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TiTaAlN (+Y) nanocomposite thin films for mechanical applications in severe environement

P. Choquet, V.Khetan, R.Animat, N.Valle, D.Duday

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Belvaux - Luxembourg

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NATURE MATERIALS | VOL 13 | MARCH 2014 | www.nature.com/naturematerials

commentary

Materials science in Luxembourg

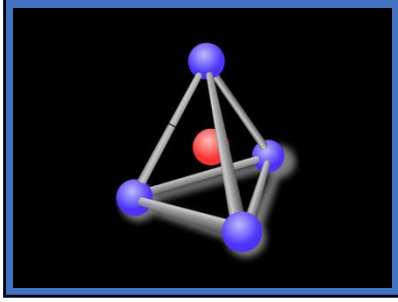
Jens Kreisel, Ludger Wirtz and Marc Schiltz

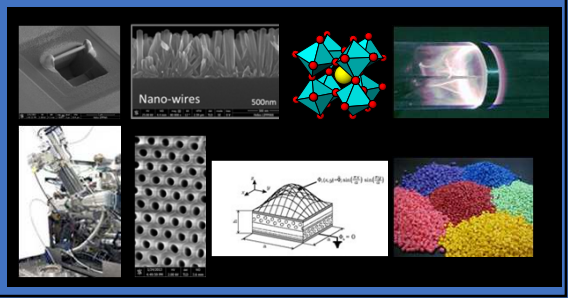
With its strategic location and firm commitment to investing in research, Luxembourg has ambitious plans to become a significant player in the international research arena.

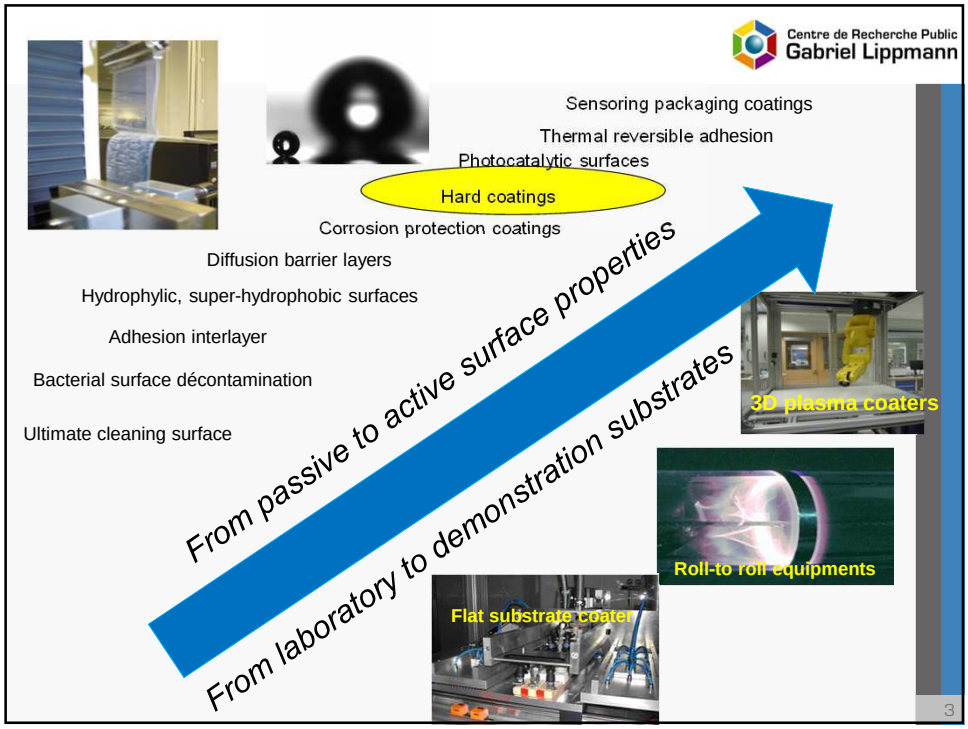
Materials Science

Luxembourg Institute of Science and Technology (LIST)

A Key-Enabling Science and Technology - For excellence and impact



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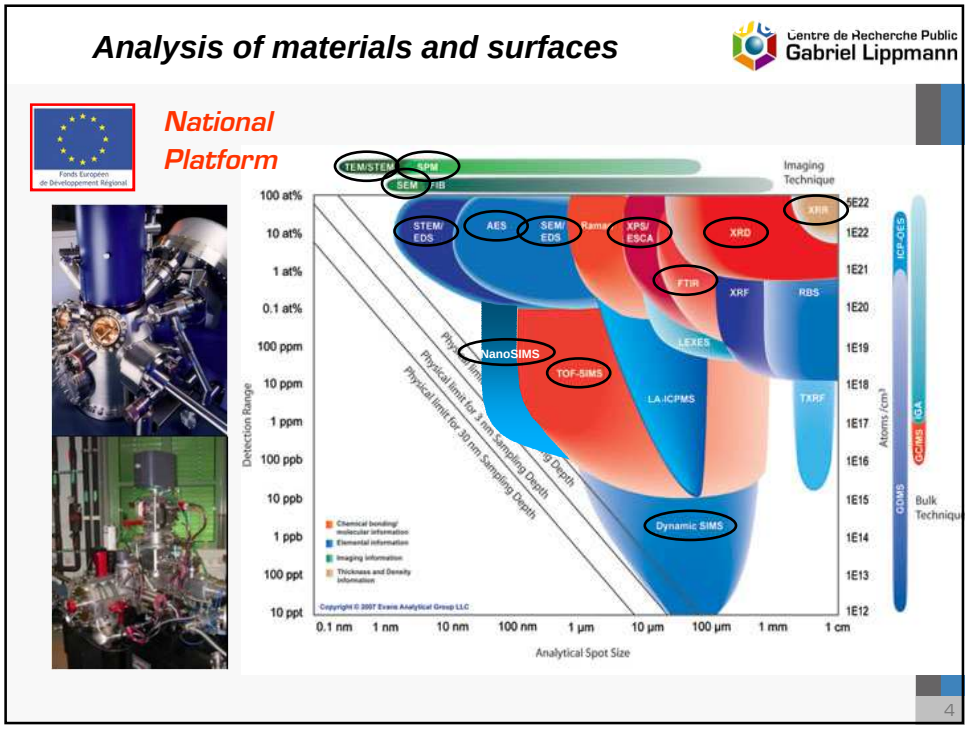
Sensoring packaging coatings
Thermal reversible adhesion
Photocatalytic surfaces
Hard coatings
Corrosion protection coatings
Diffusion barrier layers
Hydrophylic, super-hydrophobic surfaces
Adhesion interlayer
Bacterial surface décontamination
Ultimate cleaning surface
From passive to active surface properties
From laboratory to demonstration substrates
3D plasma coaters
Roll-to roll equipments
Flat substrate coater
3


Analysis of materials and surfaces
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National
Platform
Imaging
Technique
Detection Range
Analytical Spot Size
Atoms /cm³
Bulk
Technique
STEM/EDS
AES
SEM/EDS
XPS/ESCA
XRD
XRR
FTIR
XRF
RBS
LEXES
NanoSIMS
TOF-SIMS
LA-ICPMS
TXRF
Dynamic SIMS
ICP-OES
GDMS
IGA
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Summary

- ❑ *Interest of hard and protective nanocomposite coatings*
- ❑ *Deposition conditions of the coatings*
- ❑ *Oxydation and wear resistance at high temperature*
- ❑ *Conclusions and perspectives*

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Interest of hard and protective nanocomposite coatings

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❖ **Potential applications of these coatings:**
- ❑ Dry machining at very high speed
- ❑ Energy, Aerospace, … activity sectors

http://www.sears.com

❖ **Requested properties**
- ❑ High hardness and wear resistance
- ❑ High thermal stability
- ❑ High oxidation reisistance

http://shop2x52.blogspot.com

❖ **Benchmak situation**

Film	Hardness	Thermal stability	Oxidation resistance
TiN	≈2000HV [1]	Stable (T^m=2930°C)	T≲550°C [1]
TiAlN	≈3200 [1]-3300HV [2] *after deposition* ≈3600HV [1] *after thermal treatment*	Phase decomposition between würtzite and cubic à T>950°C [1]	T≲700-950°C [1] *(depending of chemical compo.)*

❖ **Interest of adding tantale to TiAlN**
- ❑ Higher oxidation resistance [3] (partial substitution of Ti^{4+} by Ta^{5+} into TiO_2 oxide phase)
- ❑ Improvement of the thermal stability until 1100°C [4]

❖ **Interest of adding yttrium to TiAlTaN**
- ❑ Higher oxide scale resistance during thermal cycle

[1] Moser, *Materials* (2010), 3, p 1573-1592 [2] S. PalDey, *Mat. Sci. and Eng.*, A342 (2003) [3] M. Pfeiler, *J.Vac. Sci. & Tech A*, 27 (2009)
[4] R. Rachbauer, *Surf. and Coat. Tech.*, 211 (2012)

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Deposition of (Ti,Al)N coatings by PVD doped with Si or Ta to obtain NANOCOMPOSITE structures

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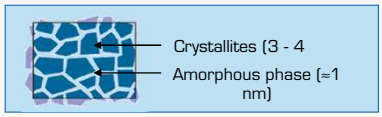
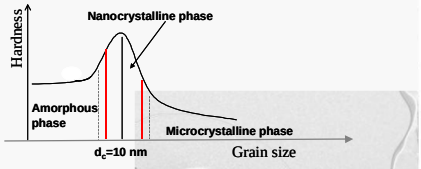
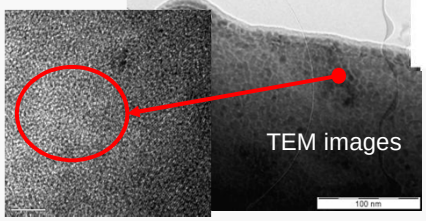
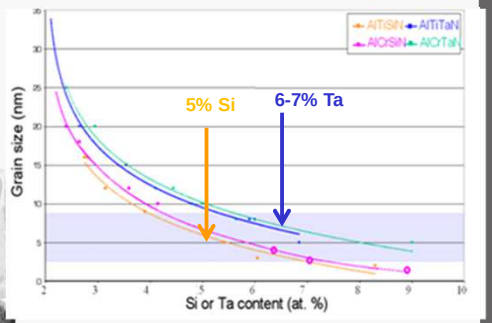






❑ *Interest of adding tantale to TiAlN*



[1] V. Hody, M. Martinez Celis, P. Choquet, D. Duday, C. Michotte, M. Penoy: "**AlTiTaN, AlCrTaN, AlCrSiN and AlTiSiN Hard and Oxidation-Protective Coatings: Effect of Bias voltage and composition on the microstructure, oxidation resistance and the hardness**", First European conference on NanoFilms, **March** (2010) Liege, Belgium.

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Deposition of (Ti,Al)N coatings by PVD doped with Y to improve the high oxidation resistance

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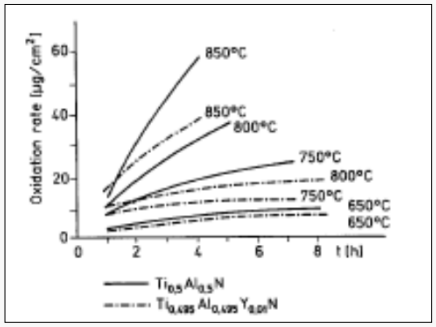
❑ *Interest of adding yttrium to TiAlN*



Münz, Werkstoffe und Korrosion, 1990

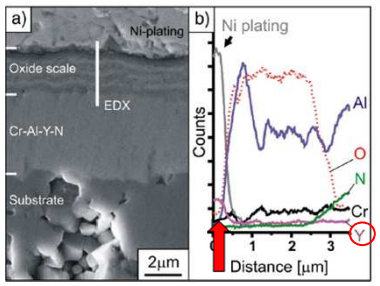


Fig. 10. SEM-cross section morphology of a $Cr_{0.45}Al_{0.53}Y_{0.02}N$ film after oxidation at 1060 °C for 50 h, b) SEM-EDX line scan profile.

Rovere, Surf. Coat. Techn., 2008

❑ Decrease of the oxidation kinetic with Y:
- ✓ Y Segregation at the grain boundaries
- ✓ Limitation of the cationic diffusion to the external surface
- ✓ Limitation of the anionic diffusion to the internal interface
- ✓ Improve the oxide scale adhesion

❑ Authors reported the possible diffusion of yttrium until the external surface

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Summary

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- *Conclusions and perspectives*

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TiAlTaN (+Y) deposition conditions

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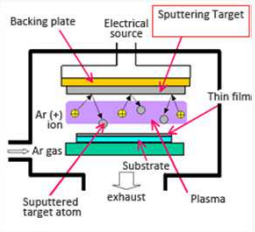
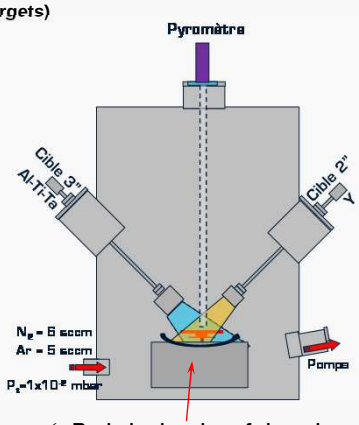
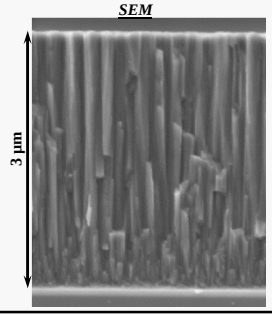
- Réactive Magnetron Sputtering by DC (or HIPIMS+MF)



- Synthesis of the AlTiN (+Ta, Y) by codeposition (2 *targets*)



- Compact and dense coatings with a fibrous structure



- ✓ Resistive heating of the substrate >450°C
- ✓ OES control of the reactive mode
- ✓ In-situ stress measurements by MOS

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TiAlTaN (+Y) structure and chemical compositions

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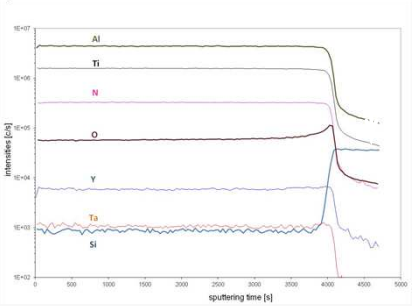
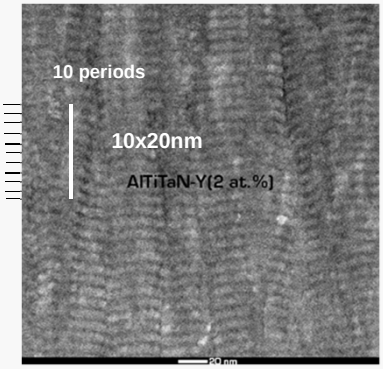
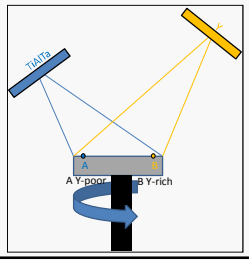
t the scale of SIMS profil, homogeneous
patings

on:







- ❑ **At the scale of TEM images, multilayer structure**

- ✓ ***The multilayer structure is the result of the substrate rotation during the deposition process***

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X-ray diffraction pattern of TiAlTaN-Y coatings with different Y contents

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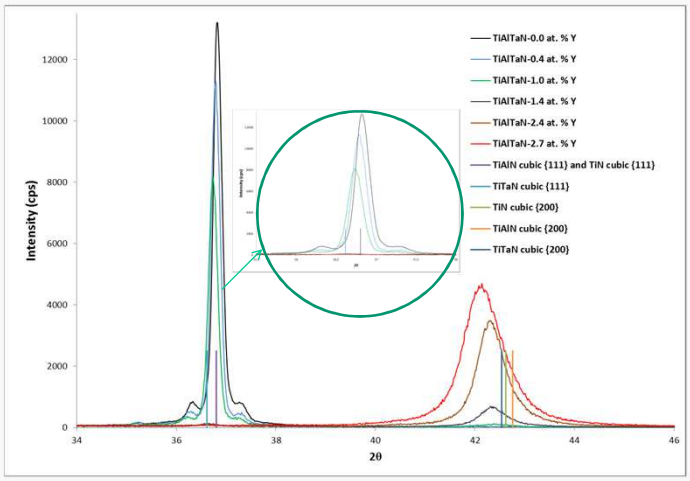

- ✓ **Diffraction measurements show only the presence of crystallites with a single-phase cubic structure as TiN and peak shifted because of Al and Ta substitution (TiAlN or TiTaN)**
- ✓ **Preferential crystallographic orientation switch from {111} cubic phase to {200} cubic phase with addition of Y > 1.4 at.%.**

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Ex-situ stress measurements and hardness of TiAlTaN-Y coatings with different Y contents at RT

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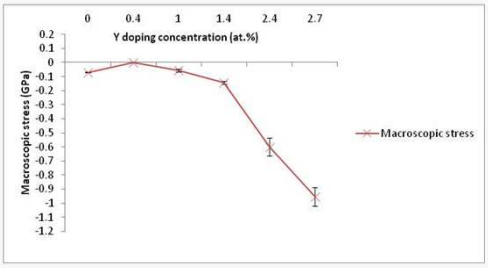
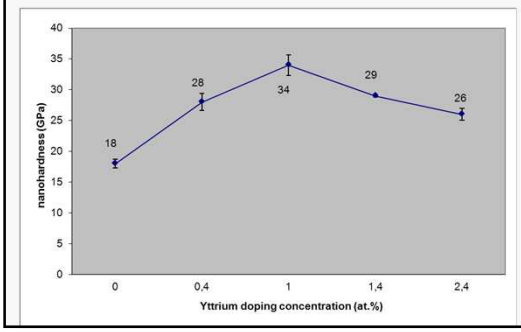


- ❑ **Macroscopic stress variation as a function of Y content**
  - ✓ ***An increase of the compressive stresses within the samples with 1.5 at.% Y to 3.0 at.%.***



- ❑ **Nanohardness evolution as a function of Y content can be linked to :**
  - ✓ **Compressive stress**
  - ✓ **Defect density**
  - ✓ **Multi-layered coatings**
  - ✓ **Crystallographic orientation <111> to <200>**

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Oxidation mechanisms of TiAlTaN (+Y) coatings

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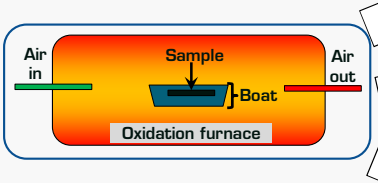
❑ **Why oxidation is important during wear ….**

✓ *During the process of dry machining at high speed, high temperature can be reached in the area where appears the contact between the piece and the tool (« flash point »)*

→ *consequently, the oxidation properties (kinetic and oxide scale mechanical behaviour) play an important rule*

❑ **Experimental study**



X diffraction (XRD)
- ❑ Crystalline phases (oxydes, nitrure)
- ❑ Crystallite size and texture

Masse spectroscopy (SIMS)
- ❑ Depth chemical profiles of nitride coating with the oxyde layers
- ❑ Isotopic measurements

Transmission electronic miscroscope (TEM)
- ❑ Local observation of the oxide layer
- ❑ Electronic diffraction
- ❑ HAADF mapping

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Oxidation mechanism, (Gracing incidence XRD)

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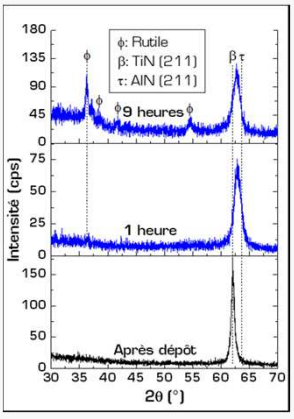
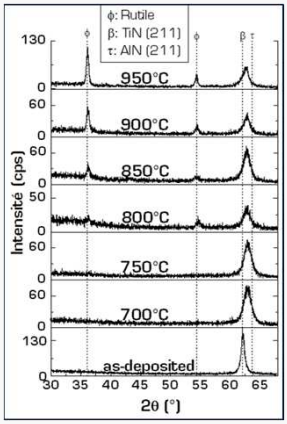
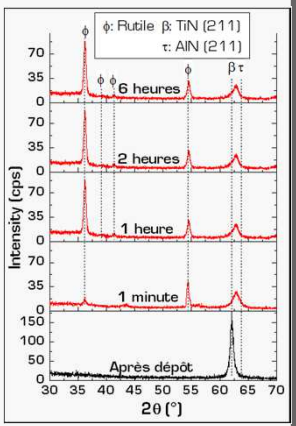
1 hour oxidation & different temperatures

Evolution with time at 750°C





Evolution with time at 900°C



- ❑ **700°C: amorphous layer formation**
- ❑ **750°C: low growth mechanism of the rutile oxide phase**
- ❑ **900°C: high oxidation growth mechanisme No yttrium influence**

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Oxidation mechanism, (SIMS analysis)

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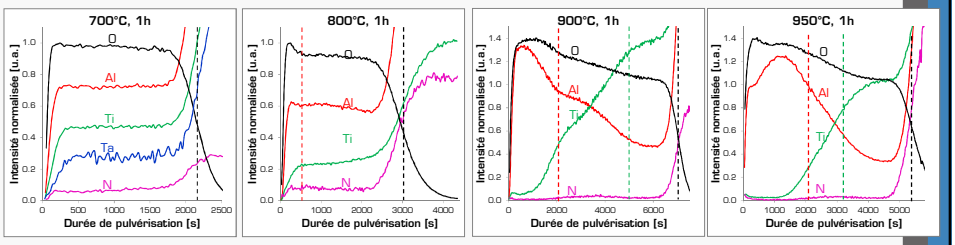
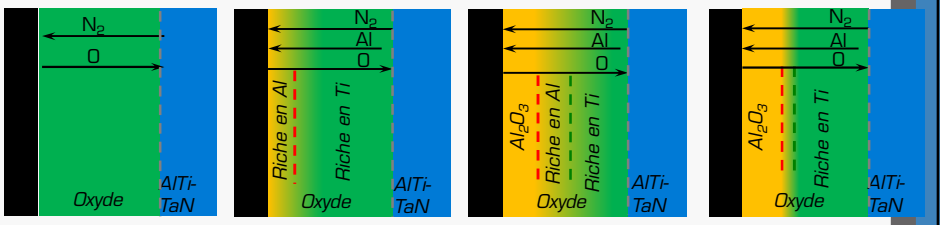
Profiles of oxidized samples after 1 hour oxidation at different temperatures



- 700°C, Uniforme mixed oxide
- 800°C, une couche superficielle riche en Al se forme
- A 950°C, deux oxydes uniformes assez nettement séparés, un oxyde d'Al a la surface et un oxyde de Ti/Ta a l'interface avec le nitrure



Profils SIMS et diagrammes explicitant les mécanismes d'oxydation à 700°C, 850°C, 900°C et 950°C après une heure

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Oxidation mechanism at 900°C (SIMS isotopic analysis)

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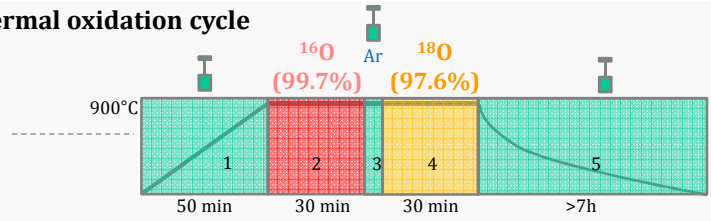
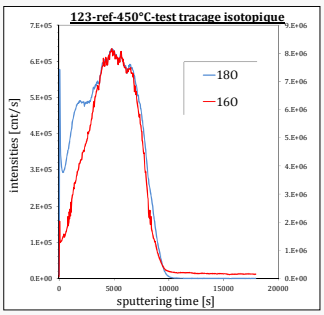
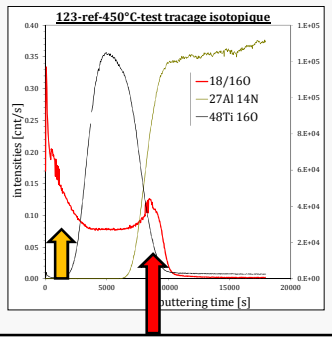
❖ **Thermal oxidation cycle**

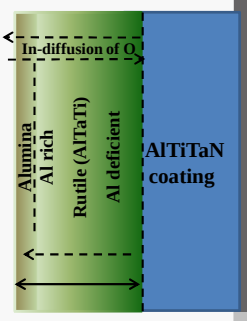


O16 & O18 depth profiles



O16 / O18 ratio





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Wear behaviour at high temperature

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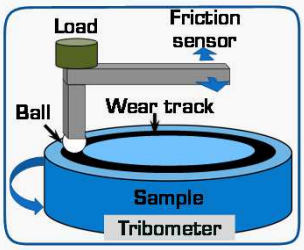
- **Les revêtements sont destinés à l'usinage de pièces à haute température** → tests d'usure par « ball on disk » à haute température pour se rapprocher de ces conditions



- **Paramètres de test:**
  - **Machine:** CSM High Temperature tribometer
  - **Vitesse linéaire** 10 $cm.s^{-1}$
  - **Rayon piste d'usure:** 7mm
  - **Charge:** 2N
  - **Bille:** alumine
  - **Substrat du revêtement:** carbure de tungstène
  - **Températures testées:** 700°C, 800°C et 900°C
  - **Durées de test:**
    - 5000 tours à RT, 700, 800 et 900°C

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Variation of wear depth at high temperature

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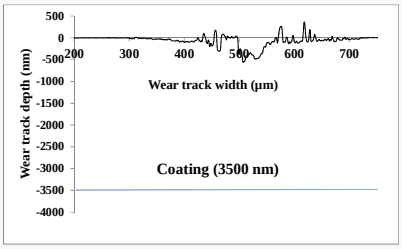
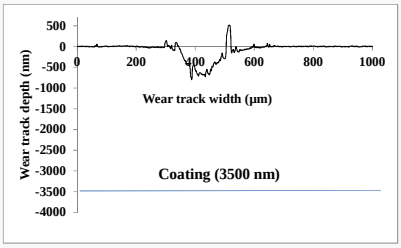
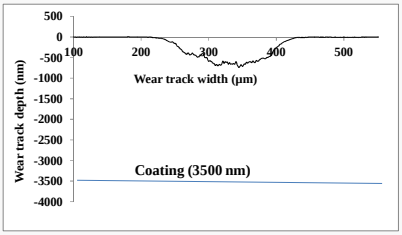
RT



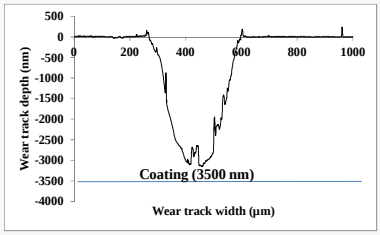
700°C



800°C



900°C



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Wear behaviour at high temperature

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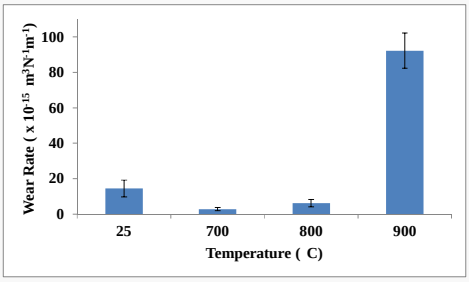
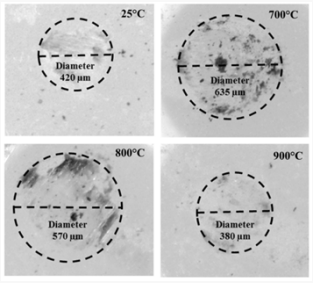
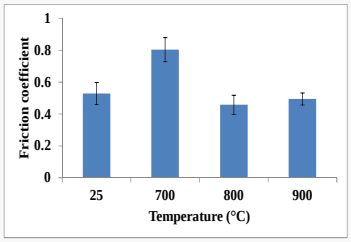
❑ *wear rate of the AlTiTaN coating*





Average friction coefficient for AlTiTaN coating



❑ *Optical microscope images of wear scars on the alumina ball obtained after ball on disk wear tests performed at various*

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Detection of a groving mechanism during wear

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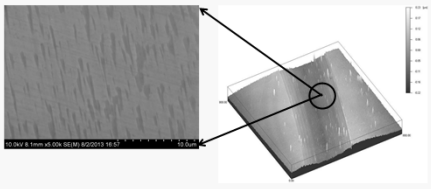
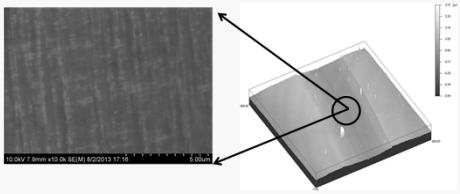
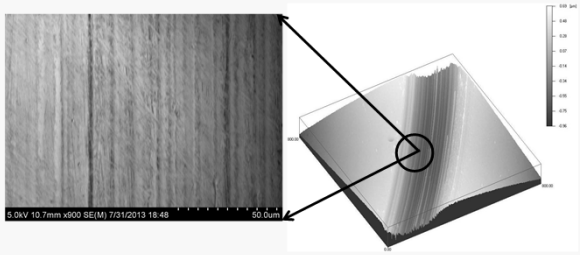
700°C



800°C



900°C



❑ Confocal microscopy images with corresponding zoomed SEM view of wear tracks after ball on disk wear tests at 700°, 800° and 900°C performed for 1000 laps.

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Conclusions and perspectives

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- ✓ The magnetron sputtering process is an adapted process for the synthesis of new protective coatings for severe environment
- ✓ The development of new HV pulse generator can bring a complementary parameter for a better control of the microstructure
- ✓ The TiAlTaN coatings offer an improvement for oxidation protection until 850°C, at 900°C the oxidation kinetic is largely increased
- ✓ Below 800°C, a complex oxide layer (Ti,Al, Ta, O) with an amorphous structure is formed. With time, crystallites of rutile phase can be detected
- ✓ Upper 800°C, the oxide layer is totally cristallized (Rutile phase),. With time, an amorphous alumina layer is formed at the external surface. With the increase of the oxidation temperature, this alumina layer begins to be crystallized
- ✓ The oxidation kinetics are control by the inner diffusion of oxygen and at higher temperature, also by the outside diffusion of aluminium
- ✓ The wear resistance is very good until 850°C, and it is largely controlled by a grooving mechanism
- ✓ The doping by Yttrium of the TiAlTaN coatings does not largely modify the oxidation and wear performances

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THANK YOU….

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