Vacuum Cathodic Arc Deposition: Fundamentals and Applications

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Introduction.
Energy characteristics of CAD process.
Geometric effects.
Effects of the magnetic field.
Pressure effects.
Temperature effects.
Effects of ion bombardment.
Macroparticles.
Summary and conclusions.
Introduction

Grupo de Capas Finas e Ingeniería de Superficies (CFIS-UB)  
Thin Films and Surface Engineering Group

- Member of the Department of Applied Physics and Optics UB.
- Over 35 years of experience in technology and characterization of thin film coatings
- Techniques: CVD: PACVD, HFCVD, PVD: DC & RF Magnetron Sputtering, Laser, Arco Cathodic
- Some Hard Materials: TiN, TiAlN, DLC, BN, B₄C, WC, CrN, Cr₃C₂, ....

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Introducción

- This course: no systematic or comprehensive.
- The basics of vacuum technology are assumed to be known.
- Objectives: Overview of relations between:
  - technological parameters
  - Physical properties of the plasma
  - Functional properties of coatings
Much more than carbon arc lamp ...

... and arc welding

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**Vacuum arc process**

- **Vacuum arcs** (cathodic arcs): high current self-sustained discharges between cold electrodes.
- Cathode: formation of "spots":
  - "micro-explosions," microscopic craters
  - lifetime: $10^{-8}$-$10^{-6}$ s.
  - Spot size: 1-10 microns.
  - Intensity:
    - minimum (40 A) (to keep the process on)
    - Maximum: limited by refrigeration (100 A typical)
      Current density: $10^6$-$10^8$ A/cm².
    - Voltage: 10-30 V (after plasma bridges anode-cathode)
- Plasma originates from “cathode spots” —
  - electrons and ions emitted from cathode surface
    - highly ionized, multiple charge states.
    - supersonic ions.

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Two types of spots:

the type I has higher mobility, life times shorter, and smaller sizes than type II. Typically the spots are occurring type I. Type II the spots are generated when cathodes are used with special geometries, or cathodes at high temperatures.
energetic Characteristics

Energy
- Heat (cathode) 34%
- electron emission 21%
- Evaporation 3%
- Vapor Ionization 7%
- Energy: ions 23%
- electrons 10%

Schematic of the regions found in a spot: (Boxman, 2007)
1. Cathode (black arrows indicate the current flow),
2. Molten metal layer (thickness 0.2 - 0.5 μm),
3. space charge layer (thickness 0.005 - 0.01 μm)
4. ionization and thermalization layer (thickness 0.1 - 0.5 μm)
5. dense spot Plasma
6. plasma expansion region (white arrows indicate plasma flow
7. ejection of molten droplets.

Effects of pressure. Thermalization

<table>
<thead>
<tr>
<th>Material</th>
<th>Charge (e)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.47</td>
<td>106</td>
</tr>
<tr>
<td>Cr</td>
<td>2.02</td>
<td>76</td>
</tr>
<tr>
<td>Ti</td>
<td>1.79</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>1.58</td>
<td>62</td>
</tr>
<tr>
<td>Ta</td>
<td>2.72</td>
<td>178</td>
</tr>
<tr>
<td>Mo</td>
<td>1.99</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>2.89</td>
<td>152</td>
</tr>
</tbody>
</table>

1 eV ⇔ 12000 °C
Geometric effects

- Target: Ti (180 mm).
- Uniform thickness for L > 300 mm.
- High roughness for L < 500 mm.

Fig. 4. Dependence of the Ti deposition rate \( P_d \) on the distance to the cathode \( z \) and transversal distance \( R \) from the symmetry axis of the substrate, \( T = 150^\circ A \).

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Effects of B

- On the target: a key role: driving spot.
- On the plasma volume: Interaction with electrons: helicoidal trajectory around field \( B \) (ions practically not directly affected).
  - higher ionization efficiency (+ dissociation).
  - plasma Confinement.
  - higher ion bombardment.

Table 1

<table>
<thead>
<tr>
<th>Magnetic field (Gs m⁻¹)</th>
<th>Element</th>
<th>Plasma species</th>
<th>Average discharge per m² (W)</th>
<th>Ionization fraction (%)</th>
<th>Plasma density ((10^{18} \text{m}^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrated arc (3.5)</td>
<td>Ti⁺</td>
<td>2.0 0.2 0.0</td>
<td>1.4</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>Balanced arc (56%)</td>
<td>N⁺</td>
<td>3.4 0.4 0.1</td>
<td>2.0</td>
<td>80</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Effects of B

- Target Ti. Permanent samarium-cobalt magnets surrounding the substrate holder.
- Magnetic confinement improves thickness uniformity.

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Enhanced Arc Deposition

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Effects of pressure. Composition.

![Graph showing the composition of CrN and Cr2N](image)

**Target Cr; P(N2)= 0-0.86 Pa; V_s=-100V, I(arc)=120 A, T_s=380ºC**

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Effects of pressure: Color.

![Graph showing color variations](image)

**TiN UB: Blanco Ti; P(N2) = 5x10^{-4} - 5x10^{-2} mbar; V_s = -300V, I(arc) = 60 A, T_s = 400 ºC**

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Effects of pressure: reactive processes

- Reactive processes: metallic target + reactive gas.
- Target poisoning (nitruration ...) ⇒ Pressure/Flux not linear (hysteresis).

- **Region A-B**: metallic target. Gas is trapped by evaporated material. Increasing flow pressure does not cause target contamination.

- **Region B-C**: when the composition of the compound in the coating (B) is reached, two feedback phenomena occur:
  - increasing the flow, the excess gas causes increasing pressure.
  - Target is poisoned ⇒ evaporation rate decreases ⇒ pressure increases.

- **Region C-D**: reducing pressure, target keeps poisoned until reaching a point D (lower flux than B!). (evaporation rate increases reducing pressure).

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Effects of Pressure: Density and size of macropart

Title: Reducing the macroparticle content of cathodic arc evaporated TiN coatings
Author(s): Harris, SG; Doyle, ED; Wong, YC, et al.
Source: SURFACE & COATINGS TECHNOLOGY Volume: 183 Issue: 2-3 Pages: 283-294 Published: MAY 24 2004

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Effects of Pressure: Density and size of macropart

<table>
<thead>
<tr>
<th>Chamber pressure (Pa)</th>
<th>Coating thickness (mm)</th>
<th>Adhesion strength (N/cm²)</th>
<th>Morphology</th>
<th>Number of incorporated particles per unit area (10⁶/cm²)</th>
<th>Information</th>
<th>Yield (%)</th>
<th>Yield % deviation</th>
<th>Yields Applied</th>
<th>Yields Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIN-I</td>
<td>0.1</td>
<td>1.3</td>
<td>1</td>
<td>136</td>
<td>2.8</td>
<td>10</td>
<td>33</td>
<td>24</td>
<td>47</td>
</tr>
<tr>
<td>DIN-II</td>
<td>0.5</td>
<td>1.5</td>
<td>1.0</td>
<td>134</td>
<td>2.9</td>
<td>10</td>
<td>55</td>
<td>22</td>
<td>46</td>
</tr>
<tr>
<td>DIN-III</td>
<td>0.5</td>
<td>1.6</td>
<td>1.0</td>
<td>130</td>
<td>2.1</td>
<td>13</td>
<td>38</td>
<td>29</td>
<td>52</td>
</tr>
<tr>
<td>DIN-IV</td>
<td>1.2</td>
<td>1.8</td>
<td>1.0</td>
<td>104</td>
<td>1.2</td>
<td>8</td>
<td>46</td>
<td>27</td>
<td>57</td>
</tr>
</tbody>
</table>

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Effects of Temperature

Importance of controlling Temperature:
- If too high: reduces substrate hardness, deform and even melt it.
- If too low: reduces adhesion, increases stress, decreases the crystallinity.
  - Difcult to measure when coating small objects and/or complex shapes.
  - Methods: thermocouple, radiative techniques.
  - Four energy sources:
    - Energy delivered during the cleaning process with ions (1000 V).
    - Energy delivered during the deposition process (100 - 200 V).
    - Energy delivered for whatever radiative source in the chamber.
    - Energy lost by radiation.
  - In principle it is advisable a combination of them.
Effects of Temperature. Structure

- $\text{Al}_2\text{O}_3$ coatings. Filtered vacuum arc device.
- Base pressure $3 \times 10^{-5}$ mbar. (100 A, 30 V), Al (99.999% Al) cathode 90 mm diameter. Oxygen: 30 sccm.
- Substrate Temperature: 200 to 800 °C (measured with pyrometer).

Surface and Coatings Technology, Volumes 174-175, September-October 2003, Pages 606-610

- Tetrahedral amorphous carbon. Transition graphite-like to diamond-like at T: 200-300 °C (Raman). Effects on stress, roughness and density.

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Ion bombardment: effects

Ion bombardment in CAE:
- Intrinsic: depending on the material and pressure.
- Controlled:
  - focusing plasma.
  - Substrate bias.

Effects of ion bombardment:
- Heating the substrate.
- Densification of the coating.
- Crystallographic orientation.
- Stress control.
- Increased adherence

Ion Bombardment: effects on stress

- high compressive stress:
  - hardness increases: 😊
  - May cause delaminating: 😞
Bombardeo iónico: efectos en Ti

- Catodo Ti (99.9%), 60 mm; I = 95 A,
- V_s = 0 - 250°C; T_s = 200°C; grosor 200 nm (10 μm/h)

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ión Bombardment : effects on Roughness

- Catodo Ti (99.9%), 60 mm; I = 95 A,
- V_s = 0 - 250°C; T_s = 200°C; grosor 200 nm (10 μm/h)

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Macroparticles

- Size (0.1-10 μm) emitted from the spot.
- Preferably emitted at low angles to the cathode surface.
- Depends on the cathode material. The lower the melting point and the higher the temperature, the greater size.
- For substrate temperatures <300-400 °C, causing non-adherence, presence of defects (pinholes), surface roughness, and poor corrosion resistance and wear.
- In TiN particle size is smaller for high N₂ pressure (nitridation of the cathode and increasing its melting point)
Macroparticles: effects

- "shadowing" can cause a crater in the coating.
- Weekly linked and coated with hard material. Detach easily increasing wear.
- The crater can act as corrosion center.
- Another source of macroparticles: peeling of the coating from the walls of the chamber (cold: high stress accumulation and thickness). Origin of arches. Convenience of good maintenance.

Fig. 1. AFM low magnification micrograph of a vacuum arc deposited Ti coating on the silicate glass substrate ($L = 80 \text{ mm}, l = 160 A, t = 240 \text{ s}$), showing the step between the masked and coated part. Small droplets and the smooth film formed from the ionic flux can be seen.


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Macroparticles: Methods to reduce particle size and density

- heating the substrate by radiation.
- Magnetic separation (filter)
- Electron bombardment in high density plasmas (Enhanced CAD).
- Low arc currents (70-80 A).
- Magnetic deplexión arc.

Magnetic deplexión

The rotation of the coils produces a varying magnetic field $B$ in the cathode and prevents guide the location arc thus reducing the formation of particulates.
Macroparticles: Methods to reduce

TAKAGAWA AND TANOUÉ: REVIEW OF CATHODIC ARC DEPOSITION
IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 35, NO. 4, AUGUST 2007

Shielded arc
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UB linear magnetic shielded filter

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Effectiveness of UB linear filter

Not filtered
CrCo8 450V (37 mm)
$R_a = 122.49$ nm

Filtered
CrCo4 50V (5 mm)
$R_a = 7.18$ nm

Macroparticles: Methods to reduce

Macroparticle Removal by Magnetic Filtering

“Classic” 90° Filter Duct

PtAu films 50 nm thick on silicon wafer, prepared by vacuum arc technology (down) and filtered arc technology (up). [O. Zimmer, Surface & Coatings Technology 200 (2005) 440 – 443]

Venecian blind filter
Macroparticles: effects on lifetime of cutting tools

Figure 17: Indentation hardness versus substrate grain size for TiN films deposited by ionized (■) and filtered (△) arc evaporation.

Figure 18: Vickers hardness versus substrate grain size for TiN films deposited by ionized (■) and filtered (△) arc evaporation.

Industrial Equipment

Today’s Typical Industrial Arc Coating

- Example: TiN or TiAlN on tools; reactive deposition at elevated temperature, unfiltered
- Market value added: about $1B/year

Pictures: Cobédeo, Japan
Some applications

Figure 3: Examples of AlTiN coated cutting tools (HSS and cemented carbide).

Figure 9: Examples for decorative coatings with different colours based on AlTiN.

- TiCN
- ZrCN
- ZrN

They successfully overcame friction tests ironing!
Positive report from the marketing department!
Summary and Conclusions

- The basic mechanisms of the vacuum arc process have been introduced.
- A number of examples have been presented in order to illustrate the importance of the knowledge of the physical mechanisms involved in the CAD process, and the control of them through the different technological parameters, in order to obtain coatings with good functional properties.

Thanks for your attention!