Vacuum Cathodic Arc Deposition: Fundamentals and Applications

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Introduction

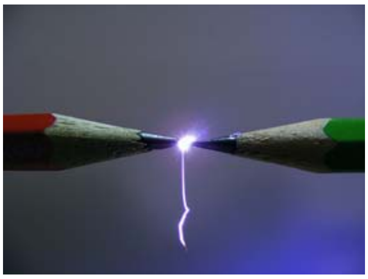
Grupo de Capas Finas e Ingeniería de Superficies (CFIS-UB)
Thin Films and Surface Engineering Group

- 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, B_4C, WC, CrN, Cr_3C_2, ...

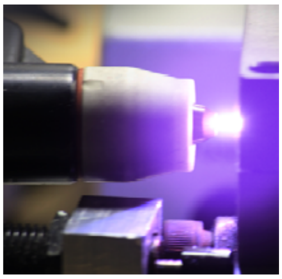
Introducción

- 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 …

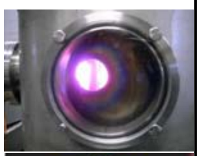


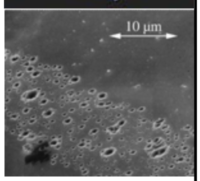
…. and arc welding

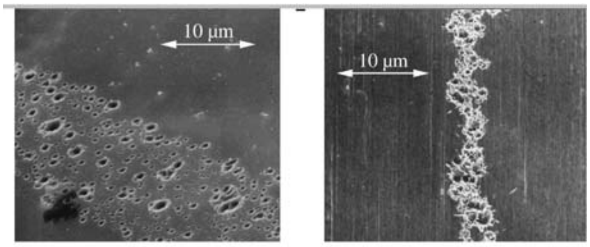


Vacuum arc process

- **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/cm^2.
  - 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.







a) Spot tipo I b) Spot tipo II

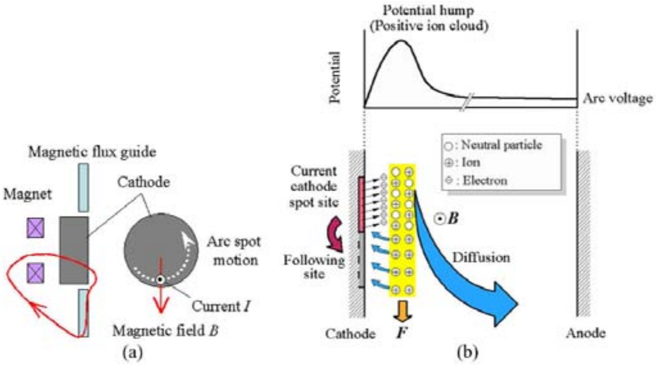
Figura 2.2. Cráteres formados por spots a) Tipo I y b) Tipo II (Anders, 2005).

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.

Spot Movement

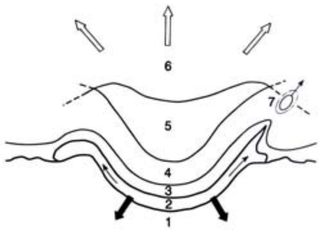
TAKIKAWA AND TANOUE: REVIEW OF CATHODIC ARC DEPOSITION
IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 35, NO. 4, AUGUST 2007



Steered Arc: B with paralell component to the cathode surface.

Avoids fixed spot and gets a uniform cathode wear

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

Energy and average charge of the ions emitted from the cathode

Material	Charge (e)	Energy (eV)
Fe	1.47	106
Cr	2.02	76
Ti	1.79	76
	1.58	62
Ta	2.72	178
Mo	1.99	156
	2.89	152

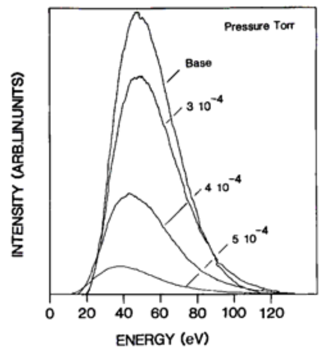


Figure 15. Energy distribution of the ion flux from a Ti cathodic arc as a function of N_2 gas pressure.[46]

1 eV ⇔ 12000 ºC

Geometric effects

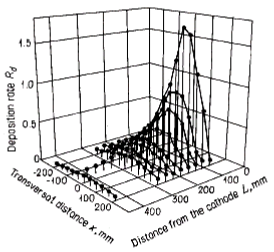


Fig. 4. Dependence of the Ti deposition rate R_d on the distance to the cathode L and transversal distance x from the symmetry axis of the substrate. I = 150 A.

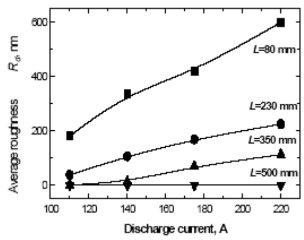


Fig. 5. Dependence of the average roughness R_a on I for different values of L.

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

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
Plasma characteristics comparison between conventional arc and enhanced arc used for TiN film deposition at 375 mm from cathode, 60 A arc current, and 2.6 Pa nitrogen pressure (after Ref. [10])

Magnetic field (Gauss)	Electron temperature (eV)	Plasma emission			Average charge per ion (e)	Titanium vapor ionization (%)	Plasma density ($\times 10^{16}$ M^{-3})
		Ti^+	N^{2+}	N^+			
Conventional arc (0)	2.5	1.0	0.2	0.0	1.6	80	0.8
Enhanced arc (1450)	25.0	3.4	9.4	1.1	2.08	99	1.7

B.F. Coll, D.M. Sanders/Surface and Coatings Technology 81 (1996) 42–51

Effects of B

Ian G. Brown
CATHODIC ARC DEPOSITION OF FILMS
Annu. Rev. Mater. Sci. 1998. 28:243–69

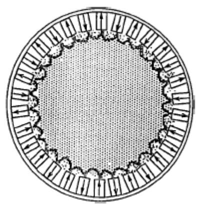


Figure 8 End view of a magnetic multicusp, with schematic plasma distribution.

Annu. Rev. Mater. Sci. 1998. 28:243–69

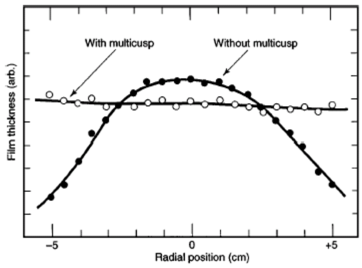


Figure 9 Radial profile of film deposition thickness with and without the use of a magnetic multicusp.

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

Effects of B

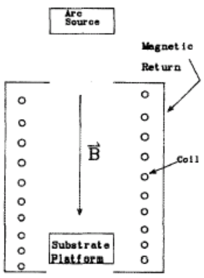


FIG. 1. Schematic diagram of magnetic enhancement apparatus.

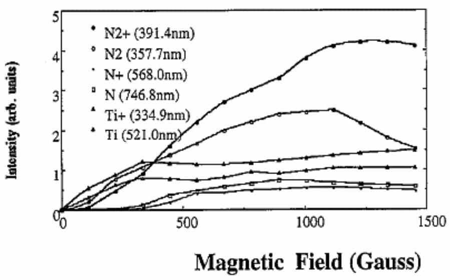


Fig. 5. Influence of the magnetic field strength on the emission intensity of reactive plasma during TiN enhanced arc deposition [10].

B.F. Coll, D.M. Sanders/Surface and Coatings Technology 81 (1996) 42–51

- Enhanced Arc Deposition

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Effects of pressure. Composition.

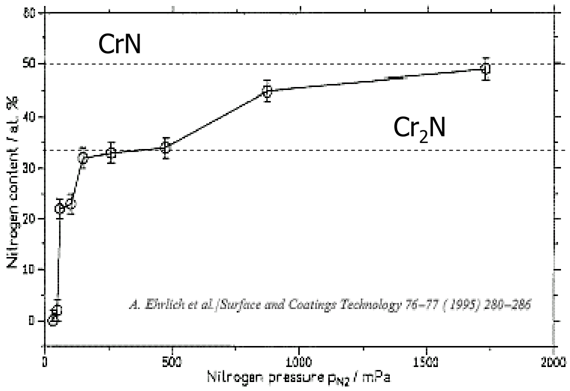

Fig. 1. Chemical composition vs. nitrogen pressure of Cr–N coatings obtained by XPS.

Target Cr; $P(N_2)$= 0-0.86 Pa; V_s=-100V, I(arc)=120 A, T_s=380ºC

Vacuum Deposition Technologies for films and coatings. Sevilla, 17-20 February 2014.

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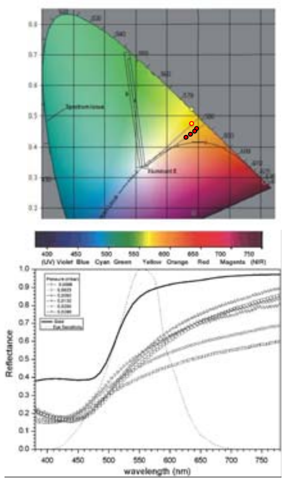
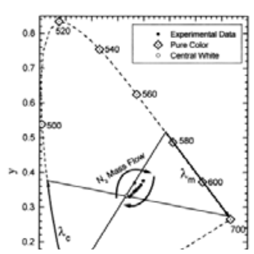
Effects of pressure: Color.

A. Lousa et al. / Vacuum 81 (2007) 1507–1510



P. Roquiny et al. / Surface and Coatings Technology 116–119 (1999) 278–283



TiNx coatings by DC reactive magneron sputtering. Magnetron cathode (90 mm diameter).. Deposition working pressure and plasma current density were maintained respectively at 0.30 Pa and 8 mA/cm2. The sample temperature did not exceed 100ºC onto grounded substrates placed at 55 mm from the sputtering target.

TiN UB: Blanco Ti; $P(N_2)$ = $5x10^{-4}$ - $5x10^{-2}$ mbar; V_s= -300V, I(arc)= 60 A, T_s= 400 ºC

Vacuum Deposition Technologies for films and coatings. Sevilla, 17-20 February 2014.

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.

B. Window/Surface and Coatings Technology 81 (1996) 92–98

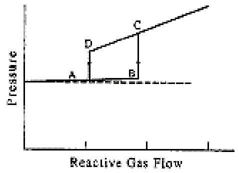
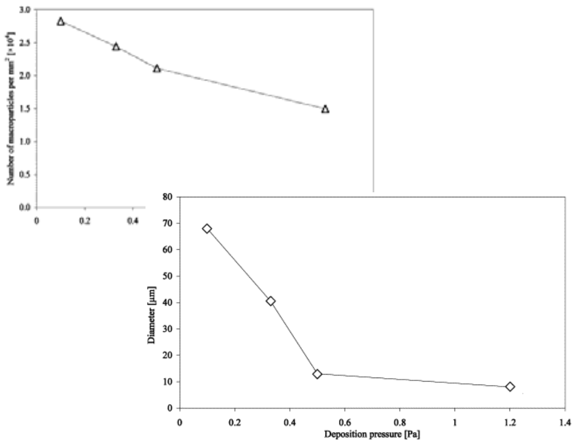


Fig. 2. A typical poisoning loop encountered in reactive sputtering at constant target power and variable reactive gas flow.

- **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).

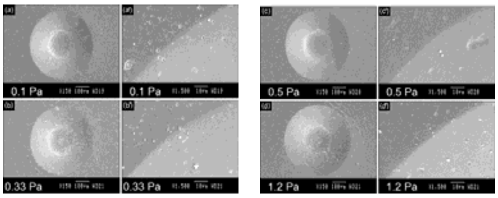
Effects of Pressure: Density and size of macropart

Base pressure	6×10^{-3} Pa
Temperature	250 °C
CAE metal ion etch	
Cathode sources	1 chromium cathode
Arc current	85 A
Time	12 min
Ar flow rate	100 cm^3/min
Substrate bias	−800 V
Followed by 30-s pump down	
TiN Coating	
Cathode sources	3 titanium cathodes
Arc current	85 A
Time	60 min
Valve opening	33%
Substrate bias	−200 V
Pressure for	
TiN-I	0,1 Pa
TiN-II	0,33 Pa
TiN-III	0,5 Pa
TiN-IV	1,2 Pa



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

Effects of Pressure: Density and size of macropart



	Chamber pressure (Pa)	Coating thickness (μm)	Adhesion ranking (VDI scale)	Roughness R_a (10^{-3} μm)	Number of macroparticles per unit area (10^4 mm^2)	Maximum macroparticle diameter (μm)	Tool life 50% outer corner wear: Holes drilled	Tool life 50% outer corner wear: Standard deviation	Tool life 'Screech': Holes drilled	Tool life 'Screech': Standard deviation
Uncoated	–	–	–	–	–	–	12	4	20	8
TiN-I	0.1	1.3	1	116	2.8	58	33	24	47	32
TiN-II	0.33	1.2	1	114	2.4	40	33	22	48	23
TiN-III	0.5	1.0	1	110	2.1	13	38	29	52	46
TiN-IV	1.2	1.0	1	104	1.5	8	46	17	57	21

Effects of Temperature

B. Window/Surface and Coatings Technology 81 (1996) 92–98

Importance of controlling Temperature:

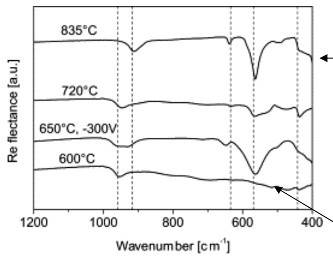
- If too high: reduces substrate hardness, deform and even melt it.
- If too low: reduces adhesion, increases stress, decreases the crystallinity.

- Dificult to measure when coating small objects and/or complex shapes.
- Methods : termocouple, 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. Estructure

- **Al_2O_3** coatings. Filtered vacuum arc device.
- Base pressure 3×10^{-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



α -Al_2O_3

amorphous

442, 569 and 635/cm: transversal modes of α -$\mathbf{Al_2O_3}$.

917 y 959/cm, longitudinal modes of γ-$\mathbf{Al_2O_3}$ y Al_2O_3 amorphous.

Effects of Temperature. Structure

- **tetrahedral amorphous carbon.**

  Transition graphite-like to diamond-like at T: 200-300 ºC (Raman). Effects on stress, roughness and density.

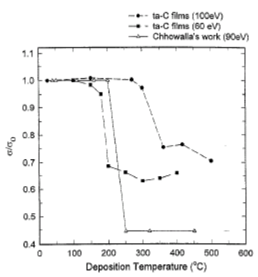


Fig. 1. Change of compressive stress as a function of deposition temperature.

Thin Solid Films 346 (1999) 155–161

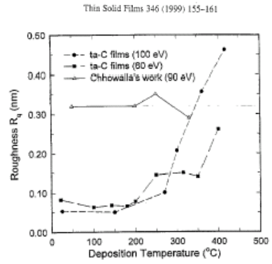


Fig. 2. The variation of surface roughness with deposition temperature.

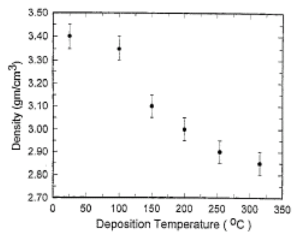


Fig. 12. The variation of density with deposition temperature for 60 eV ta-C films.

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Ion bombardment: effects

B. Window/Surface and Coatings Technology 81 (1996) 92–98

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

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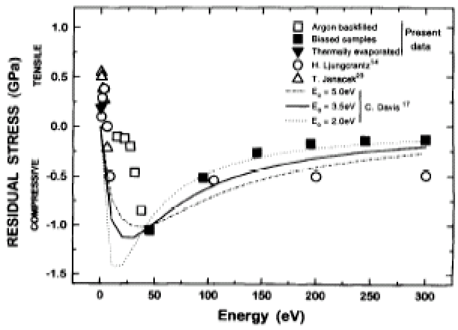
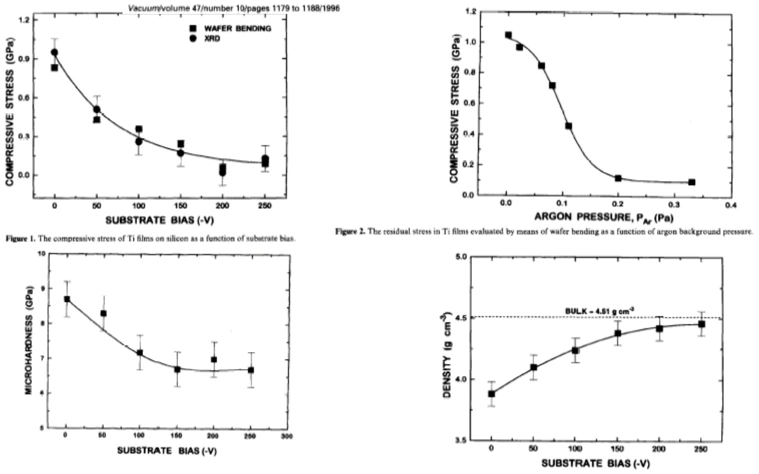
Ion Bombardment : effects on stress

Vacuum/volume 47/number 10/pages 1179 to 1188/1996



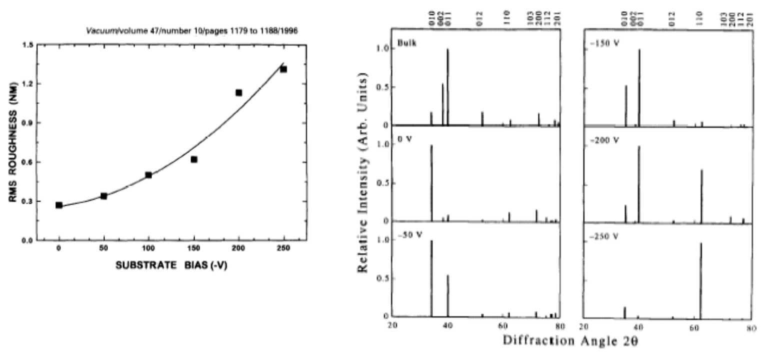
- high compressive stress:
  - hardness increases: ☺
  - May cause delaminating: ☹

Bombardeo iónico: efectos en Ti



- Cathode Ti (99.9%), 60 mm; I=95 A,
- V_s= 0 - 250ºC; T_s = 200ºC; thickness 200 nm (10 μm/h)

ión Bombardment : effects on Roughness



- Cathode Ti (99.9%), 60 mm; I=95 A,
- V_s= 0 -250ºC; T_s = 200ºC; thickness 200 nm (10 μm/h)

Macroparticles: effects

Vacuum, Volume 48, Issue 1, January 1997, Pages 7-12

Macroparticles

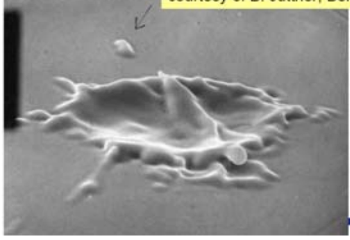
- Size (0.1-10 μm) emitted from the spot.
- Preferably emitted at low angles to the cathode surface.
- Depends on the cathode material. The lower the melting point and the higher the temperature, the greater size.
- For substrate temperatures <300-400 ° C, causing non-adherence, presence of defects (pinholes), surface roughness, and poor corrosion resistance and wear.
- In TiN particle size is smaller for high N_2 pressure (nitridation of the cathode and increasing its melting point)

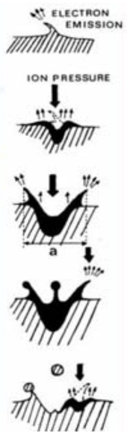
Macroparticles: formation

Macroparticle Formation

- Macroparticles are formed as part of the explosive plasma formation
- Typical: Material is ejected from the liquid pool between plasma and solid

Figure: 10 ns discharge on Mo courtesy of B. Jüttner, Berlin





Macroparticles: effects

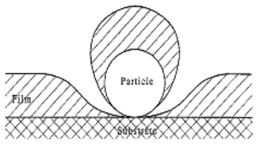


Fig. 4. The distribution of coating around a particle on a surface for a range of angles of incidence of depositing atoms.

B. Window/Surface and Coatings Technology 81 (1996) 92–98

- "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.

Macroparticles: effects

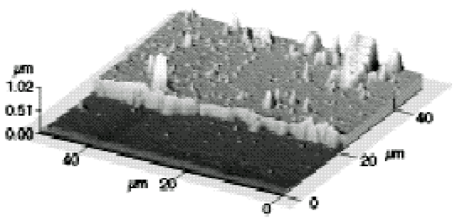


Fig. 1. AFM low magnification micrograph of a vacuum arc deposited Ti coating on the silicate glass substrate (L = 80 mm, I = 160 A, t = 240 s), showing the step between the masked and coated part. Small droplets and the smooth film formed from the ionic flux can be seen.

Mater.Phys.Mech. 5 (2002) 39-42

Macroparticles: Methods to reduce

Vacuum, Volume 48, Issue 1, January 1997, Pages 7-12

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.

Macroparticles: Methods to reduce

Vacuum, Volume 48, Issue 1, January 1997, Pages 7-12

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.

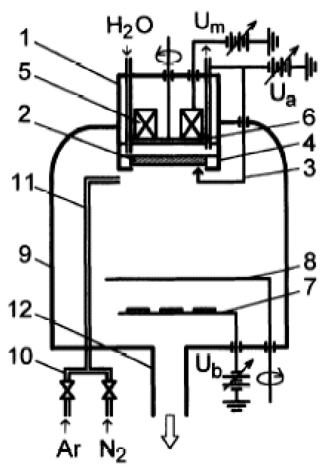


Figure 1. Schematic view of the experimental deposition unit: (1) steering arc unit; (2) water-cooled cathode; (3) trigger system; (4) cathode shield; (5) electro-magnets; (6) rotating platform; (7) substrate holder; (8) substrate shutter; (9) metal recipient; (10) working gas inlet; (11) gas pipe; (12) pump-out aperture.

Macroparticles: Methods to reduce

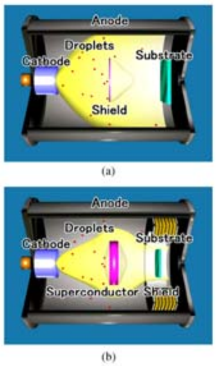
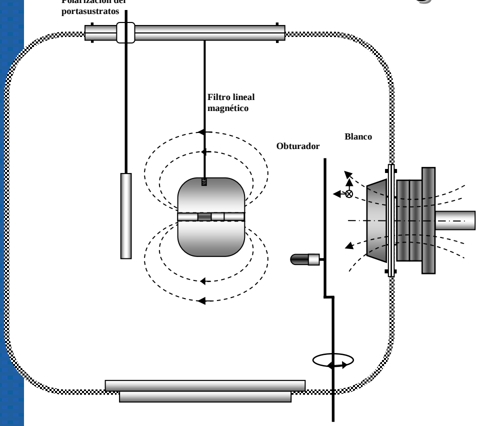


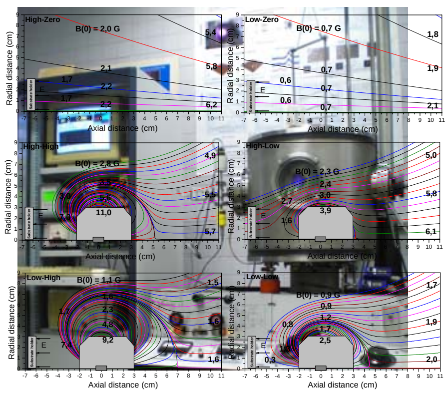
Fig. 7. Shielded arcs. (a) Simple shielded arc. (b) Superconductor shielded arc under magnetic field.

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

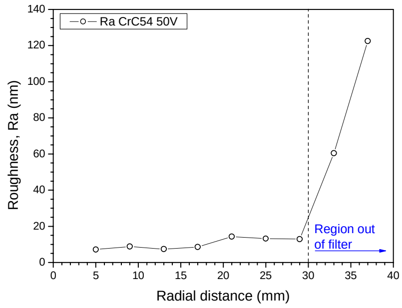
Shielded arc

UB linear magnetic shielded filter

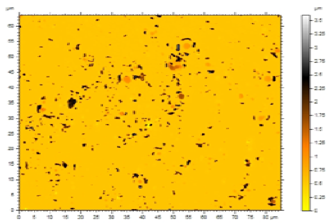




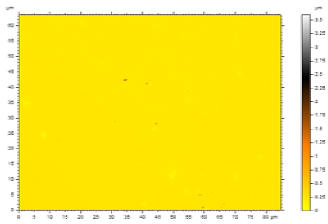
Effectiveness of UB linear filter



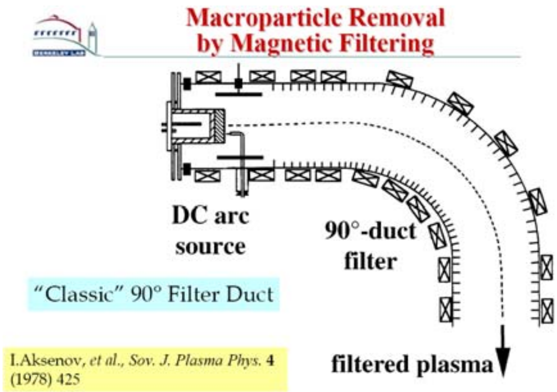
Not filtered
CrC08 450V (37 mm)
R_a = 122.49 nm



Filtered
CrC54 50V (5 mm)
R_a = 7.18 nm

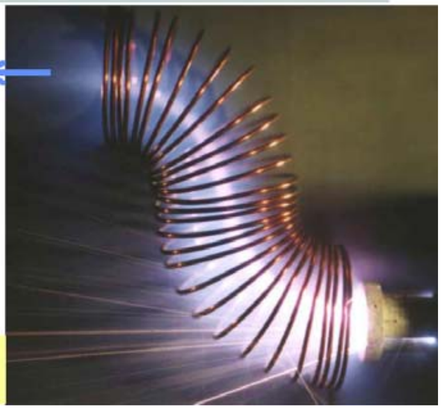


Macroparticles: Methods to reduce



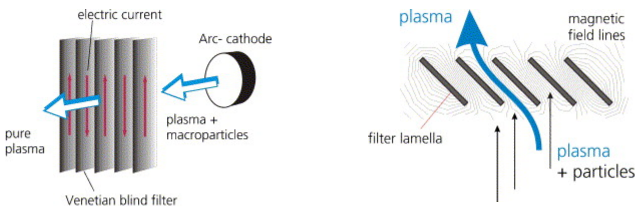
Macropartículas

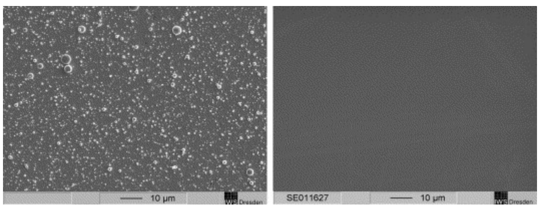
Open Filter for Cathodic Arcs



review on filters:
A. Anders, *Surf. Coat. Technol.* **120-121** (1999) 319

Macroparticles: Methods to reduce





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

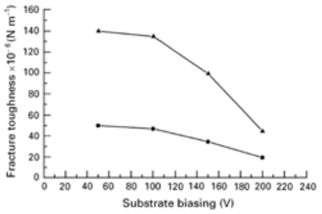


Figure 13 Fracture toughness versus substrate biasing of TiN films deposited by steered (●) and filtered (▲) arc-evaporation.

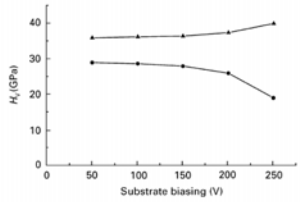


Figure 14 Vickers hardness versus substrate biasing of TiN films deposited by steered (●) and filtered (▲) arc-evaporation.

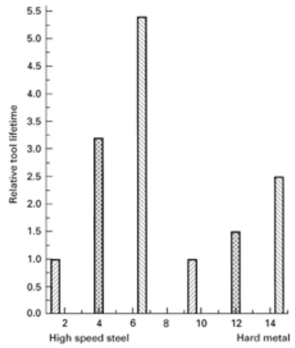
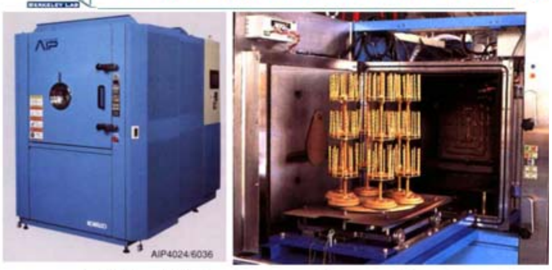


Figure 15 Lifetime of cutting tools with TiN coatings deposited by steered (▨) and filtered (▨) arc-evaporation until a flank wear of 0.8 mm is obtained for HSS tools and 0.5 mm for hard metal tools. The cutting conditions for HSS tools: turning carbon steel; cutting speed, 100 m min⁻¹; feed, 0.3 mm rev⁻¹; depth, 0.5 mm; and flank wear, 0.8 mm. Cutting conditions for hard metal tools: milling carbon steel; cutting speed, 200 m min⁻¹; feed, 0.2 mm rev⁻¹; depth, 1.0 mm; and flank wear, 0.5 mm. (□) substrate.

I. KONYASHIN, G. FOX-RABINOVICH, A. DODONOV, JOURNAL OF MATERIALS SCIENCE 32 (1997) 6029-6038

Industrial Equipment

Today's Typical Industrial Arc Coating



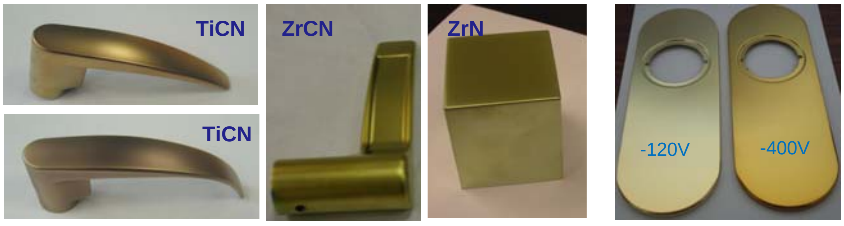
- ***example:*** TiN or TiAlN on tools; reactive deposition at elevated temperature, unfiltered
- market value added: about $1B/year

Pictures: Cobelco, 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 Al-TiN.



CrC coatings UB

- ✓ 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.

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Thanks for your attention!

Vacuum Deposition Technologies for films and coatings. Sevilla, 17-20 February 2014.