Week 14

Ceramics and colloids

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Sol-gel and thin films

References:

- J. Barton, P. Bowen, C. Carry & J.M. Haussonne - Les Céramiques. Les Traité des Matériaux, Volume 16, PPUR (2005)
- M.N. Rahaman - Ceramic processing and sintering. Taylor & Francis. Second edition (2003). Chapters 7-10
- A. Leriche, F. Cambier, S. Hampshire – Sintering of Ceramics. Reference Module in Materials Science and Materials Engineering (2017)
- M.G. Randal, P. Suri, S.J. Park – Review: liquid phase synthering. J.Mater. Sci. 44, 1-39 (2009)
- W. D. Kingery - Densification during Sintering in the Presence of a Liquid Phase. I. Theory, J. Appl. Physics, 30, 302-306 (1958)

Summary

1. Recall: sol-gel (see Section 4, slides 28-32)
2. Application of sol-gel processing (thin films)
3. Vapor phase deposition
4. Spray techniques
5. Chemical routes

Recall:

Sol-gel: preparation method for ceramics, which includes:

- preparation of a sol;
- gelation;
- solvent removal.

Sol: suspension on colloidal particles in a liquid (or a solution of polymeric molecules);

Gel: semi-rigid body formed by linked colloidal particles in form of a network (or linked polymers);

Typical example: silica (see Section 4, slides 28-32);

Multicomponent sol-gel can be prepared.

Sol-gel processing (in this case sol=particles):

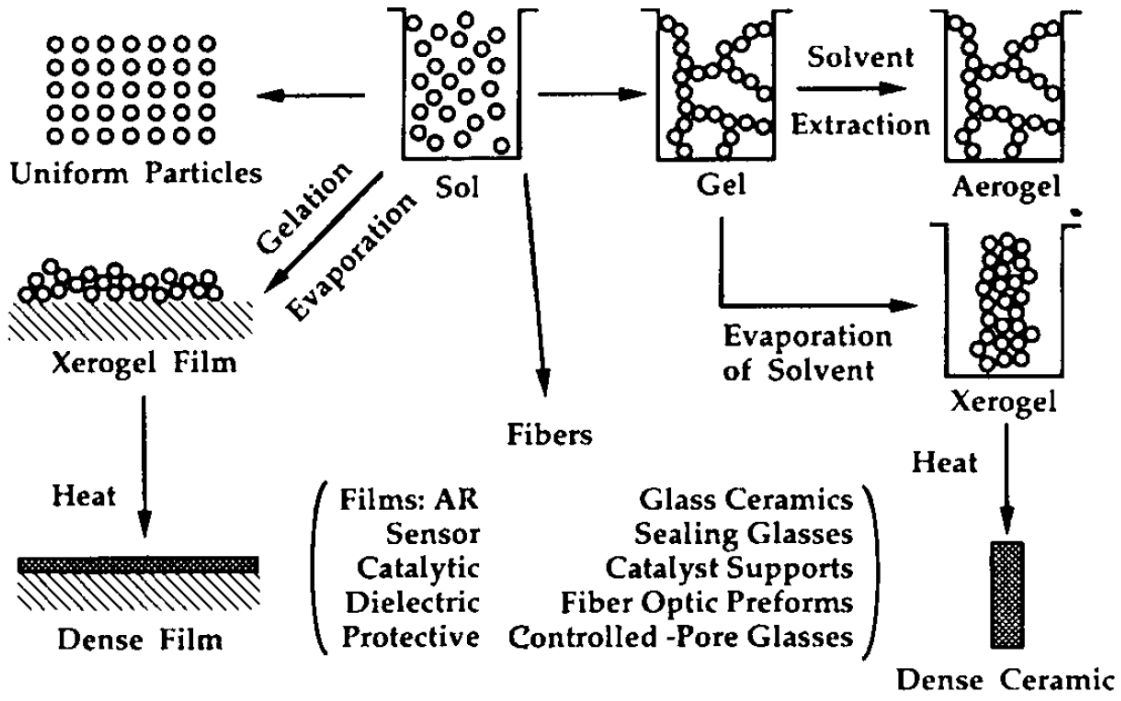
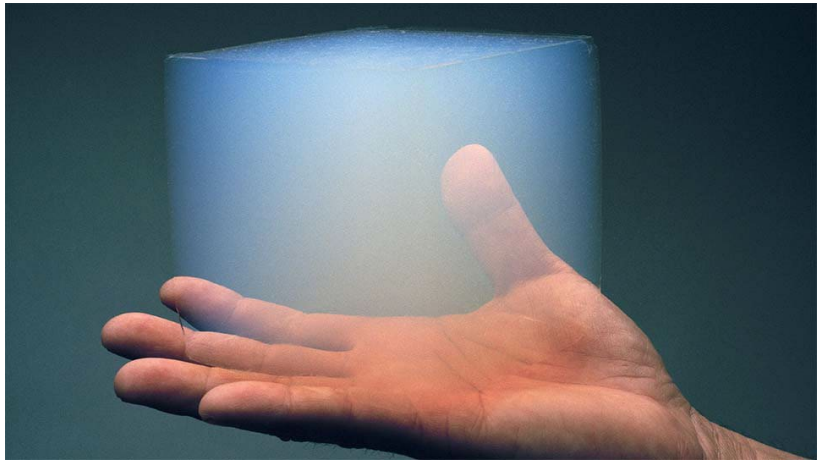


FIGURE 5.1 Schematic illustration of the routes that could be followed in sol–gel processing. (From Ref. 1.)

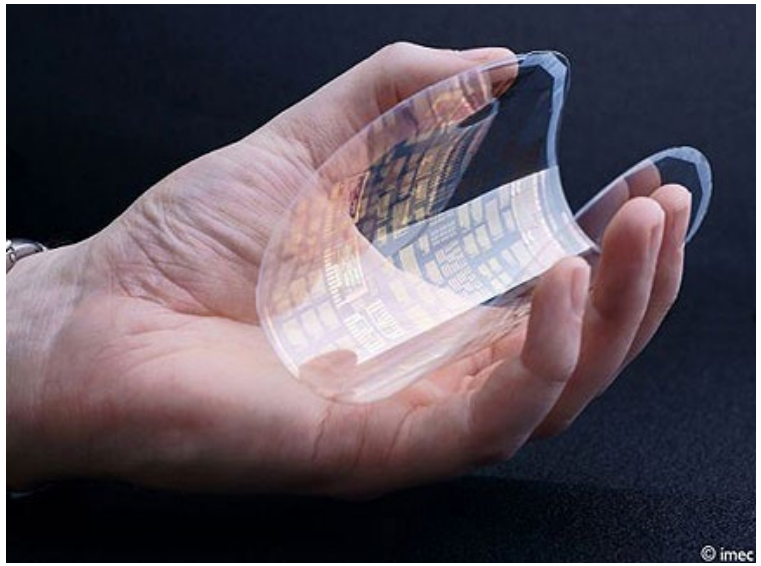
After solvent removal, a thermal treatment is needed to remove organics and then sintering. If the objective is that to produce a film, this has to be thin enough to avoid cracks (<1μm) on a compatible substrate (for instance, similar thermal expansion coefficient).
Each step, film formation, drying, debindering, and sintering have to be carried out carefully in order to obtain an optimized thin film (dense or porous).
The product can also be a massive ceramic with or without final densification.

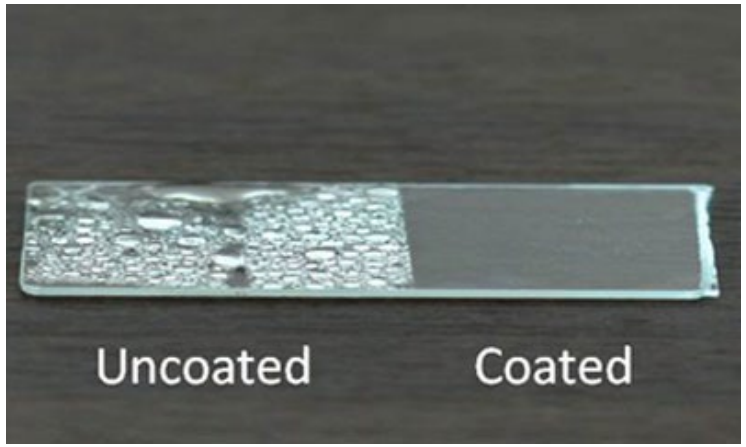
Cons: chemicals are generally expensive and moisture sensitive.

Materials obtained by sol-gel processing.
Examples: Xerogels



Examples: flexible electronics, hydrophilic/hydrophobic coatings

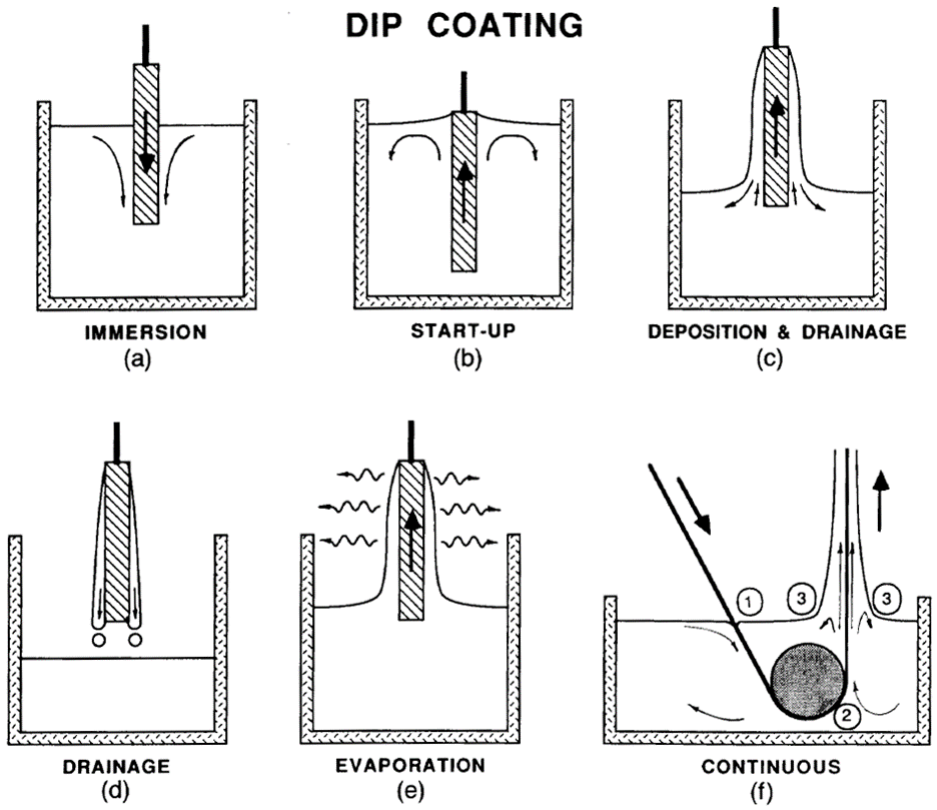




Thin films and coatings (dip coating)

Before gelation, the sol can be used to form a thin layer on surfaces by dip or spin coating. The solution needs to wet properly the surface.

Dip coating is widely used and quite easy, but the sol should not too much moisture sensitive.



In stage (c) different forces are in competitions, i.e.:

1. Viscous forces;
2. Gravity;
3. Surface tension;
4. Inertial forces;

The process can be continuous (f) up to role-to-role processing (concept similar to tape casting, but without a blade and, generally, thinner deposition)

Typical thickness: 50 -1000 nm (thin)
Compare tape casting layer thickness: 5-500 µm (thick)

Dip coating

Viscous drag force: $\frac{\eta U}{h}$

Gravity force: $\propto \rho g \mathrm{h}$

η: liquid viscosity
U: substrate speed
h: film thickness
ρ: liquid density
g: gravity acceleration
c_1: constant ~0.8 (Newtonian liquid)

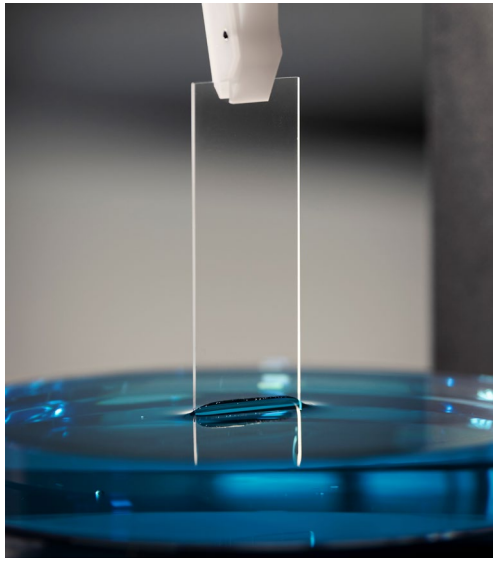
$$h = c_1 \left(\frac{\eta U}{\rho g}\right)^{1/2}$$

Nevertheless, for viscous liquid or slow substrate speed, the liquid-vapor surface tension (γ_{LV}) needs to taken into account

$$h = 0.994 \left(\frac{\eta U}{\gamma_{LV}}\right)^{1/6} \left(\frac{\eta U}{\rho g}\right)^{1/2} = 0.994 \frac{(\eta U)^{2/3}}{(\gamma_{LV})^{1/6} (\rho g)^{1/2}} = \propto (\eta U)^{2/3}$$

Extra: check how viscosity can be measured and its dimensions

Dip coating: examples



Thin films and coatings (spin coating)

Spin coating is generally used for flat discs of limited size, but the process can be done under controlled atmosphere

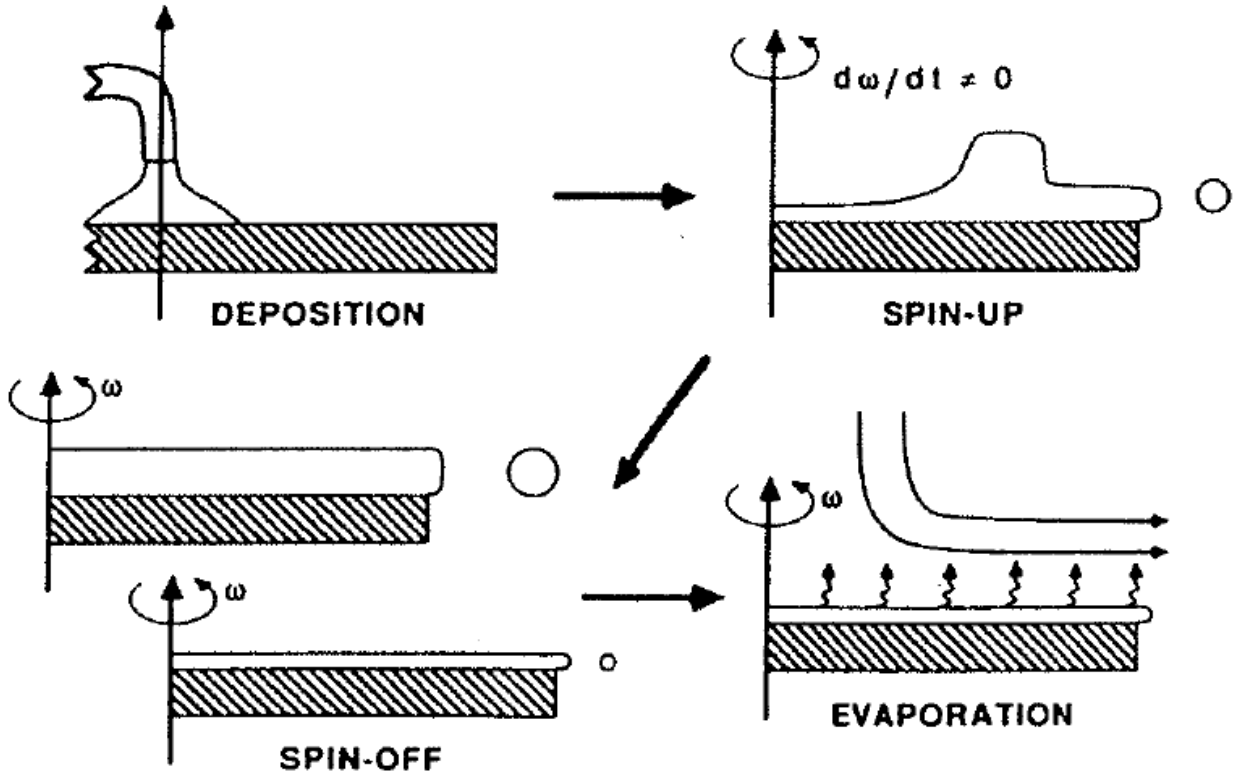


FIGURE 5.36 Stages of the spin coating process. (From Ref. 62.)

Spin coating

Rotational (centrifugal) vs. viscous.

$$h(t) = \frac{h_0}{\left(1 + \frac{4\rho\omega^2 h_0^2 t}{3\eta}\right)^{1/2}}$$

η: liquid viscosity
ω: angular velocity
t: time
$h(t)$: film thickness at time t
h_0: initial thickness
ρ: liquid density
g: gravity acceleration

ρ_A^0: mass of initial solvent per unit of volume
ρ_A: mass of final solvent per unit of volume
e: evaporation rate

Spin-off (c) is a key stage, which needs to be carried out under controlled conditions.

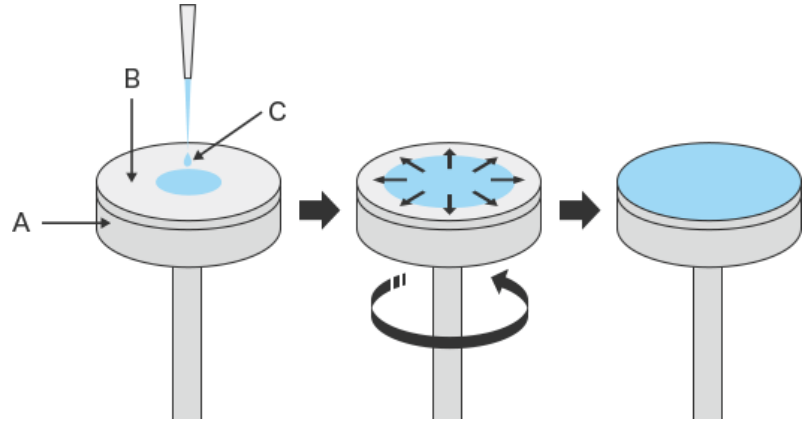
Competition of forces: rotational (centrifugal) vs. viscous.

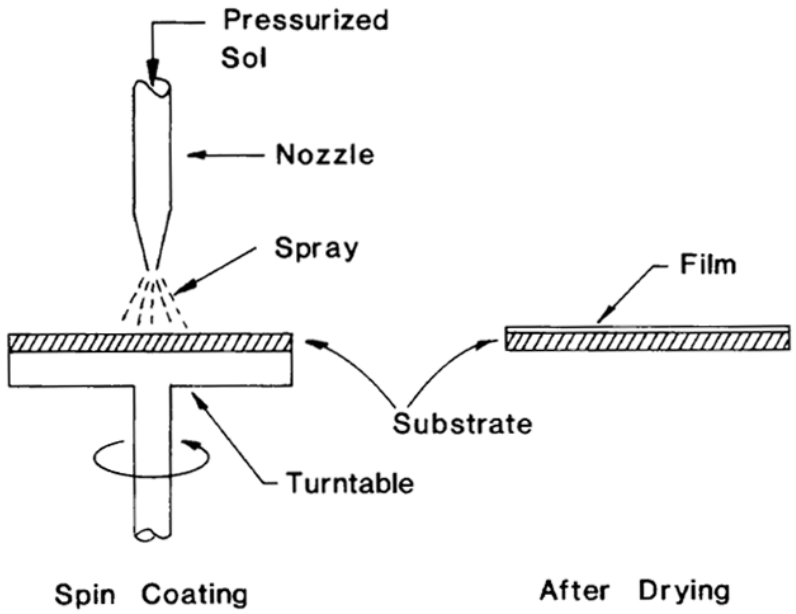
As a result, films with high thickens homogeneity are obtained.

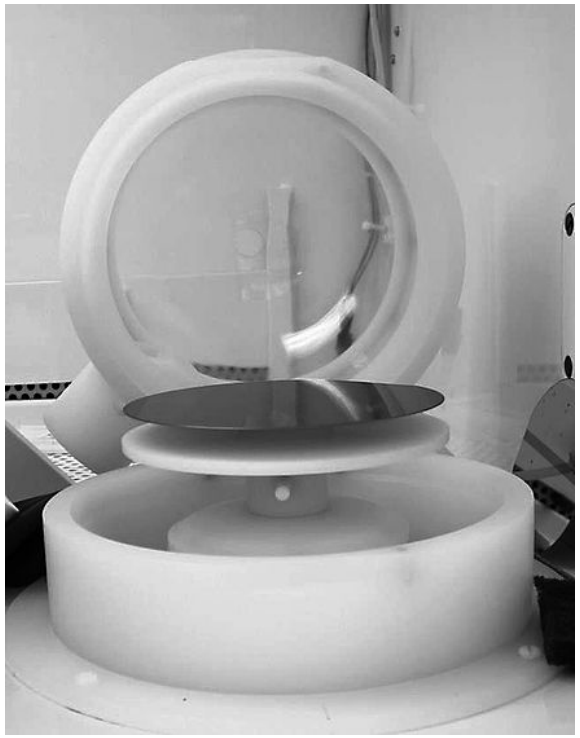
Then, evaporation takes place

$$h_{final} = \left(1 - \frac{\rho_A^0}{\rho_A}\right)\left(\frac{3\eta e}{2\rho_A^0\omega^2}\right)^{1/3} = \propto \omega^{2/3}\eta^{1/3}$$

Spin coating: examples



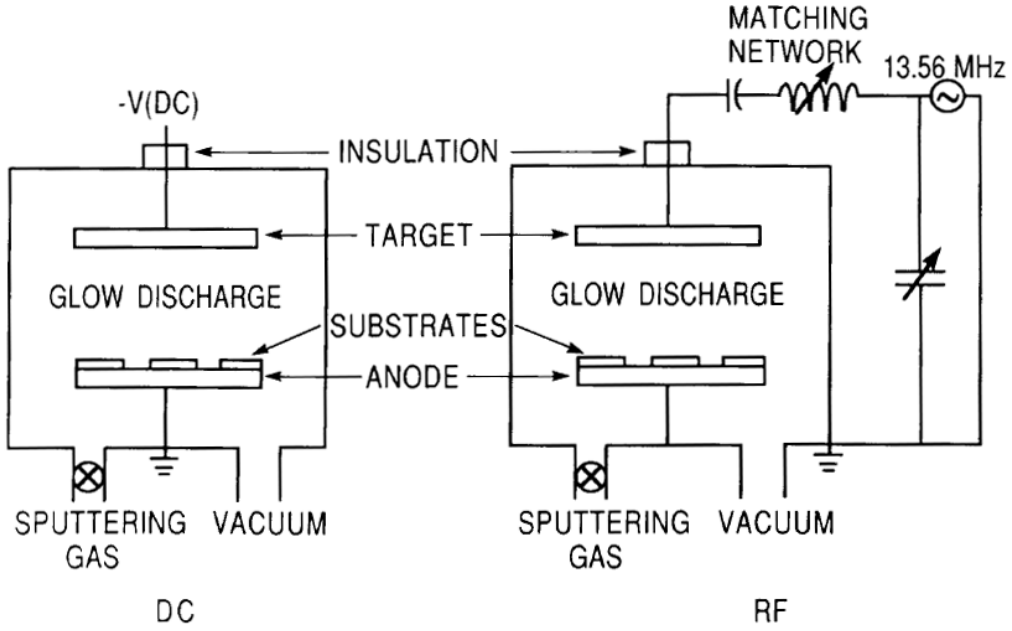




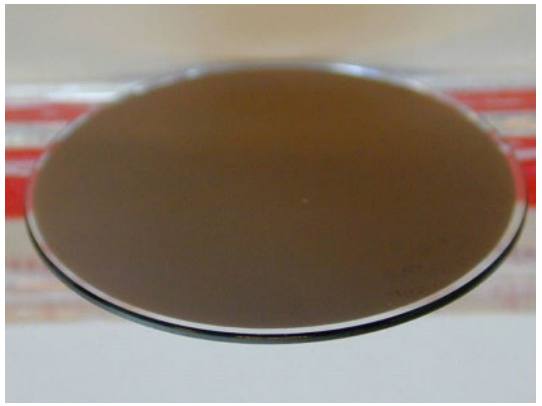
Typical thickness: 50 -1000 nm

Vapor phase deposition (Physical, PVD)

Different methods and principles.



Example of sputtering targets, they might be produced by SPS



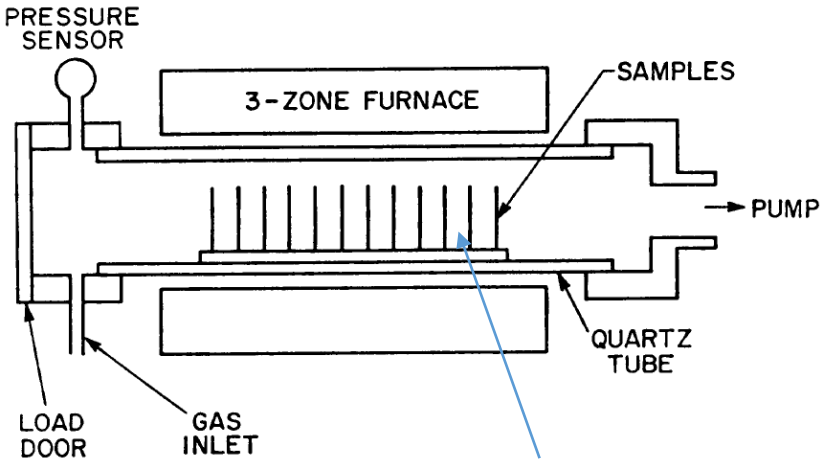
Coated substrate

Deposited material of the same nature of the target. Typically, metals and metal oxides (sputtering)

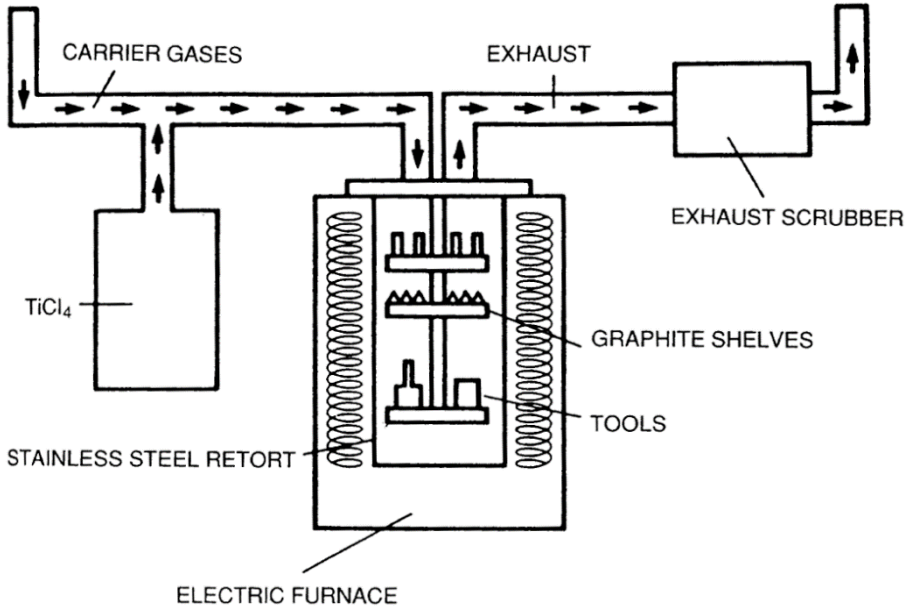
- An ion source bombards the surface of the target and a matter flux is produced and projected on the substrate;
- The deposition is strongly directional;
- Even complex oxide can be deposited (the appropriate target is needed).

Vapor phase deposition (Chemical, CVD)

- The substrate is exposed to a volatile precursor of the material to deposit;
- Vapor precursor react on the substrate (e.g. thermal decomposition or surface reaction), forming the layer (example $TiCl_4$ → TiO_2);
- By-product are produced (that might be corrosive or/and toxic);
- Can be done at atmospheric pressure or low pressure (variants as plasma enhanced or photochemical have been developed as well);
- Is not directional and complex object can be coated;
- Generally, high temperature is applied and deposition rate is rather low;
- Allow deposition of material well below the melting temperature;
- High purity, high dense deposition, economical production.



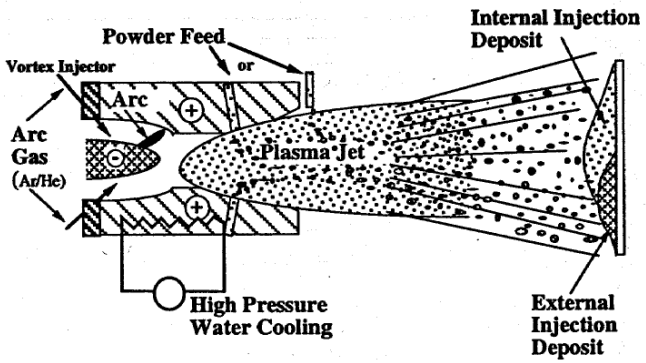
Vertical wafers

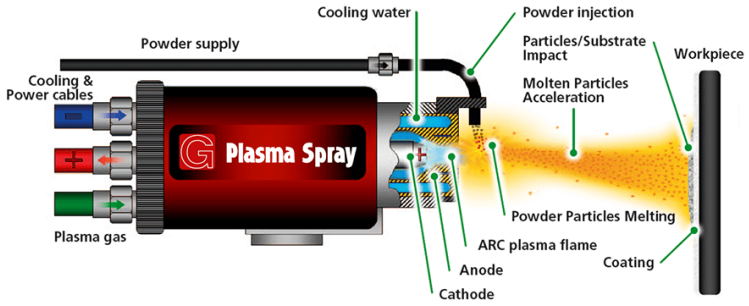


Thermal spray

Plasma

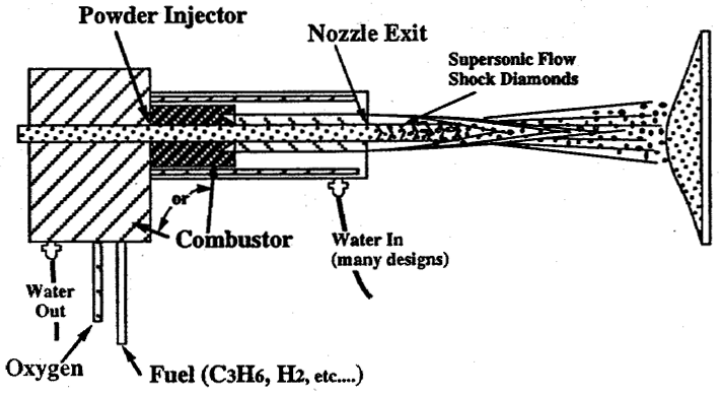
T=10000 °C

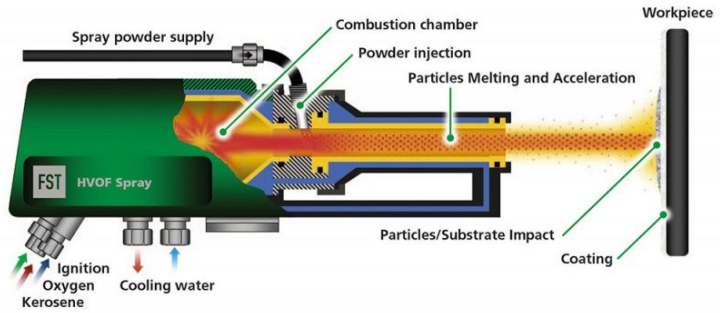




Flame (HVOF, High velocity Oxygen Fuel)

T=3000 °C





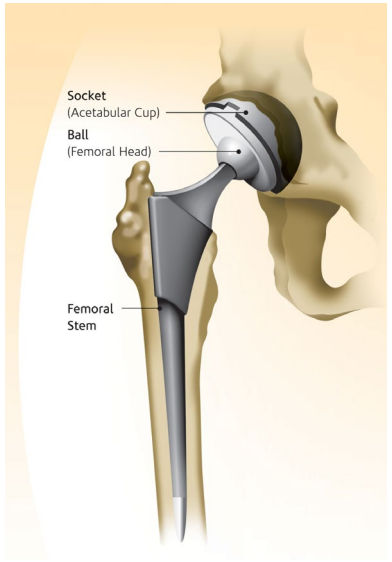
High speed of particles (even supersonic);
Generally, no reaction with the substrate, mechanical adhesion;
The substrate needs to be pre-treated (appropriate roughness obtained e.g. by sand blasting)
Coating thickness, several microns (50 – 3000 μm)
For powders and/or substrates thermal sensitive, HVOF offers a lower operative temperature

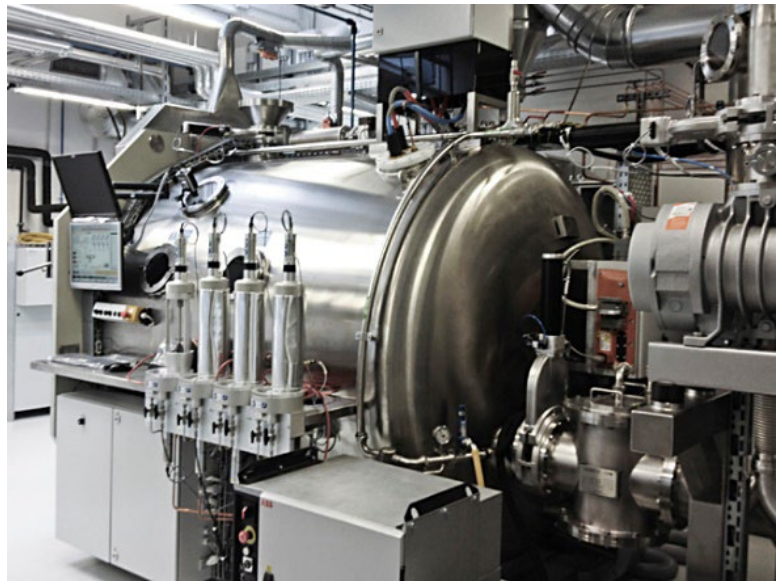
Applications (plasma most used):

- Abrasion resistance, ceramic coating: Cr_2O_3, TiO_2, Cr_3C_2, TiC, TiN, Mo_2C
- Functional interfaces to promote biocompatibility: e.g. Ti implants coated with hydroxyapatite;
- Electrically and thermal insulation: jet engines, gas turbines and diesel engines. Composition: Al_2O_3, MgO or very often ZrO_2 (6-8% Y_2O_3)

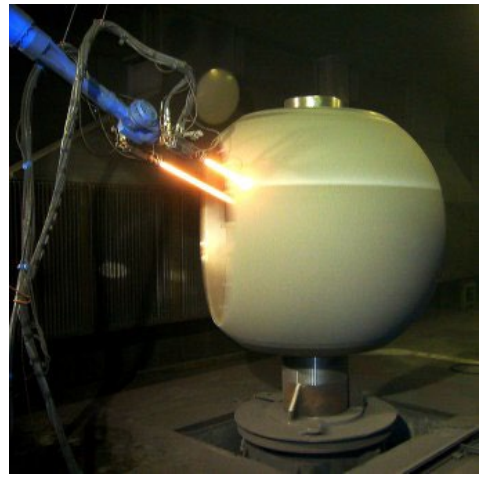
Thermal spray: examples

Plasma





HVOF



Gas Turbine Engines - power and aircraft

Loads on Blades in Gas Turbine

Efficiency:

$\lambda = (T_{max} - T_{min})/T_{max}$

T_{max} - gas exiting combustion chamber

T_{min} - gas exiting engine

First stages:

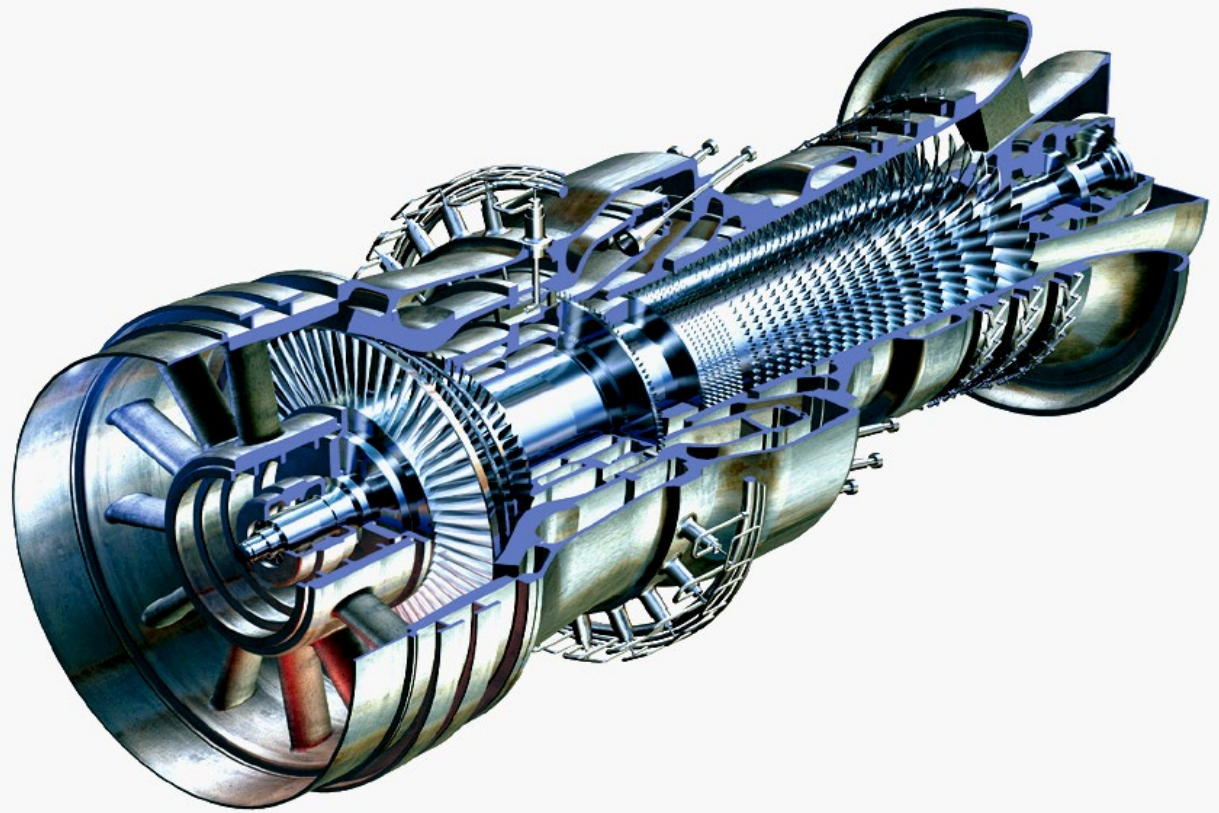
$T_{surface} = 1300$ K

- Pressure
- Oxidation

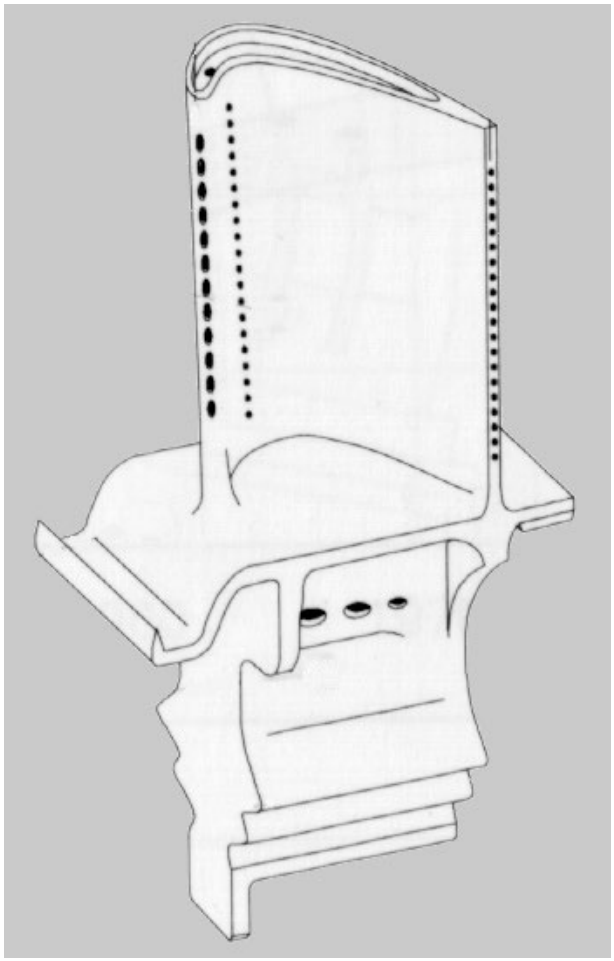
Substructure of turbine blades
– cooling channels
– gas at 650°C allows operating temperatures up to 1600°C

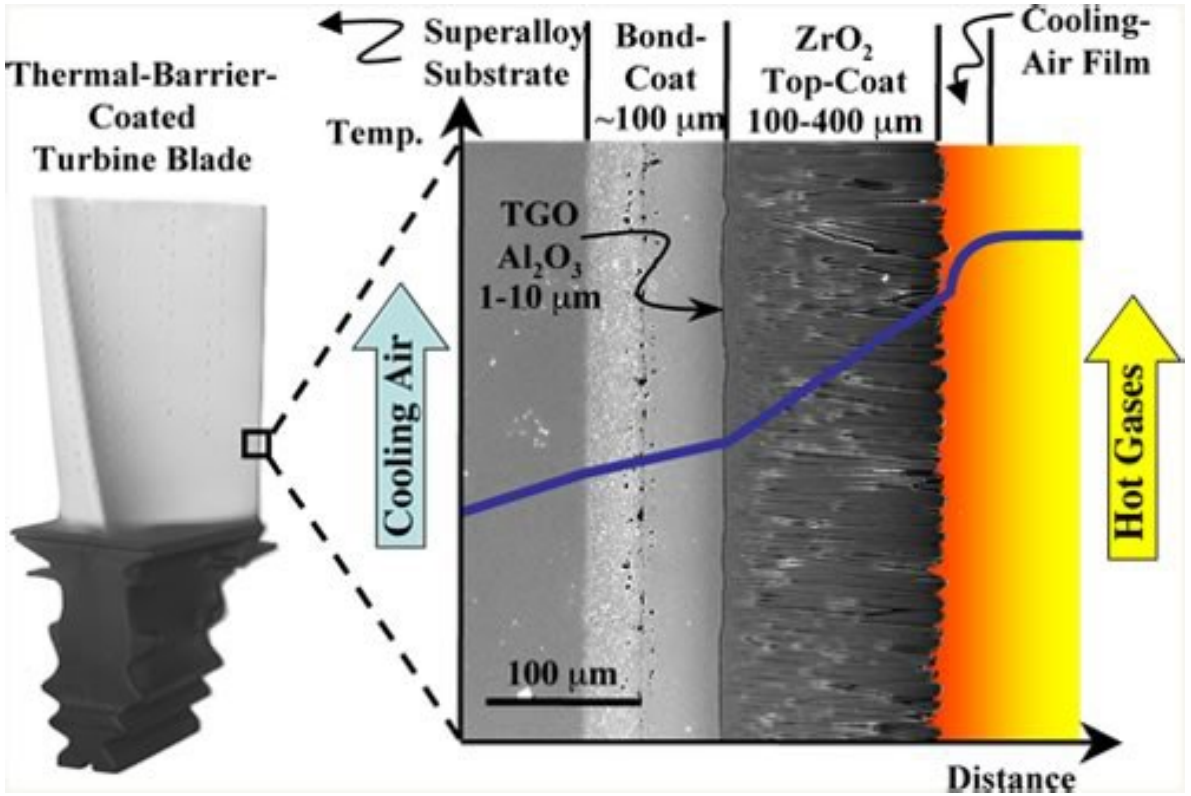
CHALLENGE

1-2% increase in efficiency – airplane
– 1-2 million dollars per plane per year !!! Lower Carbon footprint.



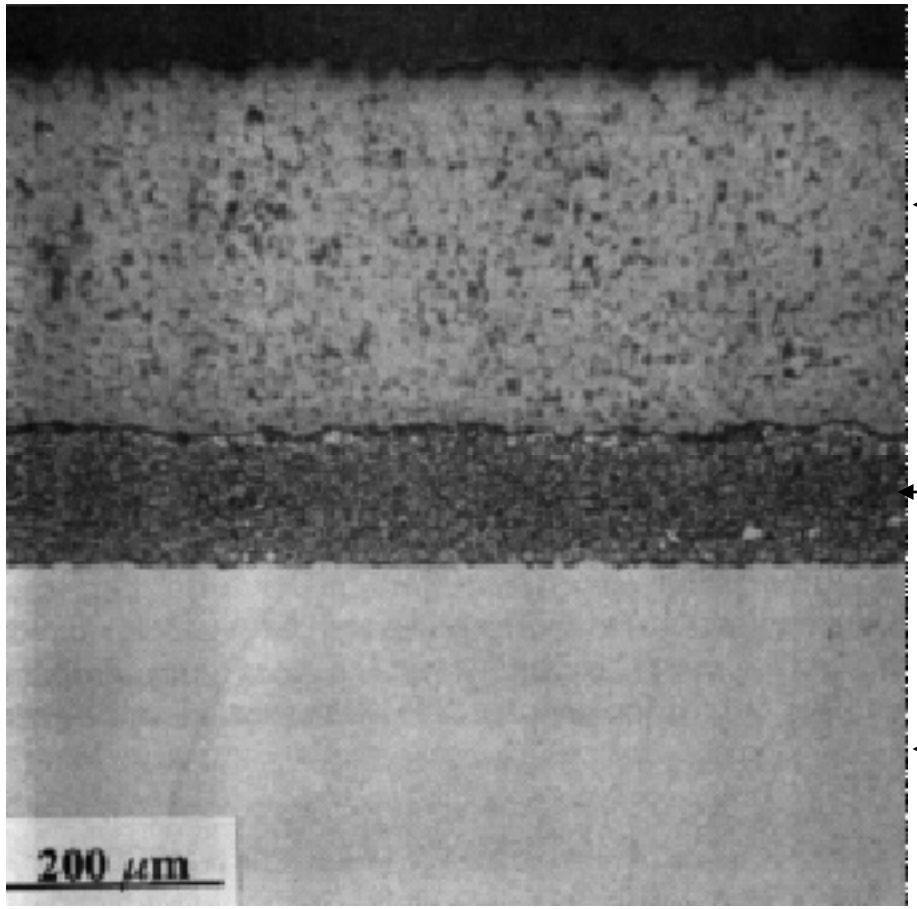
Cooling channels and Thermal Barrier Coatings





- Thermal barrier coatings (TBCs) for gas-turbine engine applications. (Padture et al., Science, 2002)

Thermal Barrier Coatings



YSZ
(ZrO_2 + 6-8% Y_2O_3)

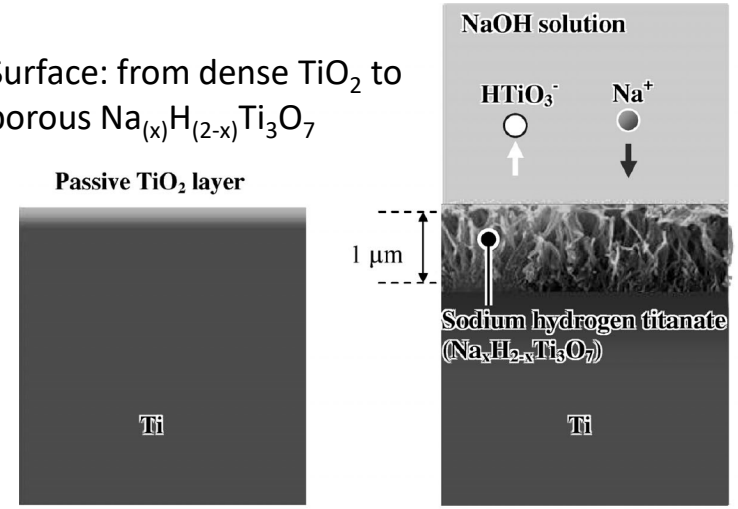
Bond coat
(MCrAlY, β-phase)

Ni-based superalloy
(γ + γ‘ phases)

Chemical coating by controlled growth

In some cases, the substrate surface (e.g. a metal) can be modified and transformed to its oxide or a chemical phase which is chemically bonded with the metal.

Surface: from dense TiO_2 to porous $Na_{(x)}H_{(2-x)}Ti_3O_7$

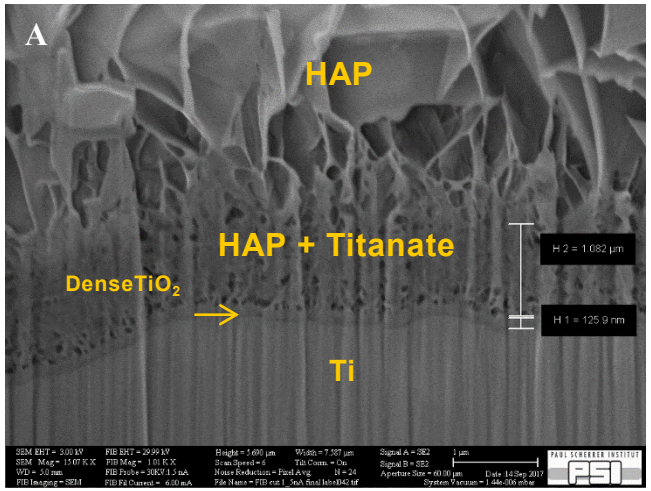


(a) Before treatment (b)After NaOH treatment

For instance, Ti surface can be converted to a porous layer of Sodium Hydrogen titanate ($Na_{(x)}H_{(2-x)}Ti_3O_7$) by soaking the metal in concentrated NaOH at 60-100 °C for some hours. The native TiO_2 layer on the surface chemically reacts and from the titanate layer.

The titanate layer is highly porous and bioactive (e.g. it promotes growth of natural bone once implanted)

Surface: from porous titanate to synthetic bone (HAP)



An additional surface modification, would be the selective deposition in-vitro of HAP (hydroxyapatite) by controlled heterogeneous nucleation and growth.

The porous ceramic layer (about 1 micron), is chemically joined with the metal and do not delaminate under mechanical stress (e.g. for dental screws).