POLYTECHNIQUE MONTRÉAL
LE GÉNIE EN PREMIÈRE CLASSE

Hard nanostructured coatings on plasma nitrided Ti6Al4V

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Outline

- Introduction
- RF plasma nirtiding
- HiPIMS treatment
- Nitriding + HiPIMS TiN
- Summary and open questions

Coating spallation

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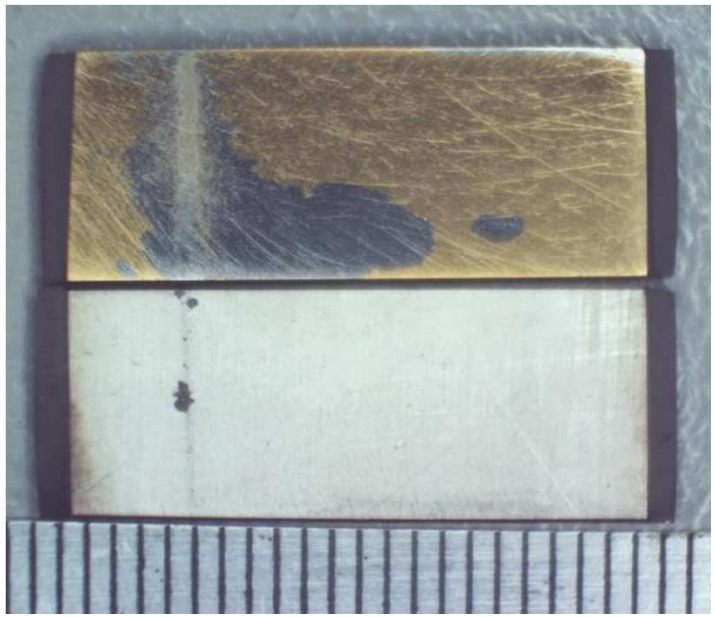
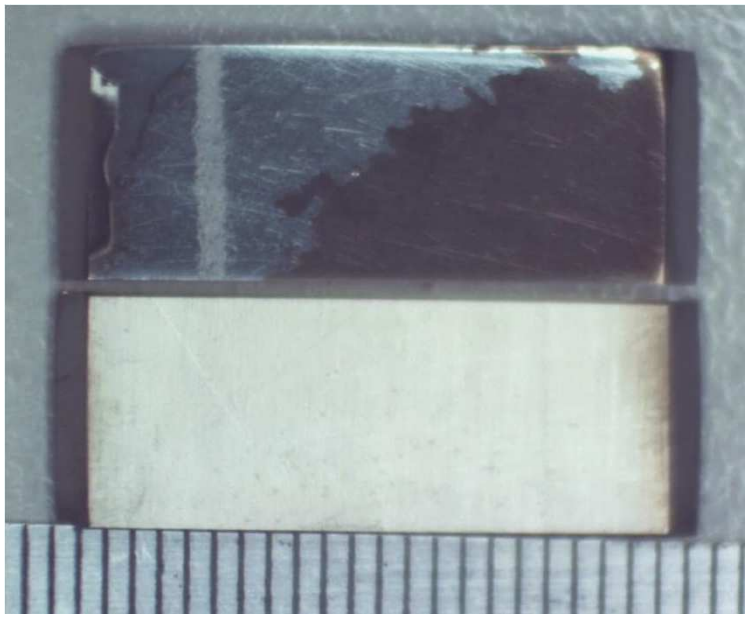
TiN-TiSiN multilayer



Ti-TiSiN multilayer



Severe spallation of coating after 30 seconds of erosion test!
Problem of coating adhesion to Ti6Al4V!

Erosion time: **30 s**
Nozzle: **400 µm**
Impinging speed: **350 m/s**
Estimated droplets size: **450 µm**
Water pressure: **30 psi**
Water flow: **0.05 l/min**

Coating spallation

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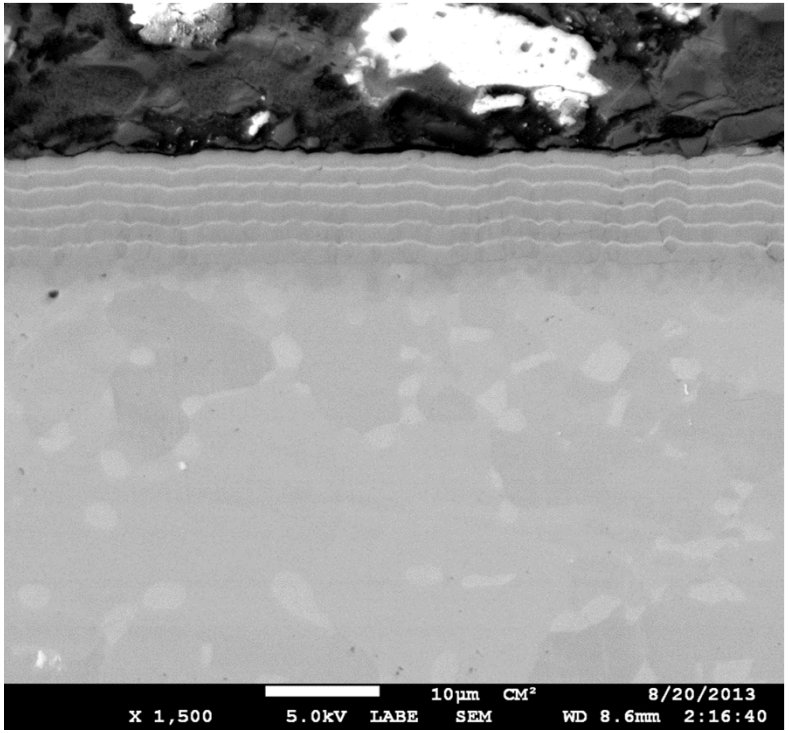
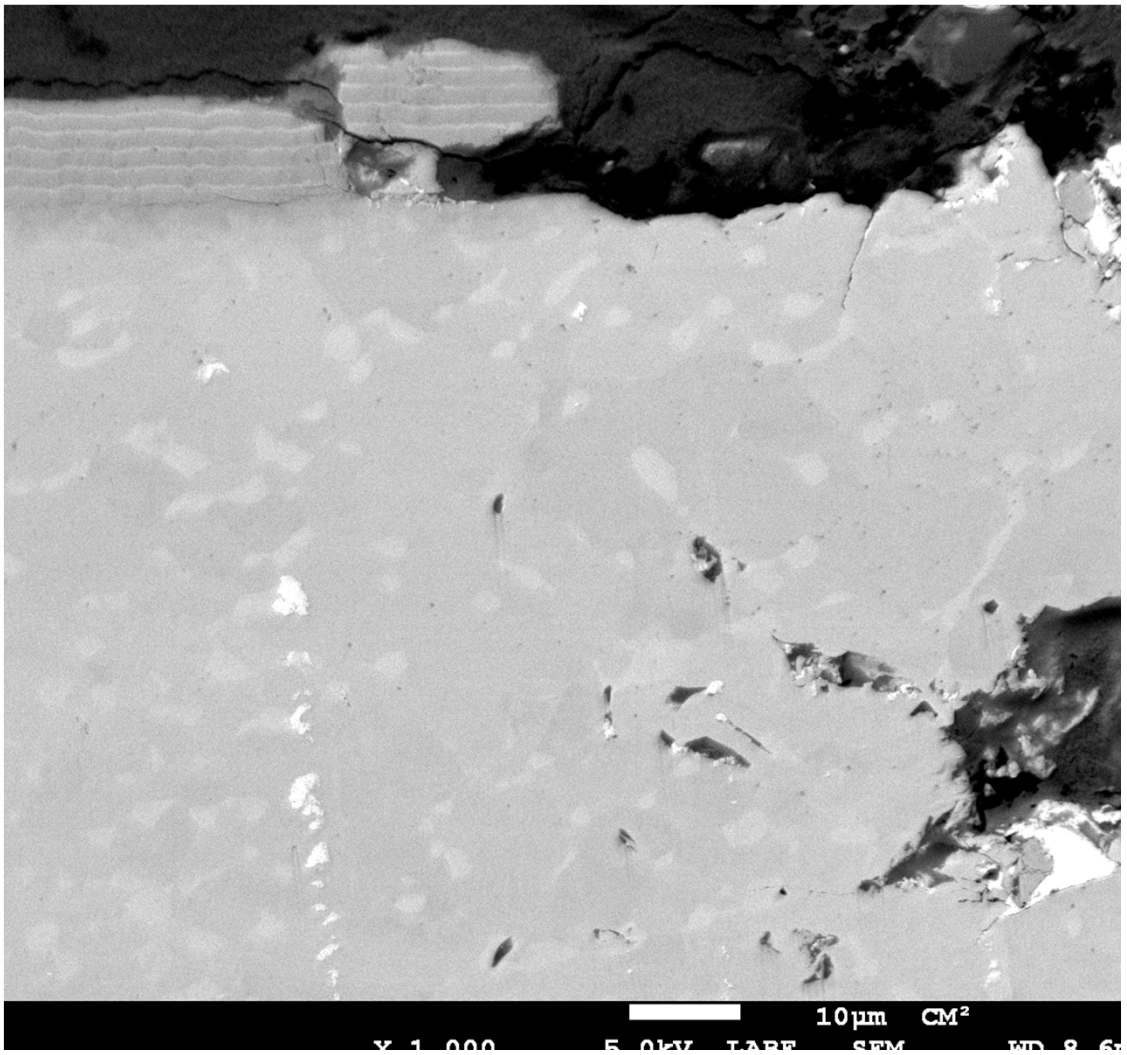
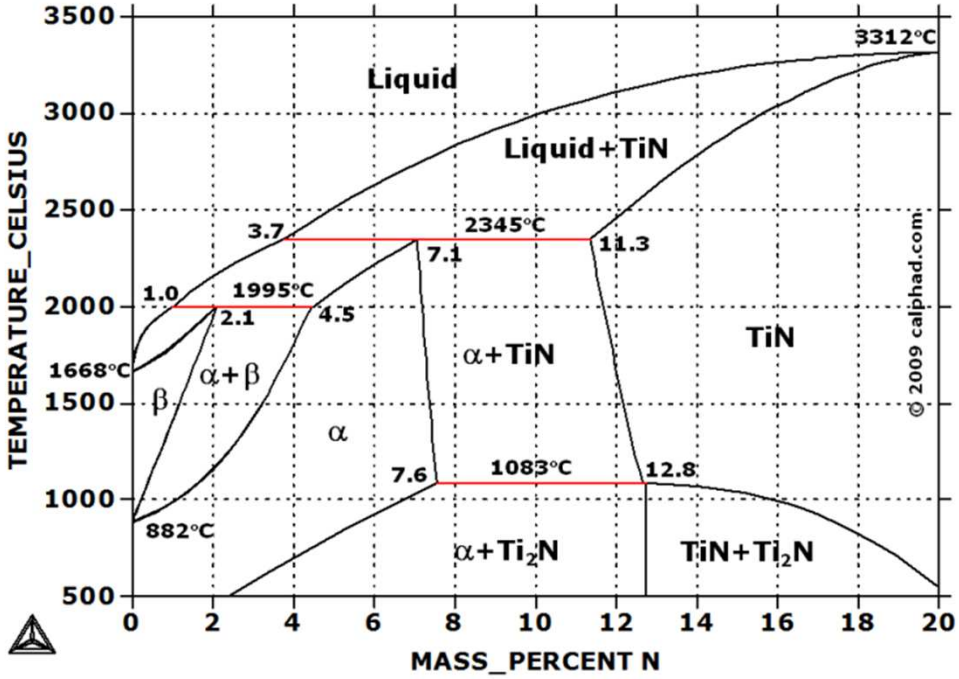
Ti-TiN multilayer, HiPIMS pre-treatment (450 ˚C)





Plasma nitriding

Plasma nitriding is a surface modification process that makes use of a glow discharge to harden the surface and subsurface of different metals by introducing active nitrogen for subsequent diffusion into the bulk.



Fick's second law

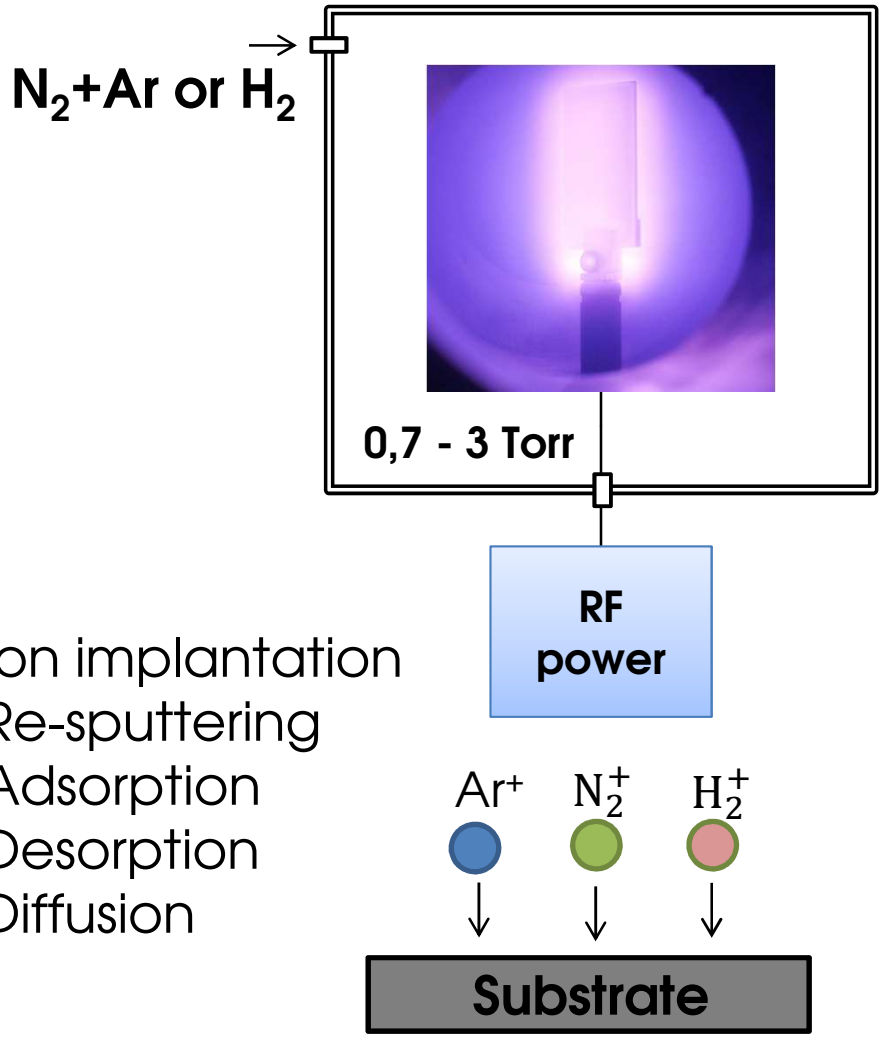
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

$$D = D_0 exp^{\left(\frac{-Q}{RT}\right)}$$

$$x^2(t) = 2Dt$$

http://www.calphad.com/titanium-nitrogen.html
A. Fick, Phil. Mag. (1855), **10**, 30

RF plasma nitriding



550 °C – 950 °C (plasma and/or external heating)

Advantages:

- Deep surface treatment (up to hundreds of µm)
- Uniformity (no rotation)
- Plasma heating
- Low vacuum
- Low price
- Ecological
- Possibility of pretreatment and deposition in one process

Disadvantages:

- High temperature required for fast diffusion may affect the overall properties of modified substrate

RF plasma nitriding

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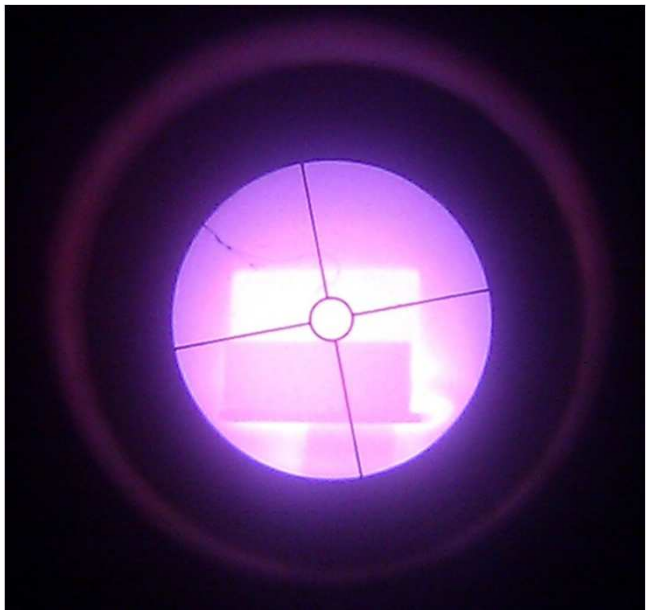
Set 1 process parameters:

No.	Gas		Temp (^{0}C)	Time (h)
#6	Ar / N_2	1 / 9	615	4
#12	Ar / N_2			8
#13	H_2 / N_2			4
#14	H_2 / N_2			8
#15	H_2 / N_2		700	4
#16	H_2 / N_2			8
#17	Ar / N_2			4
#18	Ar / N_2			8



Samples are heated only by plasma, RF power (80-120 W) is regulated to keep constant the sample temperature, measured by a pyrometer

RF plasma nitriding

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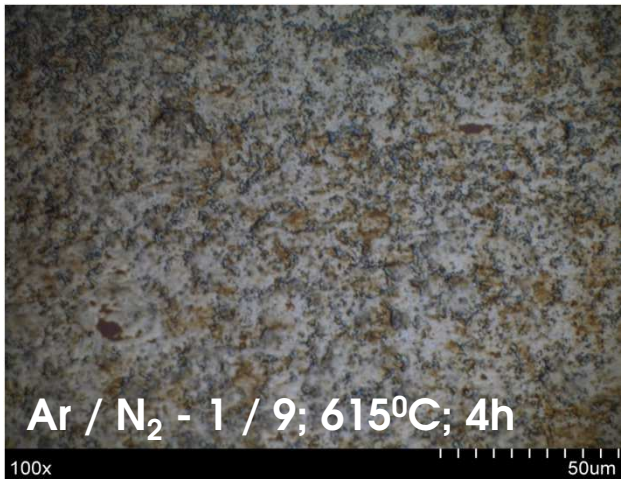

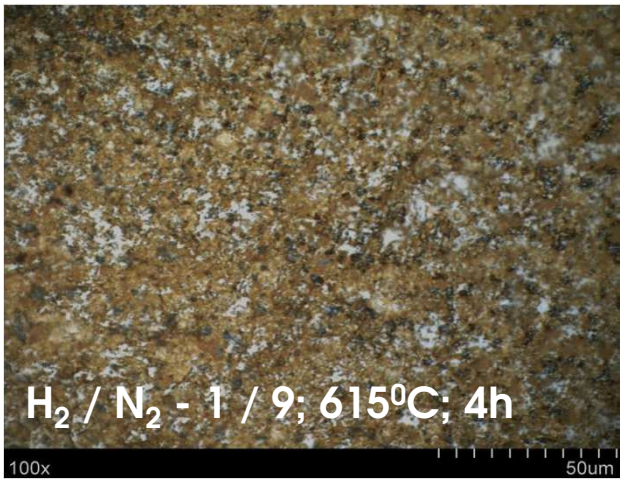

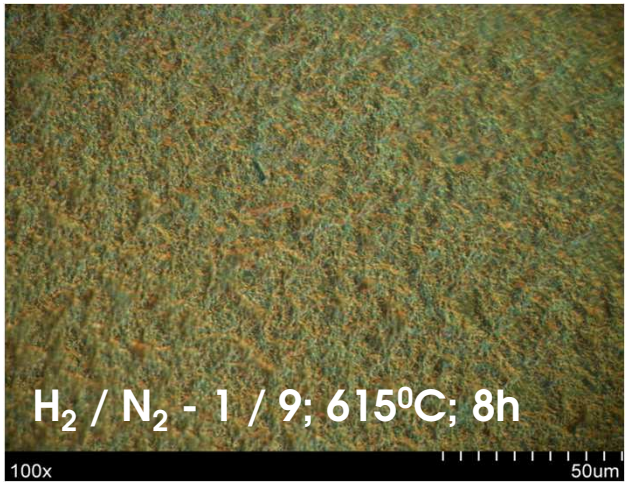

Less of golden color (TiN) when nitrided in Ar/N_2 mixture

RF plasma nitriding

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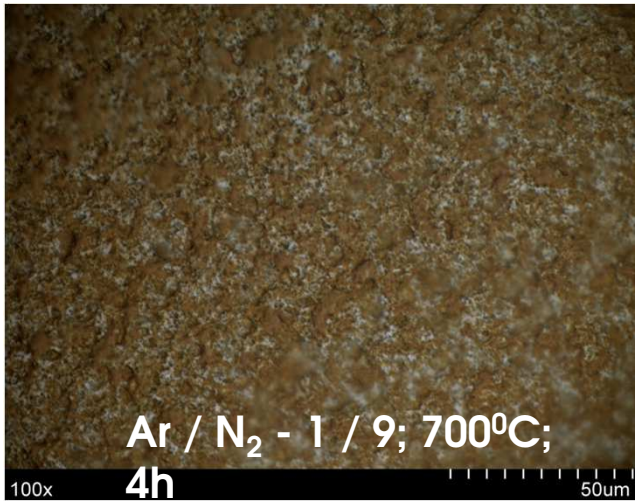

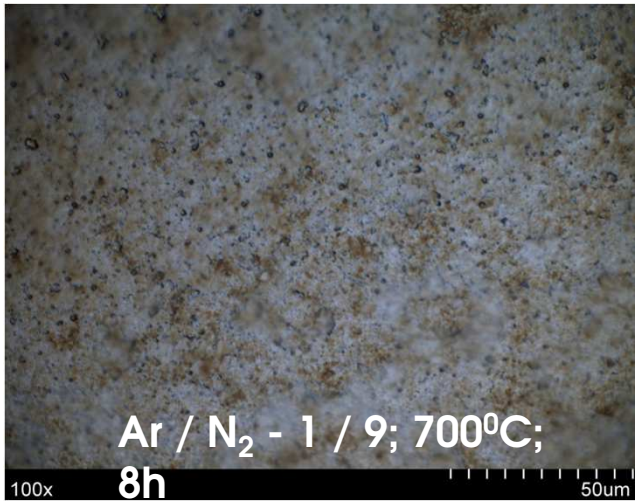

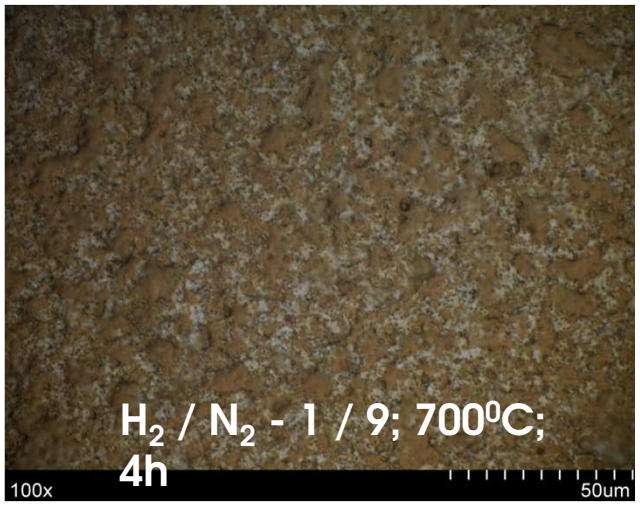

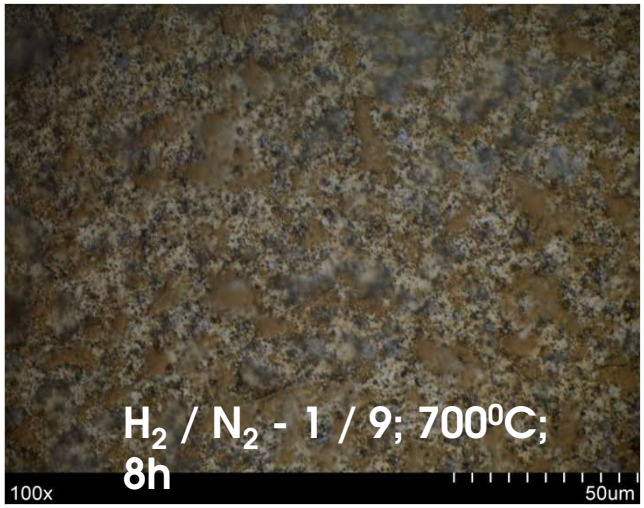

Surface roughness increased after nitriding

RF plasma nitriding

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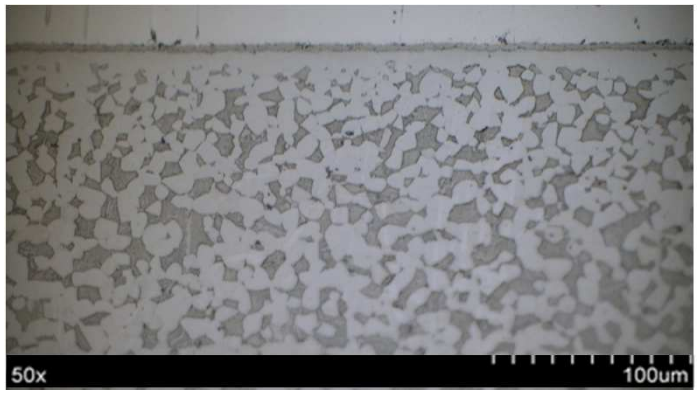
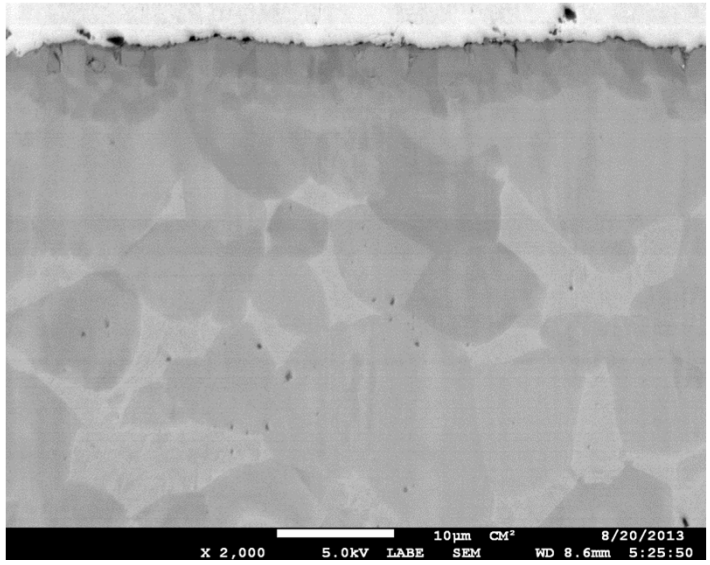
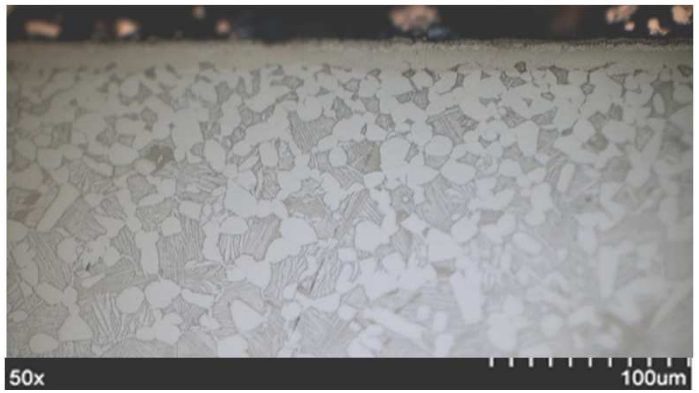
Ar / N_2 - 1 / 9; 700^{0}C; 4h





H_2 / N_2 - 1 / 9; 700^{0}C; 4h



Different zones like
- compound layer,
- alpha case,
-diffusion region,
are visible after nitriding.

Hardness profile

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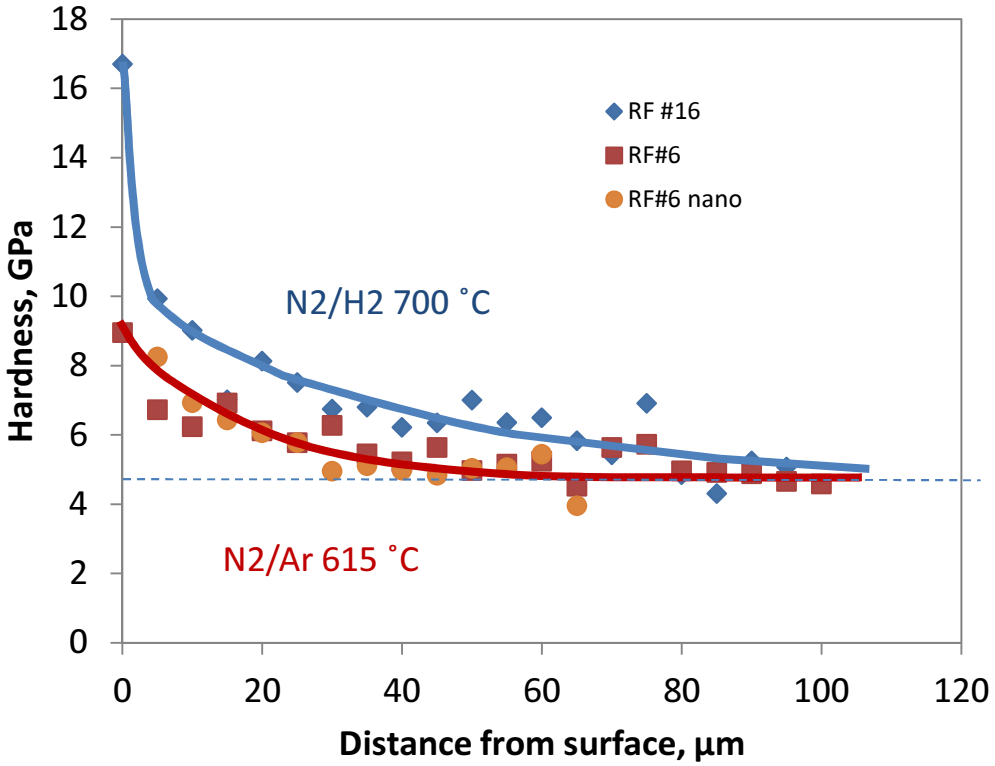

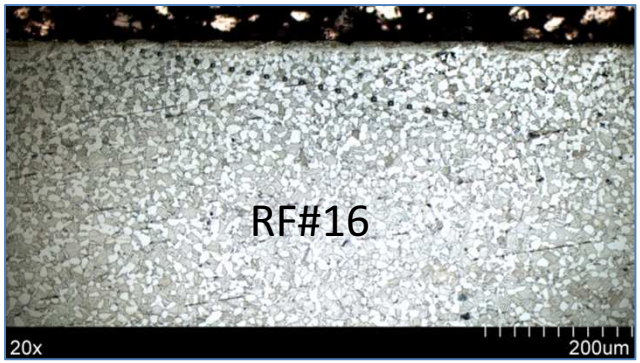

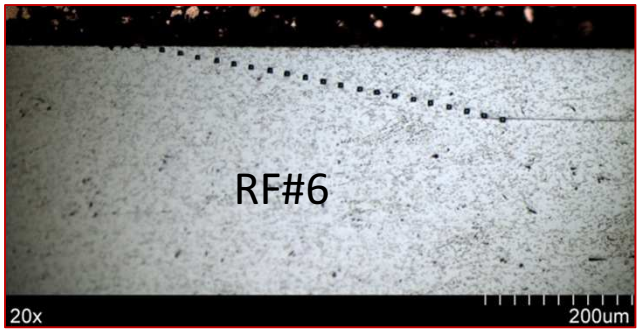

Water erosion test

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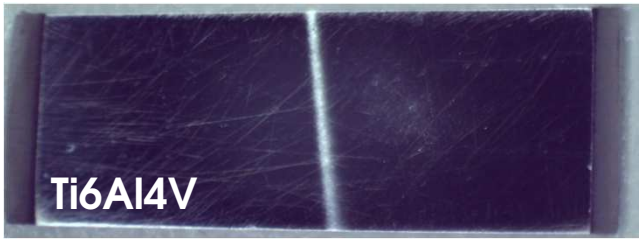
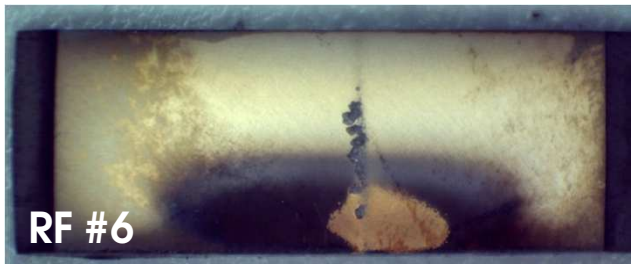
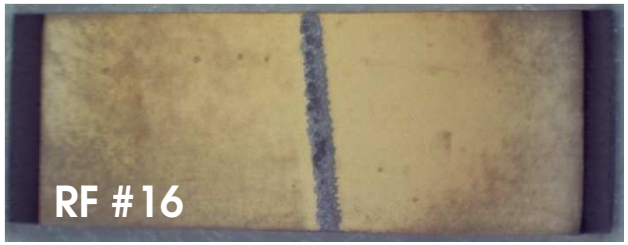


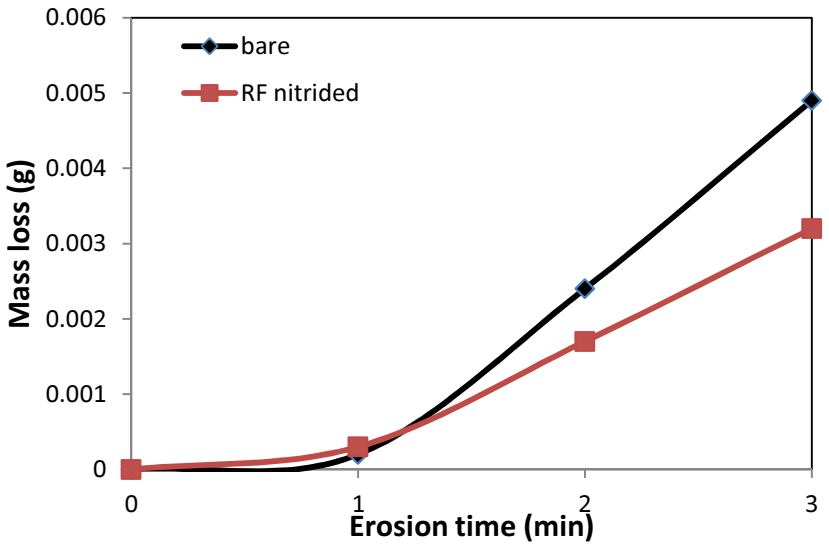
1 minute



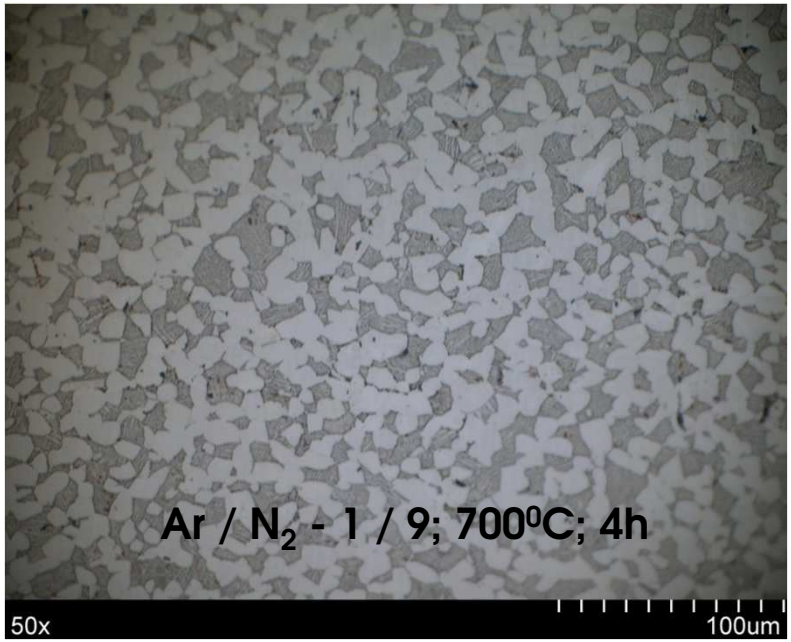
2 minutes



1 minute



Microstructure change



The proportion of beta-phase increased after the nitriding, especially at higher temperature, presumably due to the rapid quenching.

RF plasma nitriding

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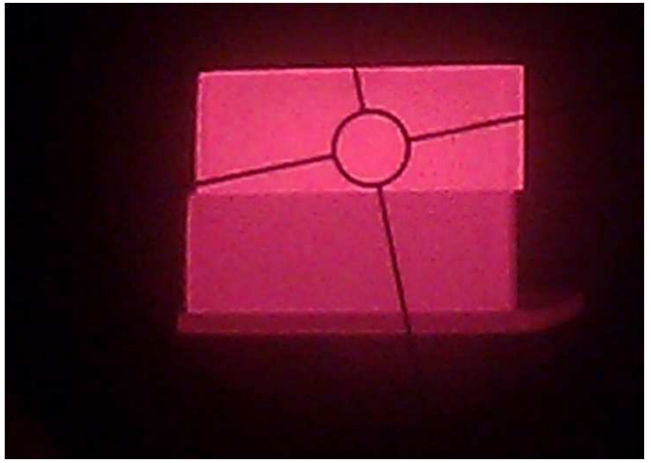
New set of plasma nitrided samples, slow cooling

No.	Gas flow ratio		Temp (^{0}C)	Time (h)
#51	Ar / N_2	1/9	580	4
#52	H_2 / N_2		580	4
#53	H_2 / N_2		700	8
#54	Ar / N_2		700	8



XRD results

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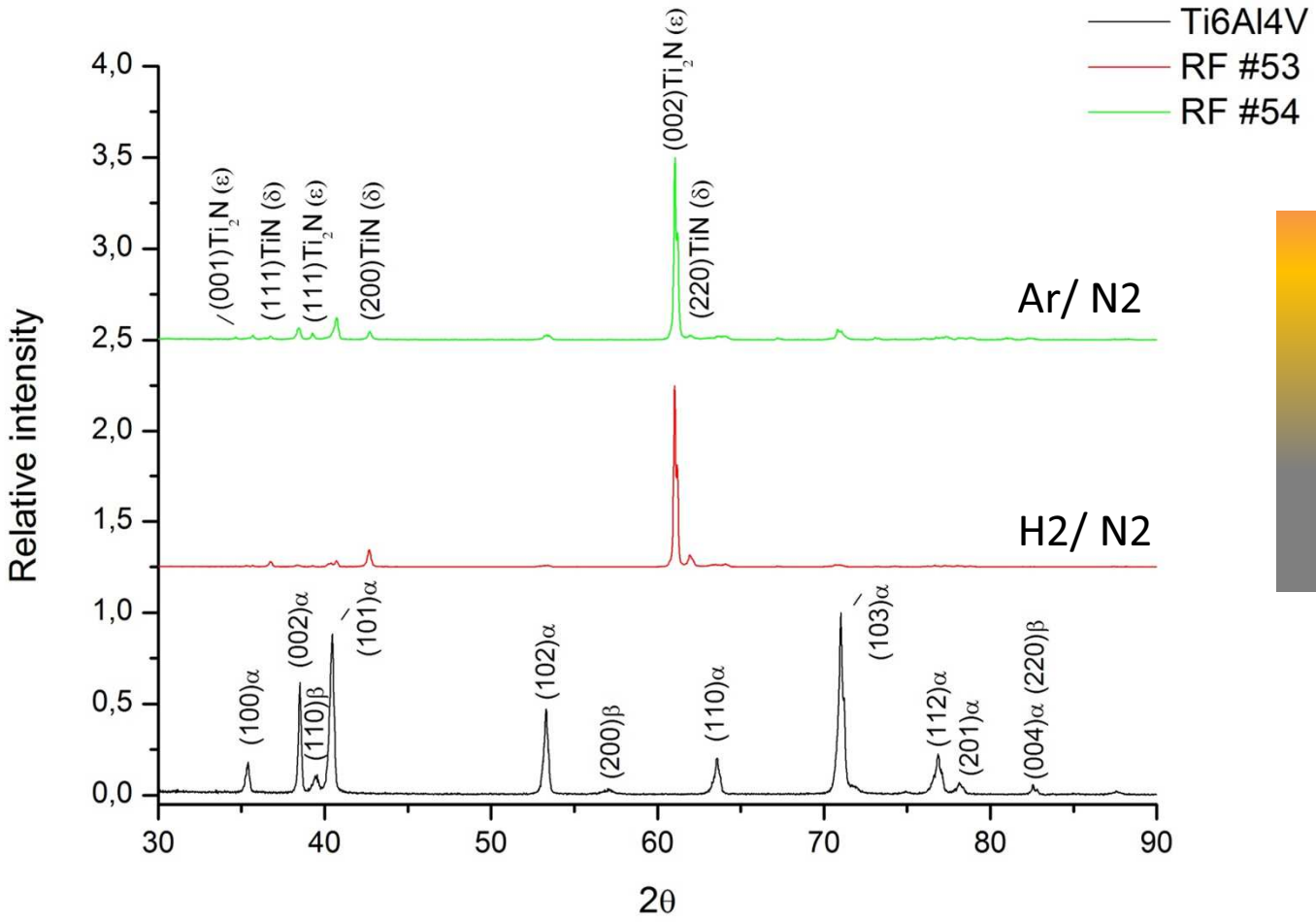
Samples nitrided 8 hours at 700 ˚C



Ti_2N + TiN compound layer

Ti(N) α diffusion layer

Ti6Al4V α + β

XRD results

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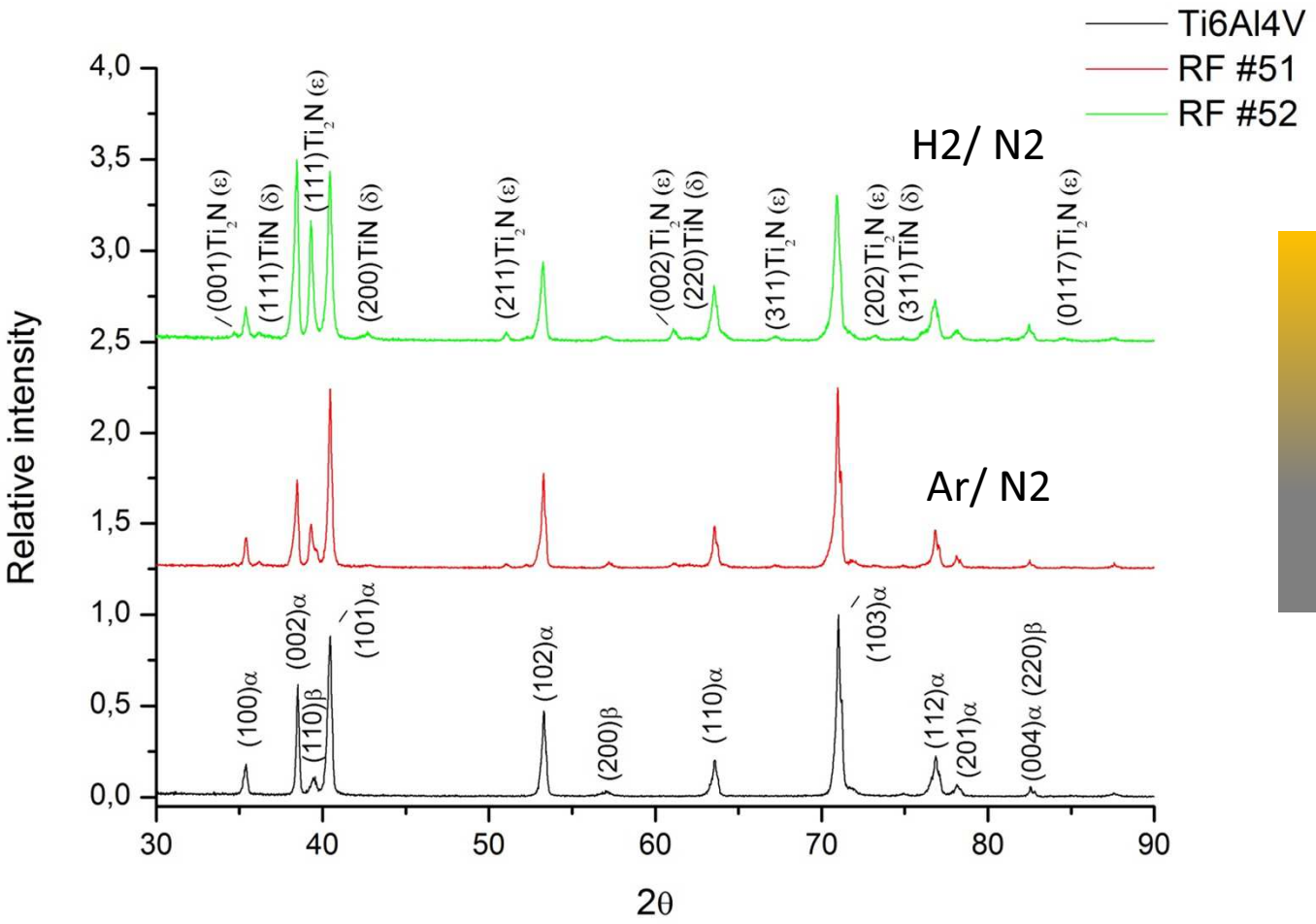
Samples nitrided 4 hours at 580 ˚C



Ti(N) α diffusion layer

Ti6Al4V α + β

Water erosion test

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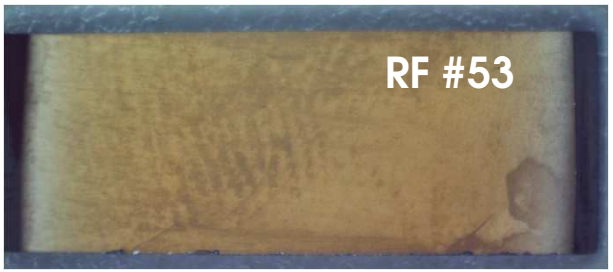
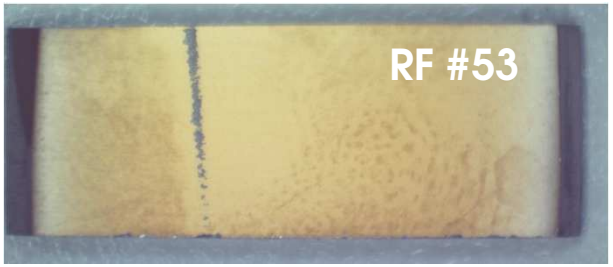
Samples nitrided at 700 ˚C

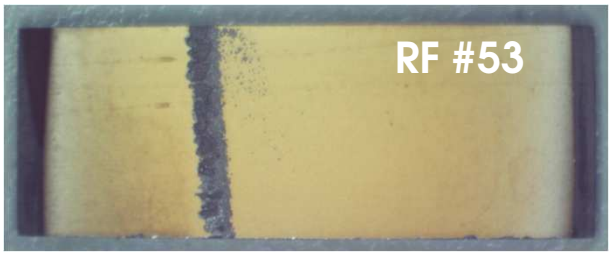
H2/ N2



Before



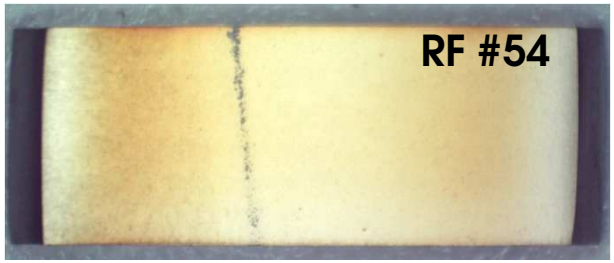
1 minute



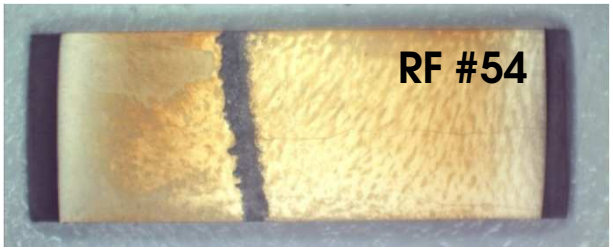
6 minutes

Ar/ N2

Before



1 minute



6 minutes

Water erosion test

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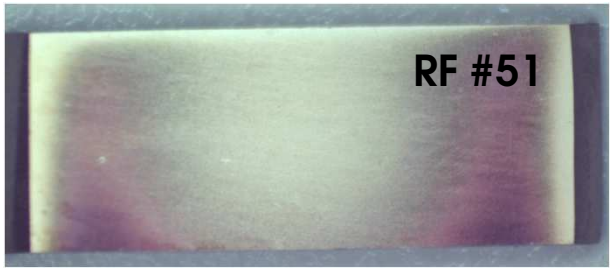
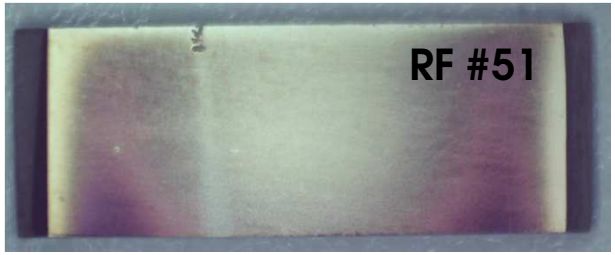
Samples nitrided 4 hours at 580 ˚C

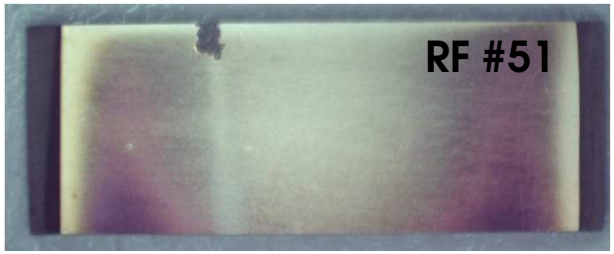
Ar/ N2



Before

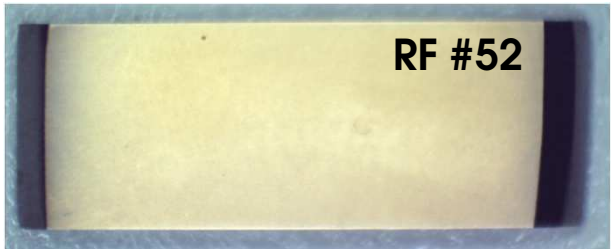


5 minutes



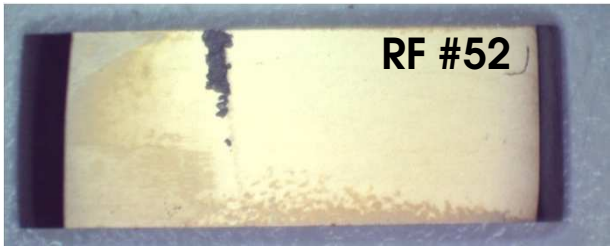
6 minutes

H2/ N2



Before

3 minutes



6 minutes

Water erosion test

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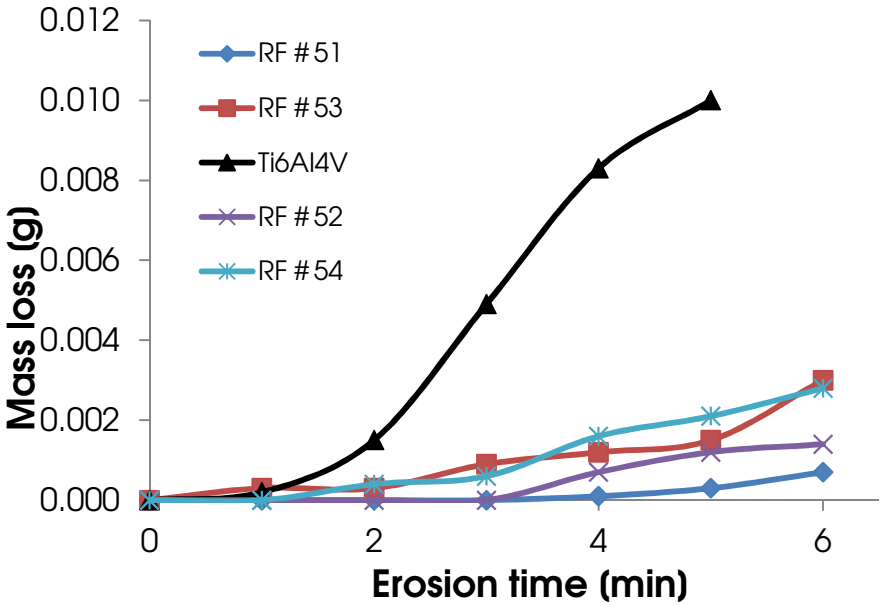

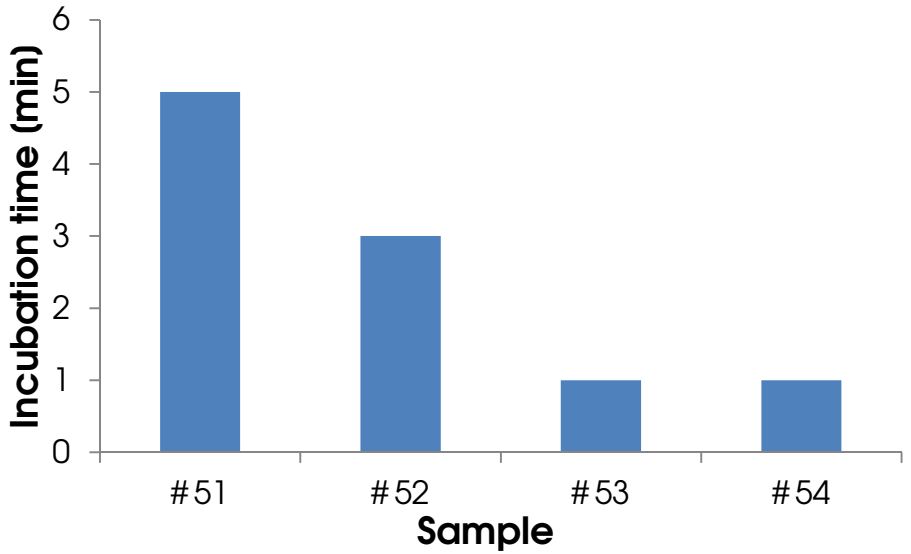

Samples nitrided at low temperature show longer incubation time and lower mass loss.

Coating deposition setup

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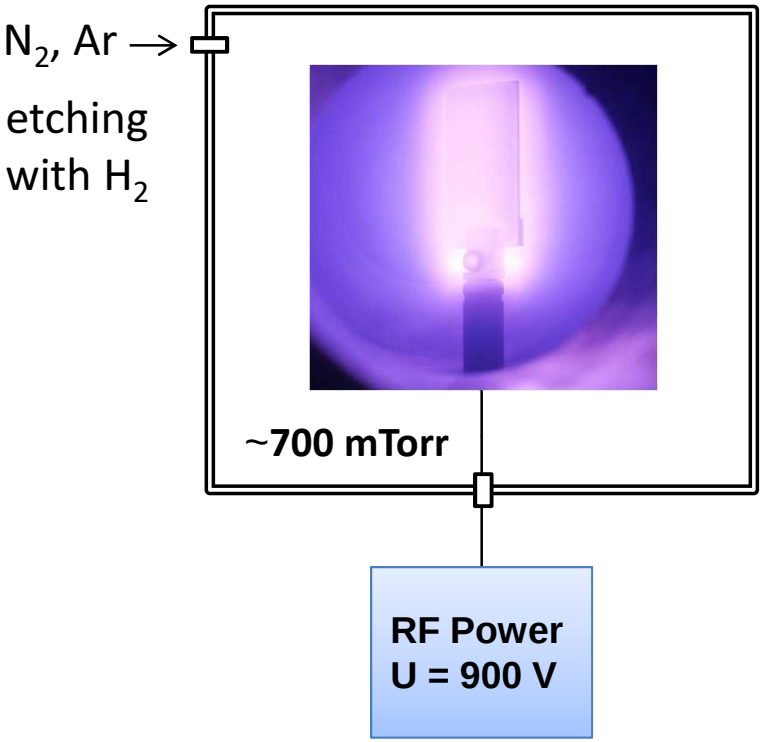
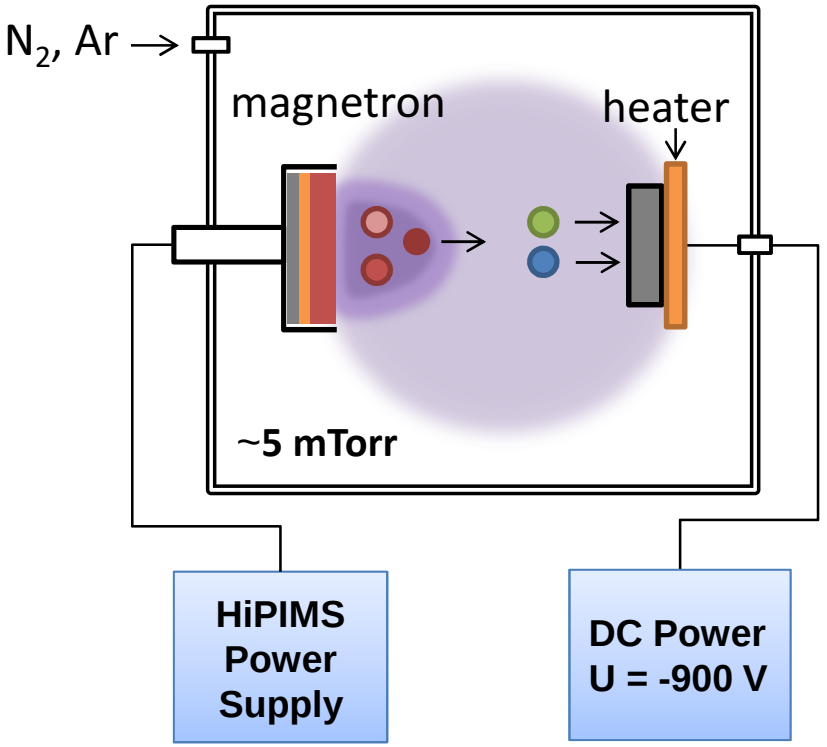
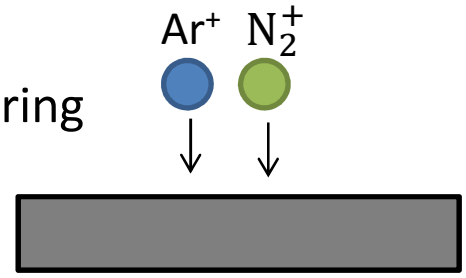
RF nitriding



HiPIMS treatment+ TiN

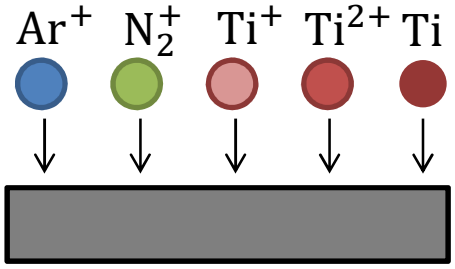


nitriding
re-sputtering



Ti6Al4V

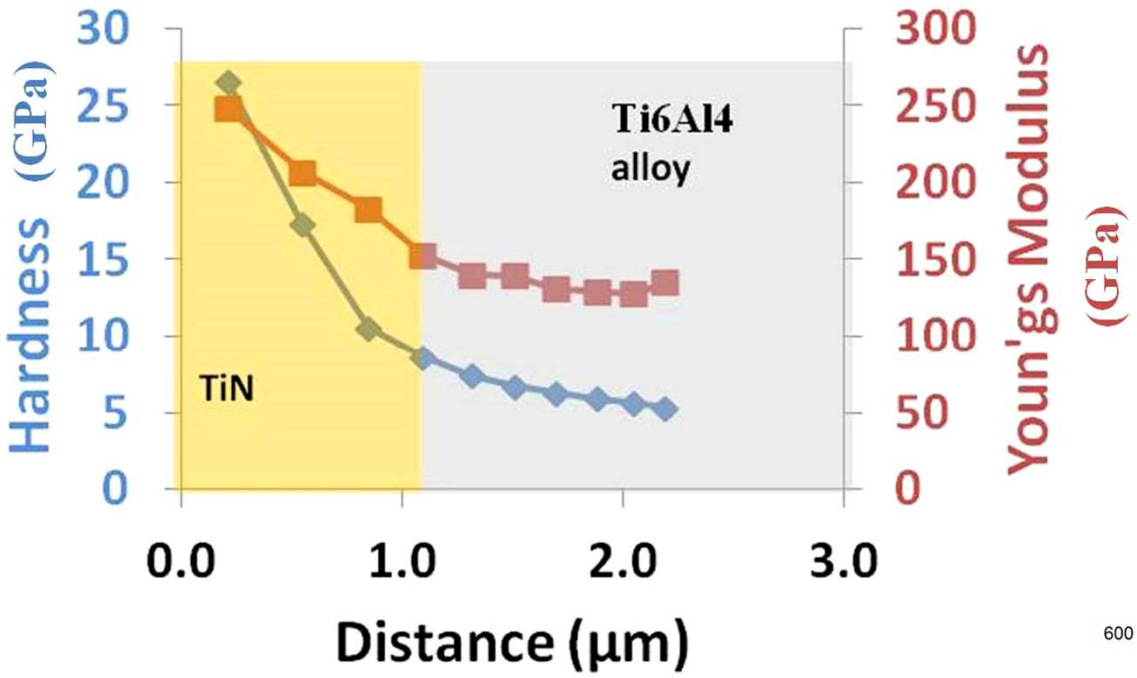
580 or 700 °C (plasma heating)



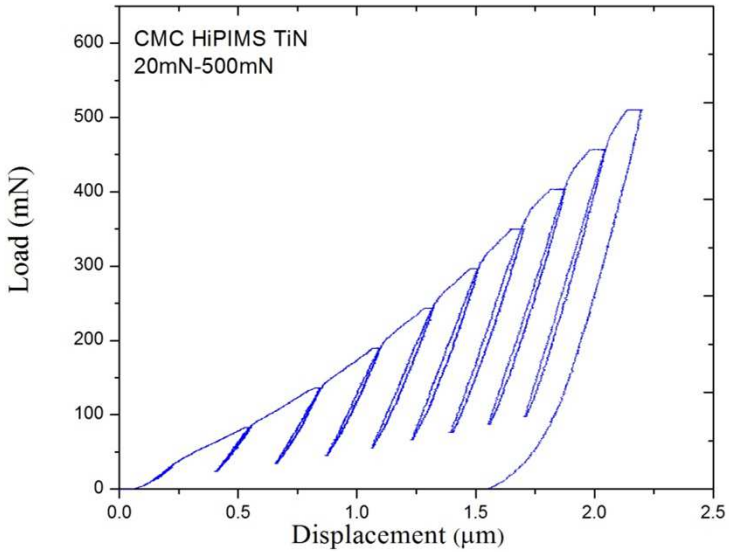
nitriding
re-sputtering
deposition

~450 °C (heater)

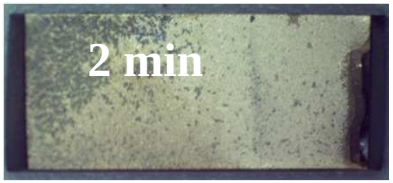
Hardness profile

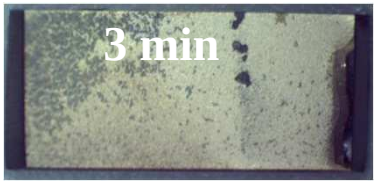


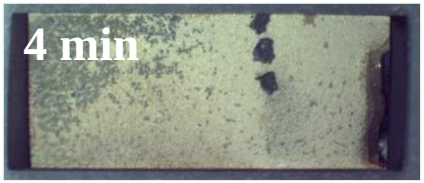
Measured by progressive load indentation on the same spot



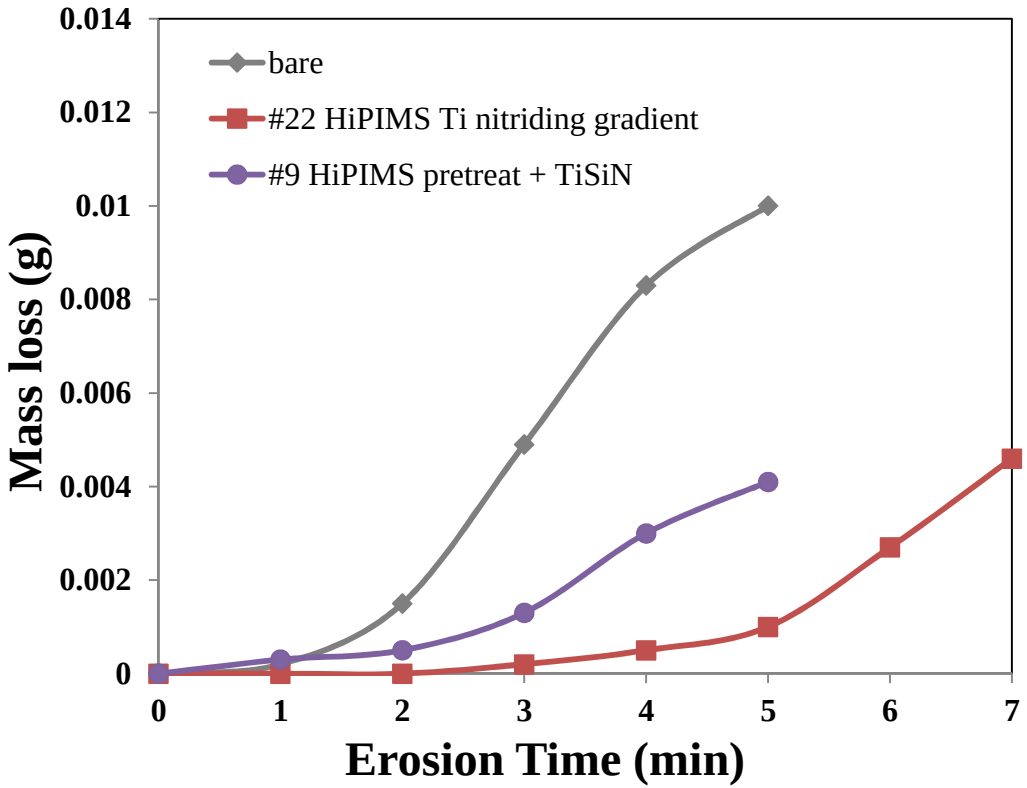
LDE for HIPIMS pretreated+ TiSiN coating on Ti6V4-alloy







After 5 min , about 3 times lower mass loss for HIPIMS deposited TiSiN Ti6V4 alloy when compared to Untreated Ti6V4 alloy



Water erosion test

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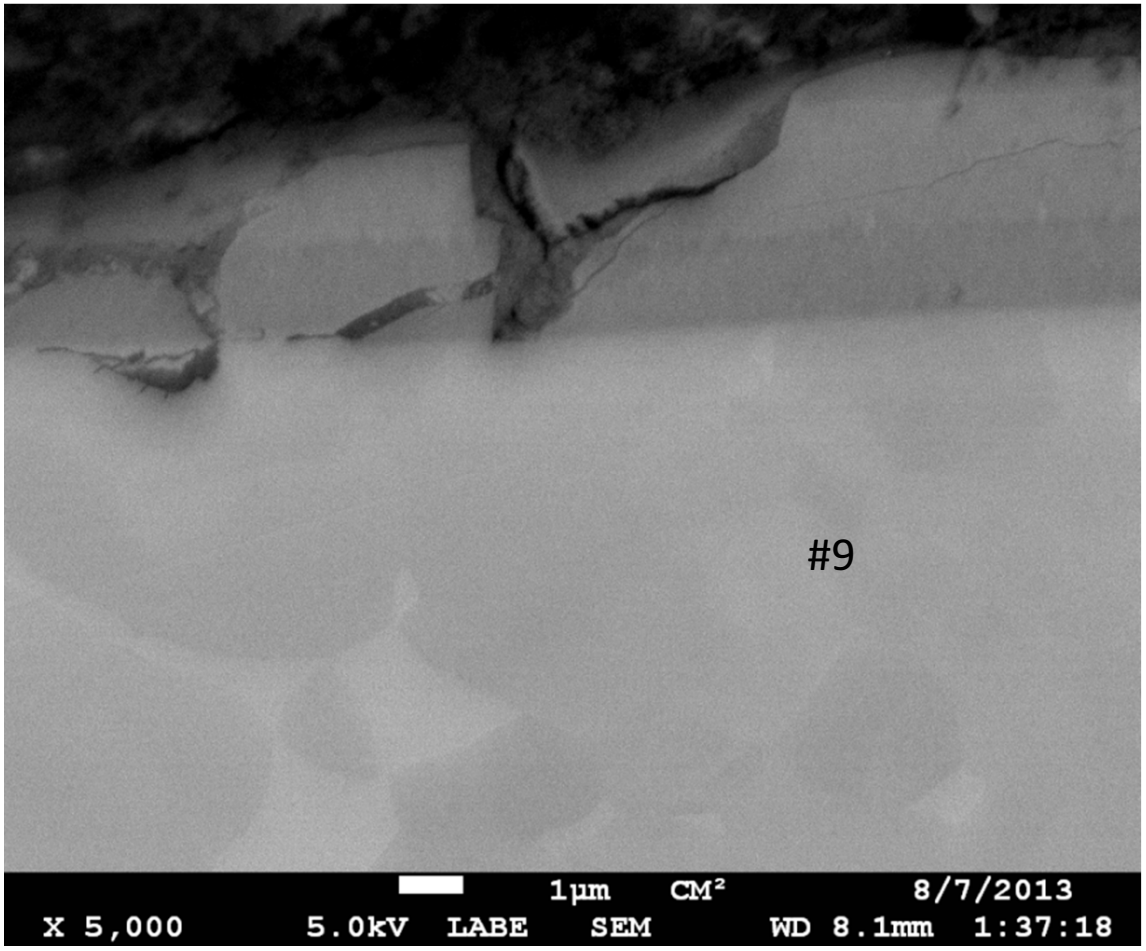
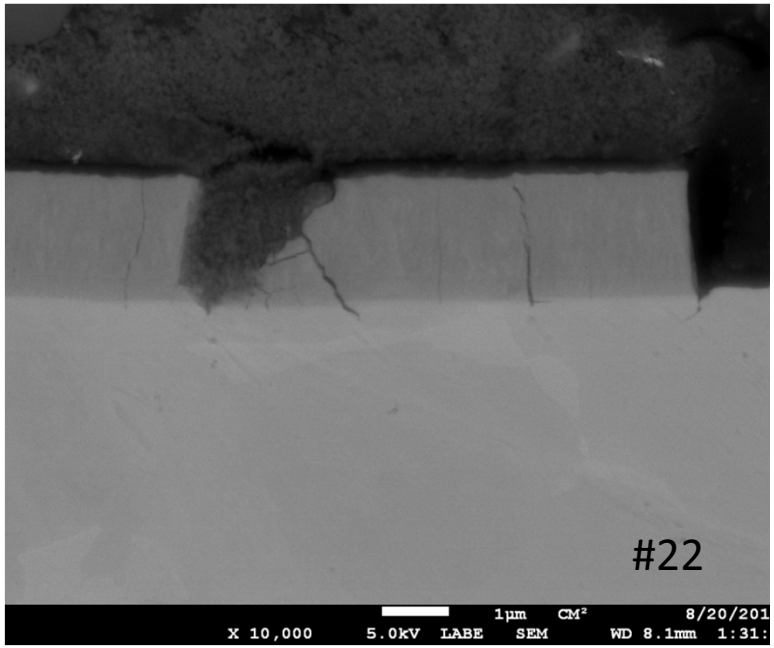
HiPIMS TiSiN after 5 min of test



HiPIMS TiN after 7 min of test



Water erosion test

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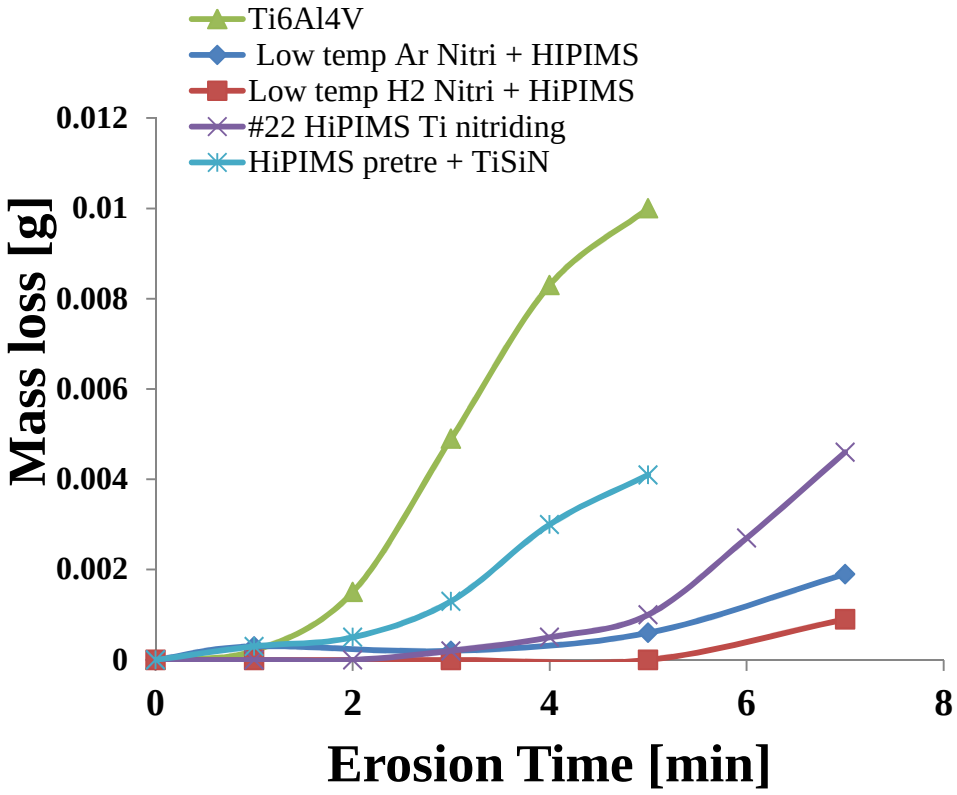
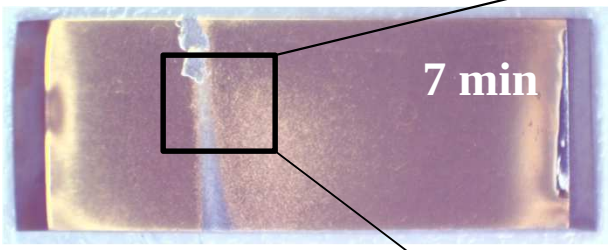
LIE for Nitriding+polished+HIPIMS pretreated Ti6V4-alloy substrate

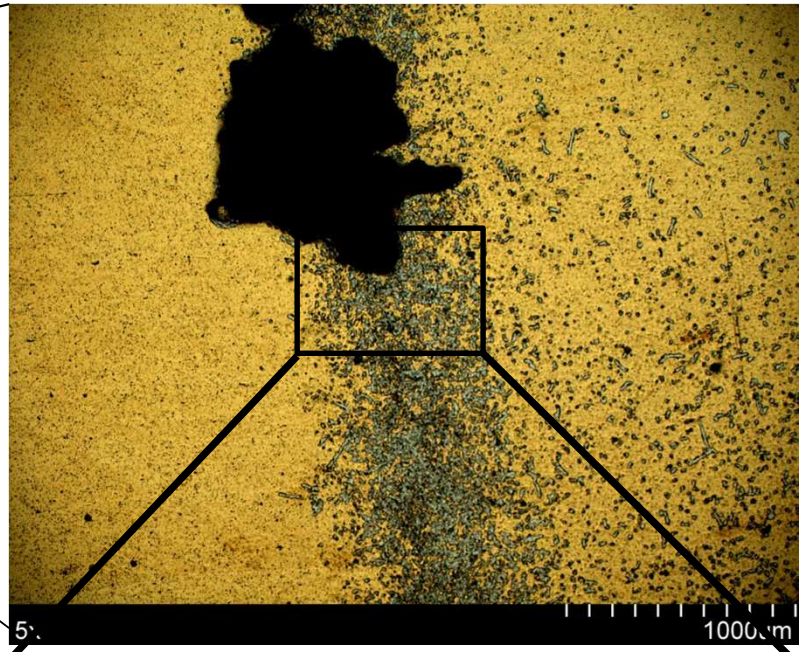
after 5 minutes test

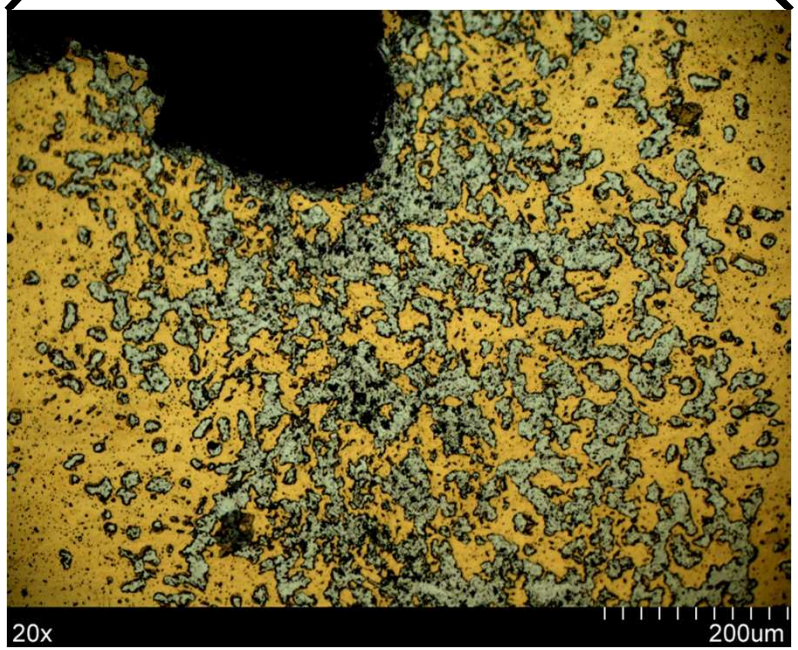
Treatment	Mass loss , mg	Mass loss reduction, times
Bare Ti-alloy	10	1
HiPIMS + TiN	1	10
HiPIMS + TiSiN	4	2.5
580C Ar RF+ HiPIMS	0.6	16
580C H2 RF + HiPIMS	<0.1	100



LDE surface of Nitriding+HIPIMS pretreated Ti6V4-alloy







TiN coating deposited by HIPIMS stays well adhere to substrate after 7 min of water impact

Best samples so far

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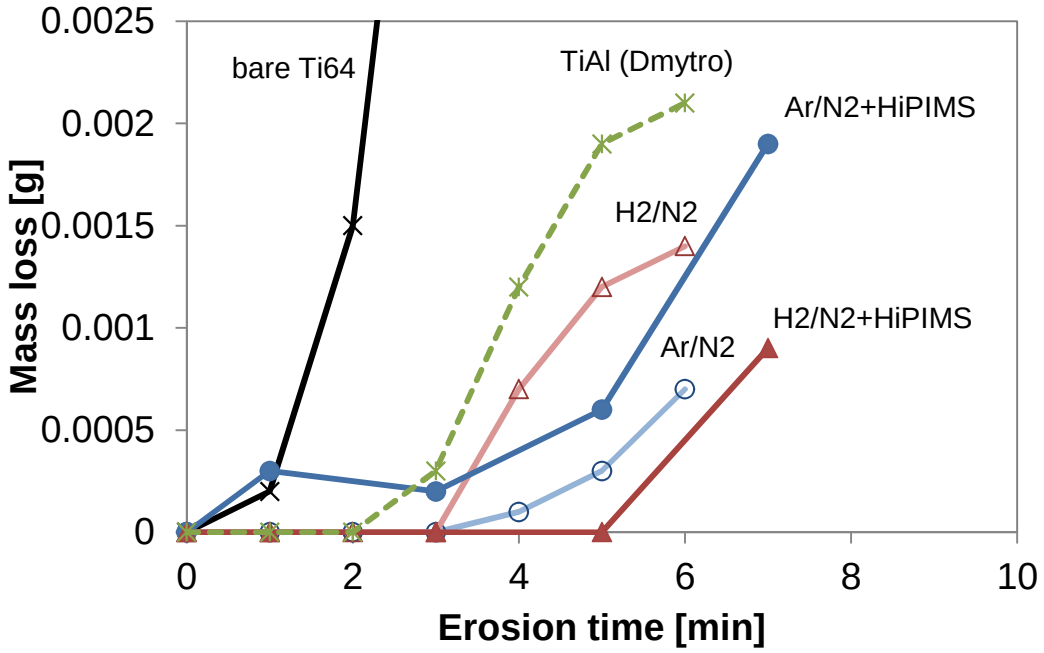
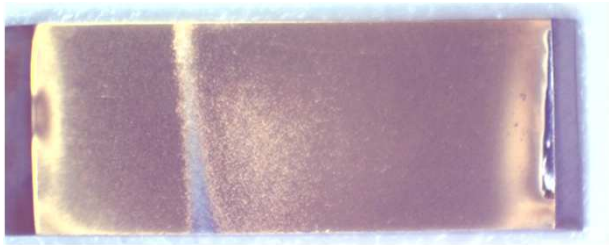


Ar/N_2 RF nitriding

5 minutes

H_2/N_2 RF nitriding +HiPIMS



5 minutes

Summary

- Hard coatings need a solid intermediate foundation to be an effective protection against LIE.
- Plasma nitriding and particularly RF plasma nitriding of Ti6Al4V alloys provides such interface layer.
- Ti6Al4V samples treated at rather mild niriding conditions (580 ˚C, 4 hours) perform the best in LIE rig test.
- HiPIMS coatings give better results than their DCMS counterparts.
- HiPIMS TiN film deposited on RF nitrided sample gives the lowest mass loss to date

Open questions

- Ar vs H_2 as a companion gas in RF nitriding
- What is the lowest nitriding temperature ?
- Polishing after RF nitriding – is it needed before deposition of (super)hard coating
- Will RF niriding work on real parts (temperature distribution)
- What properties of coatings to look for?

Papers to come

1) D. Batory, M. Panjan, O. Zabeida, J.E. Klemberg-Sapieha, ...
   “RF plasma nitrided Ti64 alloy with improved water erosion resistance”

2) G. Kamath, M. Panjan, O. Zabeida, J.E. Klemberg-Sapieha, ...
   “LIE resistant coatings deposited by HiPIMS”

3) HiPIMS on RF nitrided Ti64

RF plasma nitriding

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