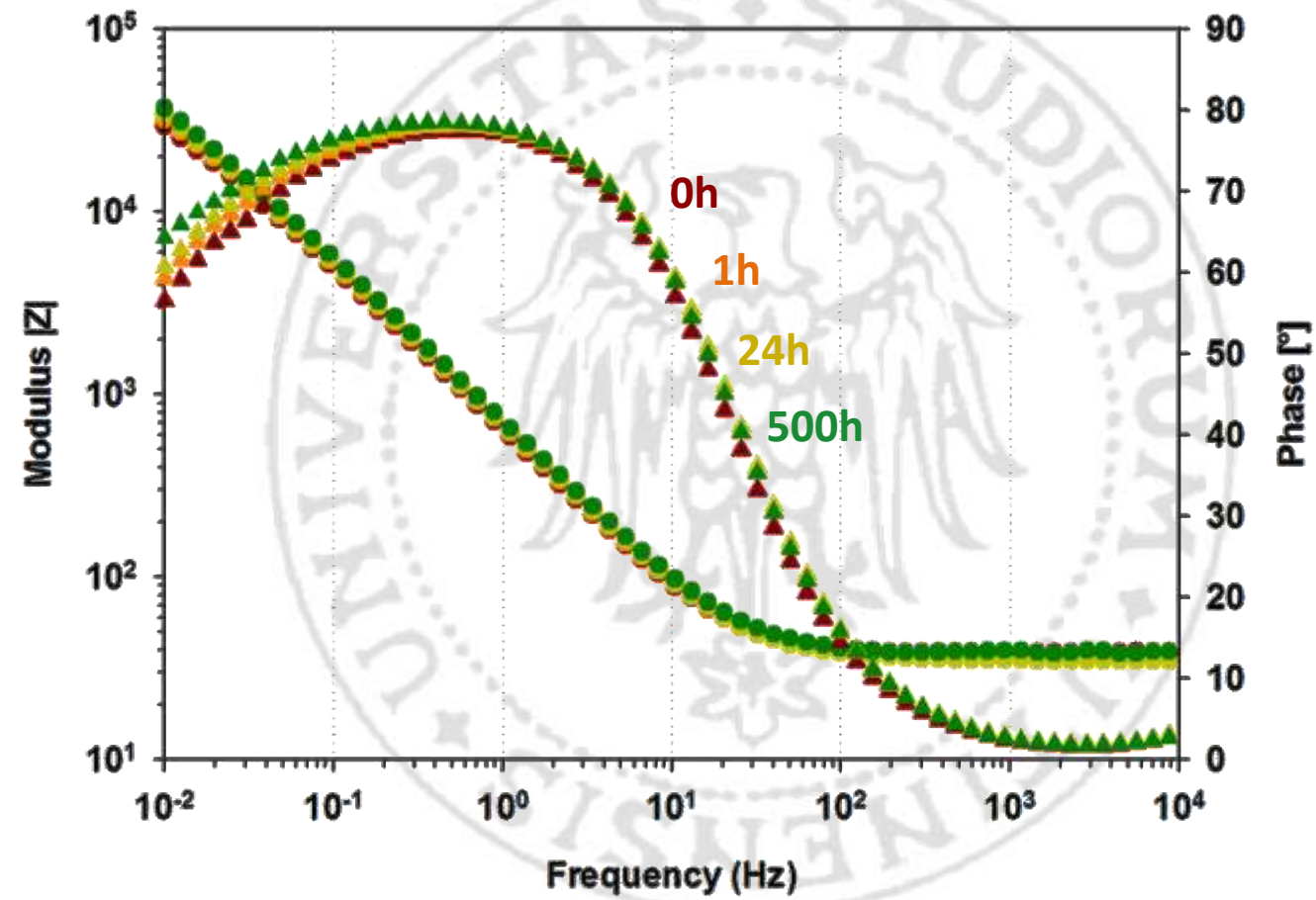
Electrolyte

9 g/l NaCl

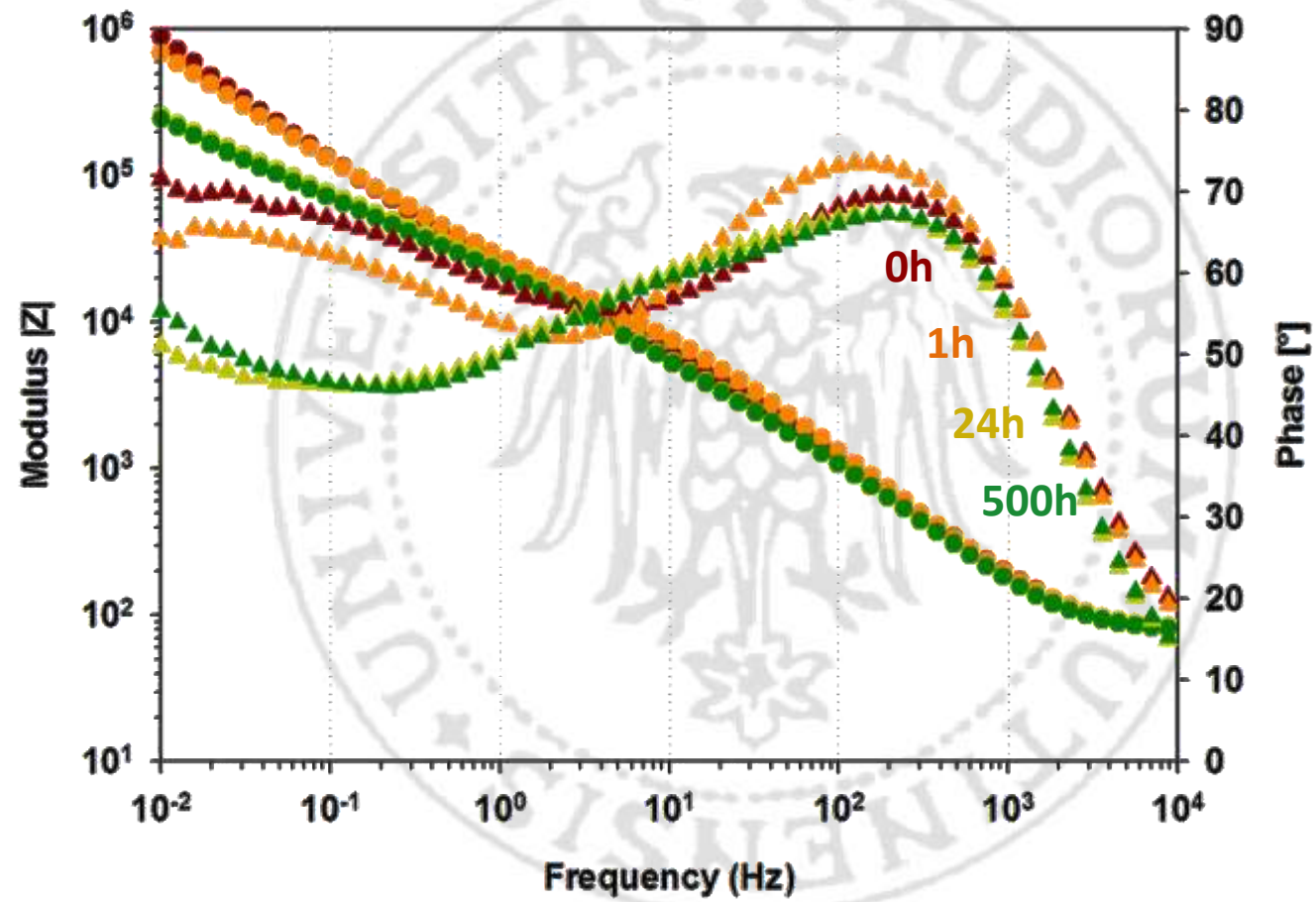
Long term corrosion behavior: Electrochemical Impedance Spectroscopy

0.2 M NaCl solution

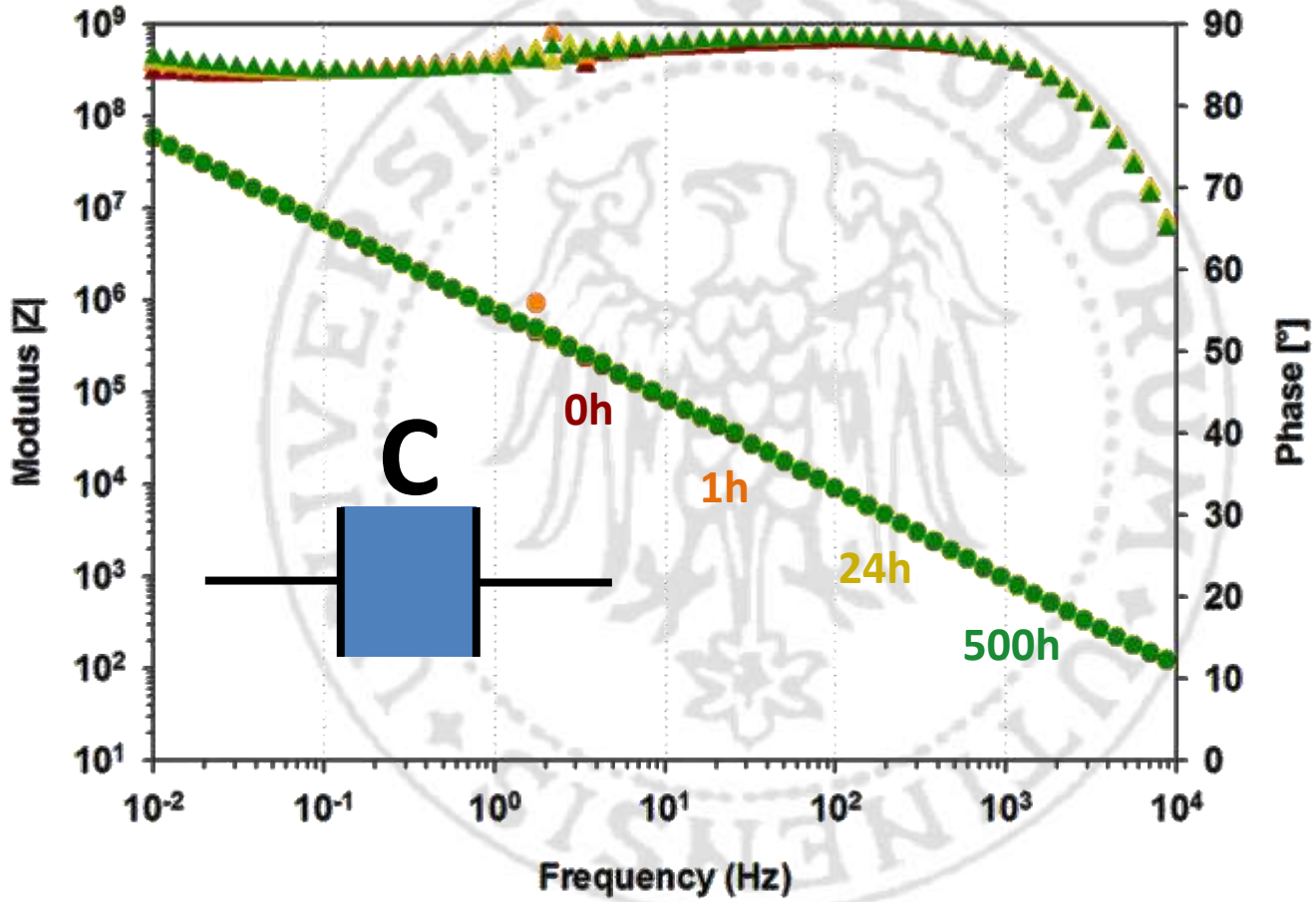
Impedance (AISI 316)



Impedance coating TiO_2



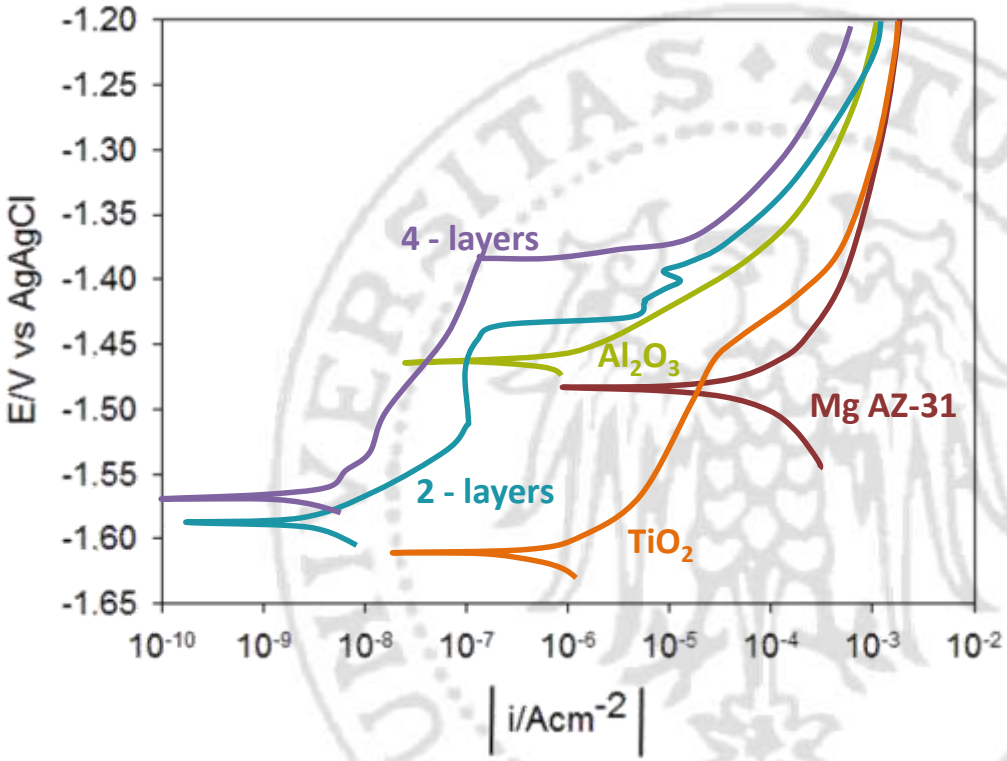
Impedance coating Al_2O_3



Reactive alloys

Short term corrosion behavior: Potentiodynamic Polarization

Effect of multilayer structures on Mg alloy



100 nm total thickness

Electrolyte

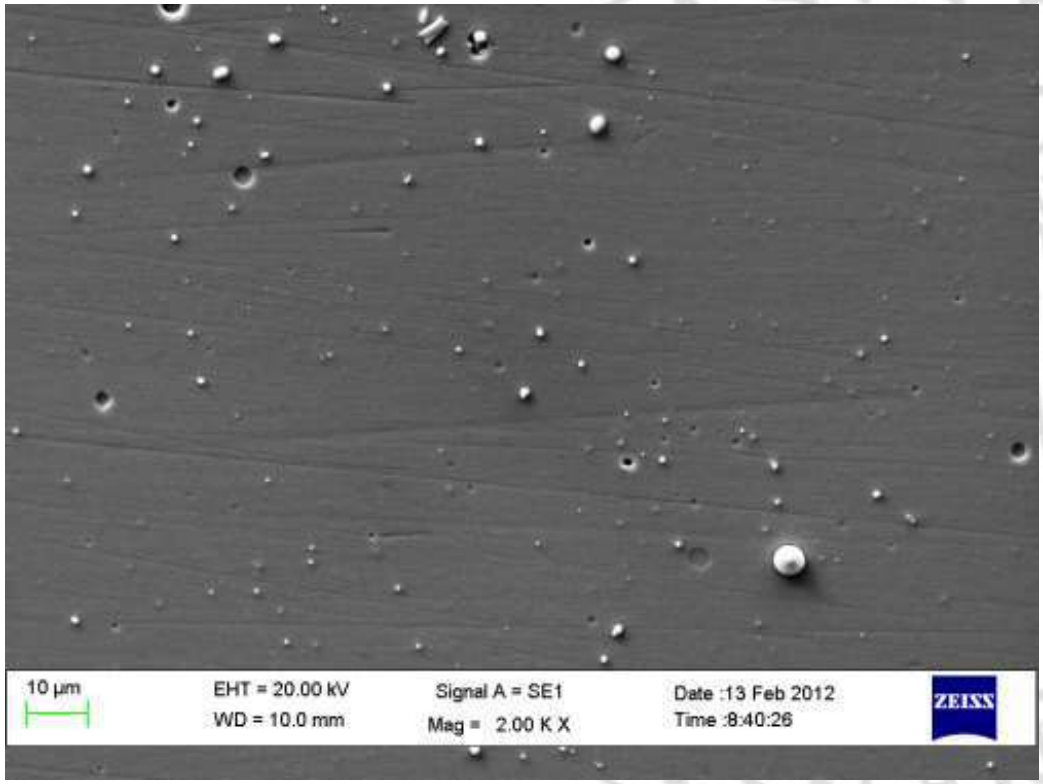
0.05 M NaCl

COMBINED COATINGS

ALD can be easily applied on substrates already protected with other coating technologies, such as PVD, CVD or sol-gel, in order to grant further corrosion protection.

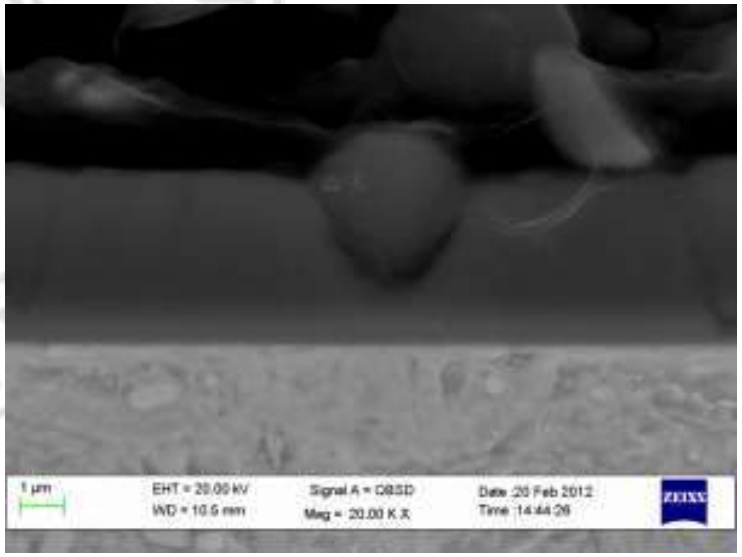
The idea is to seal the residual defects of other coating by ALD, thus increasing the life of the component.

SEM micrographs of a PVD TiAlN coating

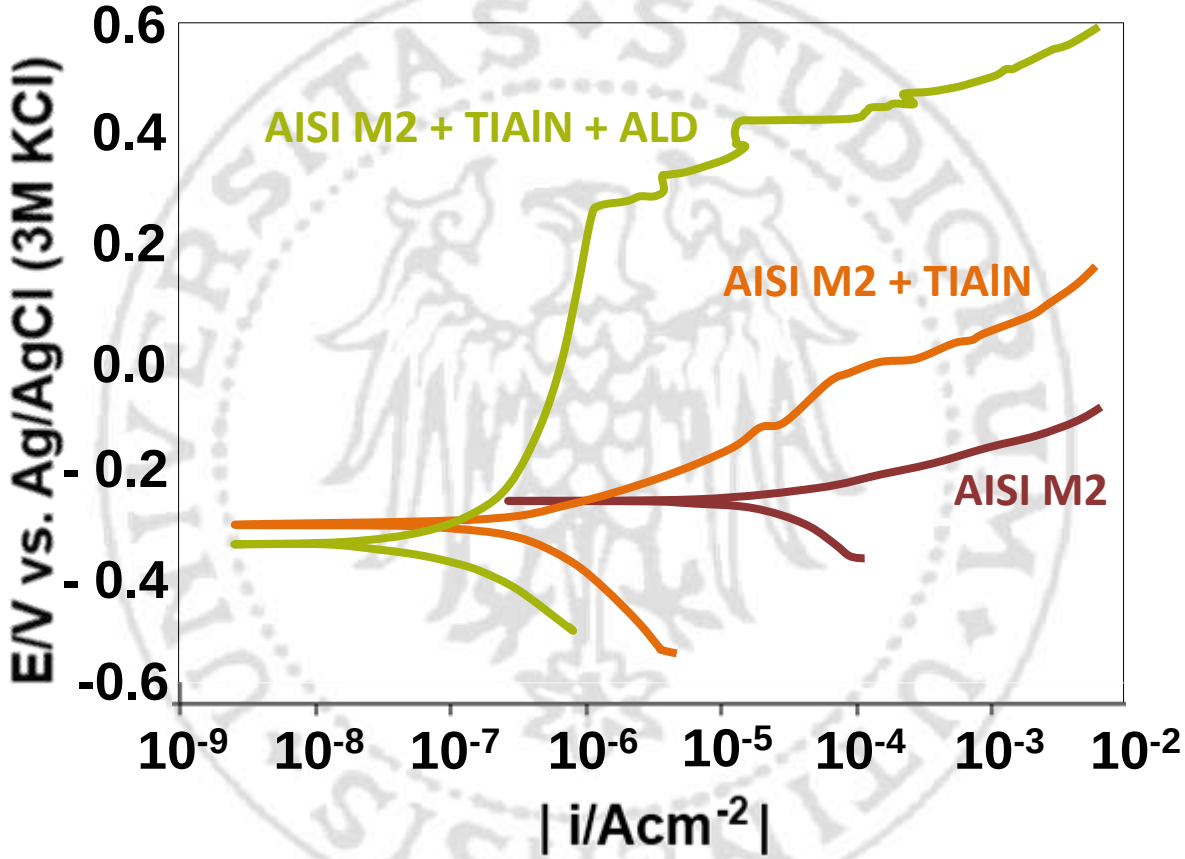


Pinholes, Pores
Droplets
Scratches

Cross section of the PVD coating

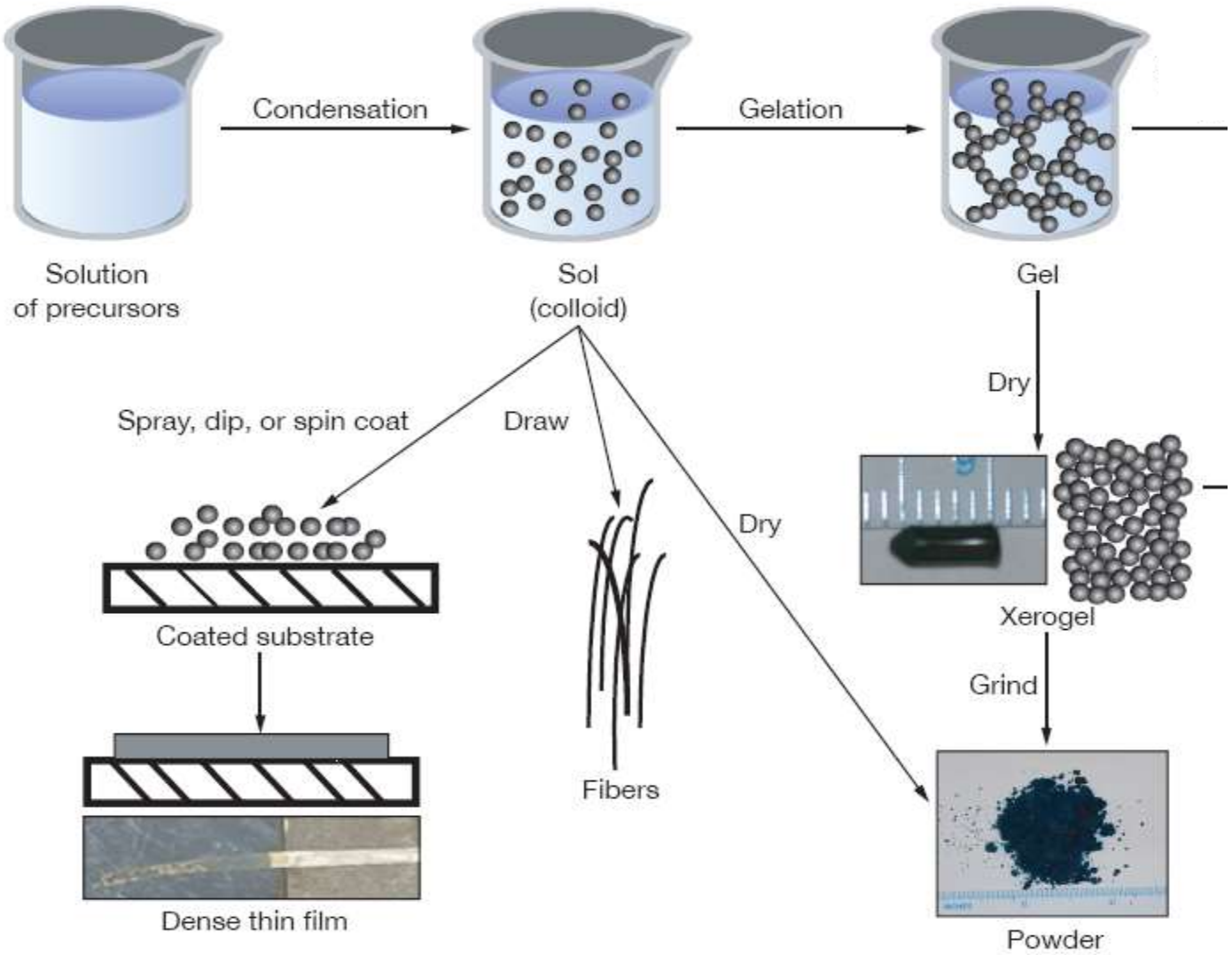


Corrosion protection of PVD + ALD



Electrolyte: 0.2M NaCl

Sol-gel technology



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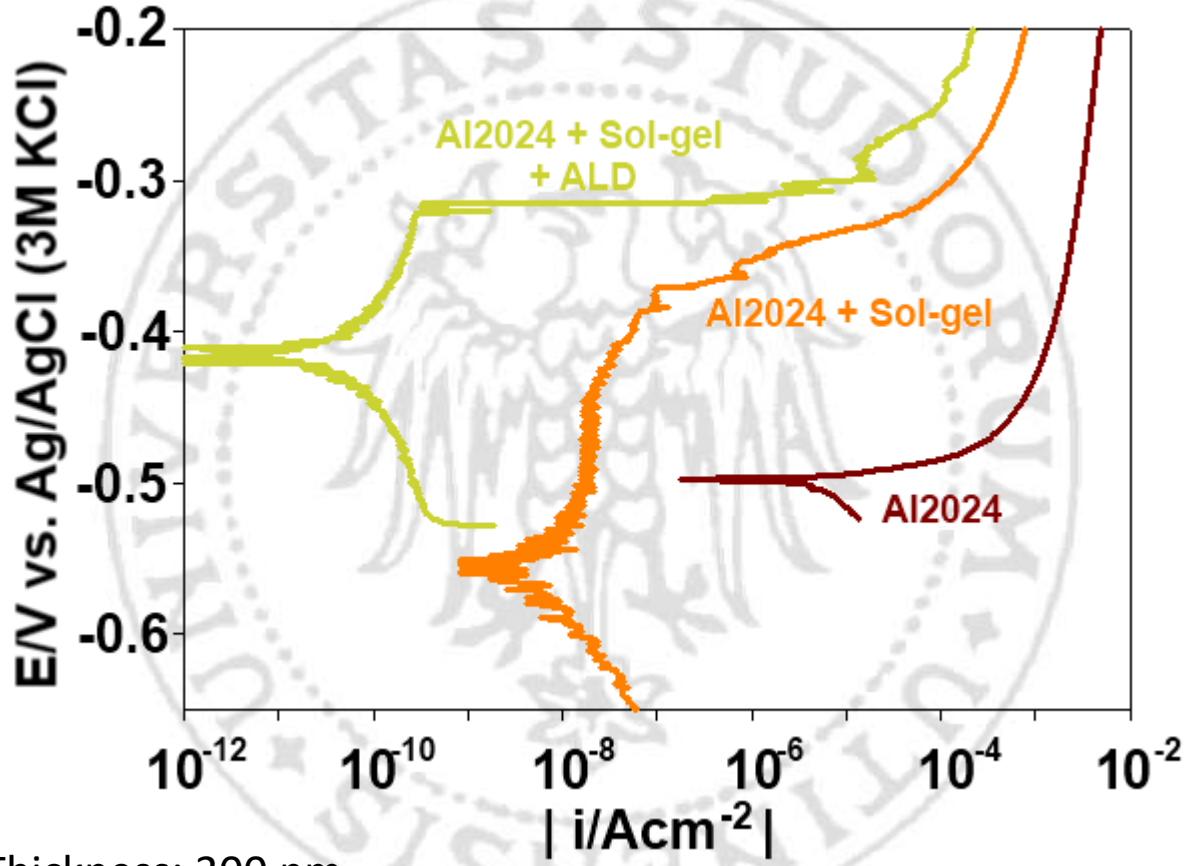
Corrosion protection of solgel + ALD



Sol-gel Thickness: 300 nm
ALD Thickness: 20 nm
Electrolyte: 0.05M NaCl

Conclusions:

- ALD seems to be a very promising corrosion protection technology as shown by electrochemical tests
- By means of electrochemical impedance measurements long term protection was also proved for stainless steels
- ALD over-deposition can strongly improve the protection behaviour given by other deposition technologies

Thank you for your attention