PVD & PaCVD technology: the clean processes of future

Romagnoli Denis - Lavalle Paolo
STS Service and Tools
Why Coat?

Coating

Save money

Performance

Quality Guaranteed

Pollution
Tribological system

- Loss of functionality
  - Obsolescence (15%)
    - Chemical Wear (20%)
      - Abrasion
  - Degradation of surface (70%)
    - Mechanical Wear (50%)
      - Adhesion
  - Accident (15%)
    - Fatigue

More than 50% of phenomena are play on the first mm of surface
Surface treatment

- Modification of base material
  - Nitriding (N on surface)
  - Carbo-nitriding (C and N on surface)
  - Phosphating (P in surface)
  - Case Hardening (C on surface)
  - Oxidation (for Aluminium)
  - Shot peening (Compressive stress)

- Heterogeneous material
  - Galvanic process (Chrome, Nickel)
  - Thermal Spray (Mo, WC, Oxide)
  - CVD (Chemical Vapor Deposition)
  - PACVD
  - PVD (Physical Vapor Deposition)
Chromium plating application

Cr Market value in Europe:
5580 mln € / year

- Automotive (engine components and decorative)
- Mechanical (components, molds, food machine)
- Oleodinamics
- Fashion
- Furnishings

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18 - 21 September
Warsaw University of Technology - Poland
The Restriction of Hazardous Substances Directive (RoHS) is a directive restricting the use of certain substances (heavy metals).

Regulation n. 348/2013 for the Evaluation, Authorization and Restriction of Chemicals (REACH). » The Regulation stipulates that the 21st September 2017 (Today!!) is the date beyond which the chromium trioxide can no longer be used - within the borders of the European Union - unless it has a specific authorization.
Dangerousness of Cr(VI)

Acute and chronic oral toxicity is available for inhalation, dermatitis, cytotoxicity, genotoxicity and, finally, of cancerogenicity. Cr (VI) is a certain carcinogen (lung, nose) by inhalation. The problem of oral cancerogenicity is established too. It has been shown that, under appropriate conditions of temperature, humidity, pH and chemical composition of the matrix, the equilibrium: Cr (III) ⇔ Cr (VI) can move to the right.

D.Lgs 152/2006 Limits for waste water from indistrial discharges for irrigation: Cr (VI): 5 µg / Lt
We need “clean technology”

ISO 10993-2005 Medical

ISO 14001-2004 Enviromental

EN 1935/2004 Food Contact

PVD Coating
PVD Coating definition

PVD coatings (Physical Vapor Deposition) are based on the evaporation of a **Metal** (Titanium, Chromium, Aluminum, Niobium ...) that reacts in a controlled atmosphere with a **Non-Metal** (Nitrogen, Carbon or Oxygen) to form a Ceramic deposit with certain tribological characteristics (hardness, toughness, friction coefficient, corrosion resistance).

- **Binary Coating**: TiN, Ti$_2$N, CrN, ZrN, HfN,
- **Ternary Coating**: TiCN, AlTiN, TiNbN, AlCrN
- **Quaternary Coating**: TiAlCN, AlTiSiN
- **Bilayer Coating**: TiN+TiCN, TiN+MoS2
- **Multilayer and superlattice coating**: TiN-TiAlN, CrN-NbN

![Steel lattice](image)
PVD Application

- **Mechanics**: Tools (mills, drills, hobs, mould), components (textile and food machine, Automotive, Oleodinamics, etc.)
- **Medical**: Prostheses and instruments for Surgery and Orthodontics
- **Electronics**: CD, Solar cells.
- **Optics**: Glass for mobile phone and televisions.
- **Chemical**: Catalysis, valves.
- **Decorative**: Watches, glasses, jewelry, knife, taps, etc.
Evolution of coating

- TiAlN
- AlTiN
- AlCrN
- TiSiN and AlTiSiN
- MoS$_2$
- PLC
- DLC
- WCC
- MoN
- TiAIN
- AITiN
- CrN e TiN
- Hardness coating
- Autolubricant coating
- TiCN

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Arc PVD coating features

Titanium Nitride (TiN)

- Melting Point: 2.930-2.950 °C
- Hardness: 2.200-2.500 HV at 20°C, 200 HV at 1.000°C
- Thickness: 1-8 micron
- Young Modul : 350 GPa
- Friction Coefficient vs 100Cr6 : 0.65
- Thermal conductivity : 0.07 cal/(s·cm·°C)
- Adhesion Critical Load: 70-80 N
- Intrinsic Roughness: Ra: 0.20 micron
TiN features

PVD-HDP TECHNOLOGY

The Titanium Nitride better known as TiN, has been on the market for decades and still occupies a position of absolute importance in the panorama of PVD coatings.

TiN has always been a reference in the field of cutting tools, and its properties also arouse much interest in many other fields of application.

The recent development of HDP technology (High Density Plasma) by STS, has allowed to improve the TiN characteristics, creating a layer with a very smooth and compact surface, which can be deposited at low temperatures (150°C).

If you associate these new conditions to the fact that TiN complies with ISO 10993 (biocompatibility) and FDA (Food and Drugs Administration), one can easily imagine how this coating turns out to be a good solution in the areas of medical, food industry, automatic machines, racing and mechanical parts.

<table>
<thead>
<tr>
<th>Basic Composition</th>
<th>Coating Structure</th>
<th>Microhardness (HV 0.05)</th>
<th>Coefficient of Friction against 100 Cr 6</th>
<th>μm thickness (microns)</th>
<th>Deposition Temperature (°C)</th>
<th>Max Temperature of use (max °C)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium nitride</td>
<td>Monolayer</td>
<td>2.200</td>
<td>0.6</td>
<td>1 - 4</td>
<td>140 - 480</td>
<td>500</td>
<td>Yellow gold</td>
</tr>
</tbody>
</table>
PaCVD coating features

Diamond Like Carbon (DLC)

- Carbon Coating Based
- \( a-C:H \), \( \text{sp}^2 \) (grafite) e \( \text{sp}^3 \) (diamond)
- Hardness: 1500-3000 HV
- Friction Coefficient vs steel: 0,1 (vs DLC 0,05)
- Thickness: 0,5-3 micron
- \( T_{\text{max working}} \): 400°C
- \( T_{\text{of deposition}} \): 180-250°C
- Hydrophobic and chemically inert (40h in Fluoridric Acid)
- Electrical resistance: \( 10^8 \) Wcm (Insulant!!)
**DLC COATING**
(Diamond Like Carbon)

**PA-CVD TECHNOLOGY**

DLC is an innovative carbon-based coating with wide spectrum of application which allows you to deal with problems related to abrasion, to chemical attack and sliding.

The low deposition temperature, the hardness and the low coefficient of friction make it of extreme interest.

It is applied on finished parts while maintaining the state of the surface finishing.

The DLC is deposited by the PA-CVD (Plasma Assisted - Chemical Vapour Deposition) technology which allows to maintain low temperature of depositing and at the same time ensures an excellent adhesion.

**TIPS/SUGGESTIONS**

The high hardness and low friction coefficient arise from the simultaneous presence of sp² hybridized Carbon (Graphite) and sp³ (Diamond). It works very well for dry contacts.

**Benefits**

- High hardness (resistance to abrasion and wear)
- Low coefficient of friction (smoothness and anti-adherence)
- Excellent chemical inertia (resistance to corrosion and chemical attack by acids, bases and salts)
- Compactness (impermeable to gases, such as to Hydrogen)
- Electrical insulation
- Biocompatible

**SUBSTRATES**

- Steels, ferrous alloys in general
- Aluminium and its alloys
- Titanium and its alloys
- Copper and its alloys (bronze, Cu -Be)
- Tungsten Carbides

<table>
<thead>
<tr>
<th>Basic Composition</th>
<th>Deposition Technology</th>
<th>Microhardness (HV 0.09)</th>
<th>Coefficient of Friction against 100 Cr 6</th>
<th>pV Thickness (microns)</th>
<th>Deposition Temperature (°C)</th>
<th>Max Temperature of use (max - °C)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-Cr</td>
<td>PA-CVD</td>
<td>1.500 - 3.000</td>
<td>0.05 - 0.1</td>
<td>0.5 - 3</td>
<td>250</td>
<td>400</td>
<td>Black</td>
</tr>
</tbody>
</table>

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DLC Automotive Application
## Choice of PVD Coating

<table>
<thead>
<tr>
<th>Coating</th>
<th>Hardness</th>
<th>Toughness</th>
<th>Sliding</th>
<th>Corrosion resistance</th>
<th>Heat resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>xx</td>
<td>xxx</td>
<td>x</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>TiCN</td>
<td>xxx</td>
<td>x</td>
<td>x</td>
<td></td>
<td>xx</td>
</tr>
<tr>
<td>CrN</td>
<td>x</td>
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<tr>
<td>AlTiN</td>
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<td>x</td>
<td>x</td>
<td>xxx</td>
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<tr>
<td>TiAIN</td>
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<td>x</td>
<td>xxx</td>
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<tr>
<td>PLC</td>
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<td>x</td>
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<tr>
<td>WC/C</td>
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<td>x</td>
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<tr>
<td>DLC</td>
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<td></td>
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<td>xxx</td>
<td>x</td>
</tr>
<tr>
<td>MoS2</td>
<td></td>
<td></td>
<td>xxx</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Micrographs

Columnar structure of Arc PVD Coating

Amorphous structure of PaCVD Coating (DLC)
Materiale di base
•Fe-C Alloy
•Al and its Alloy (Highly reactive alloy, low coating T)
•Cu and its Alloy (Highly reactive alloy, low coating T)
•Ti and its Alloy
•WC-Co Alloy

Base Material

•Magnesium
•Carbon Fiber (porosity and low coating T)
•Plastic (PEEK, high melting point)
Wear Mechanism

- **Abrasion**: removal of base material caused by hard particles coming from an antagonist or from a 3rd body
  - Hardness

- **Adhesion**: cold adhesion of antagonist particles
  - Friction Coefficient

- **Fatigue**: crack formation on the surface due to the repetition of mechanical or thermal cycles
  - Structure

- **Corrosion**: oxidation and acid-base aggression
  - Chemical Composition
Case History 1: Friction Coefficient

COF Cr vs 100Cr6 : 0.18

COF DLC vs 100Cr6 : 0.10
Case History 2: Abrasion

Component: coffee grinder
Material: C40 (Not replaceable for workability and pricing)
Problem: Abrasion Wear
Coating: Galvanic Chrome
New Coating: TiN
Result: Increase 1.5 times the component life

Hardness Cr: 1000HV
Hardness TiN: 2200HV
Case History 3: Corrosion

**Component:** Cover for Automotive

**Material:** Aluminium 6000 (NSS: 90 Hrs)

**Problem:** Corrosion (Target: 150 Hrs)

**Coating:** Galvanic Chrome or DLC

**Results:** 190 Hrs

NSS Cr: 150-170 Hrs

Salt Spray Test in accordance with ASTM B117-07
NaCl 5%, pH 6.5-7.2, T= 35°±2°, 1-2 ml/h
Case History 4: Abrasion-Adhesion

Hydraulic actuator
Wear means Fluid leakage and loss of efficiency

Cilinder
Stationary element in steel + Galvanic Chrome
Camshaft
Camshaft
Rotary element in nitriding steel + HVOF

Nitriding + DLC
DLC

Tight contact

The solution has allowed increased contact life without loss of efficiency by at least **2,5 times** the solution in use.
Case History 5: Abrasion

Component: Engine Valve
Material: Bimetallic
Problem: Abrasion Wear
Coating: Galvanic Chrome
New Coating: CrN
Result on scuffing test: CrN = Galvanic Chrome but more wear on counter part

Hardness Cr: 1000HV
Hardness CrN: 1800HV
Case History 6: Abrasion

Component: Pasta trap
Material: Bronze
Problem: Abrasion Wear
Coating: Galvanic Chrome
New Coating: TiN
Result: WIP

Hardness Cr : 1000HV
Hardness TiN : 2200HV
Case History 7: Abrasion-Corrosion

Component: Knee prosthesis
Material: CrCoMo (with Ni)
Problem: Ni leaching, Corrosion and Abrasion from HDPE
Coating: TiNbN
Result: No Ni Leaching and reducing wear can be implanted at a younger age
"Material is God's work, the surface is the work of the Devil"