Resonant Nuclear Reaction Analysis investigation of Nitrogen and Oxygen diffusion processes involved in plasma assisted multi-interstitials surface hardening of Ti6Al4V alloy

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Motivation

- The poor wear resistance of Titanium and its alloys
- Limitation of their applications

→ Surface hardening (Ti compounds like TiN)
→ Resistant underlayer: thick (100s µm) solid solution Ti(N,O)

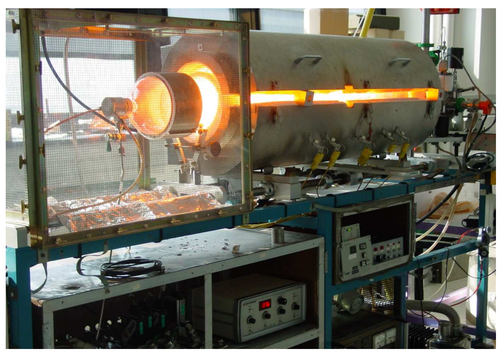
→ **Multi-interstitial diffusion using plasma processing**

Abstract

Multi-interstitials (N, O) diffusion surface treatments of titanium alloys can provide a thick and strong mechanical support to improve the wear resistance. For this purpose, low-pressure plasma assisted diffusion thermochemical treatments, using sequential O2 and N2+H2 atmosphere, were applied on Ti6Al4V samples:
In order to study the potential influence of each interstitial (N, O) on the diffusion of the other one, various sequential treatments (nitriding + oxidizing or oxidizing + nitriding) were performed with isotopic ^{15}N or ^{18}O elements in the reactive atmosphere and the resulting composition profiles were analyzed by resonant nuclear reaction analysis (NRA).
Microstructures of the modified surfaces were also characterized by optical microscopy and scanning electron microscopy (SEM) and the crystallographic structure was determined by X-Ray Diffraction (XRD); Glow Discharge Optical Emission Spectroscopy (GDOES) and Energy Dispersive X-Ray Spectroscopy (EDS) provided depth profiles of the treated surface chemical composition and were compared to the NRA results.

Experimental

The Plasma Reactor



T= 200 – 950 °C Up to 4 gas mixture
10^{-7} mbar base pressure
50 µbar (5 Pa) working pressure
700 W RF power

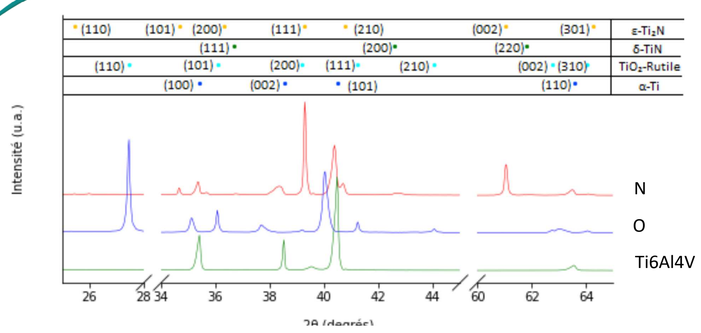
Surface treatments sequences

N = plasma nitriding (850°C ; 50 µbar ; 60% N_2, 40% H_2; total 8h)
d = vacuum diffusion (10^{-6} mbar ; 15h) ;
p = surface polishing (elimination of oxide layer)
O = plasma oxidizing (750°C ; 50 µbar O_2 ; 8h)
-16-18: O operated with ^{16}O (6h) + ^{18}O (2h)
-18-16 : O operated with ^{18}O (2h) + ^{16}O (6h)
-14-15 : N operated with ^{14}N (5h) + ^{15}N (3h)

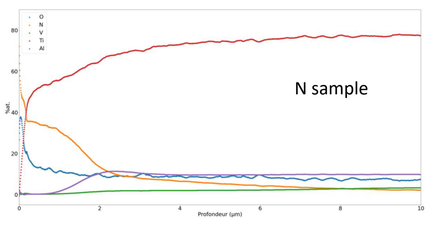
N(-14-15)	NO (-16-18)	O (-16-18/18-16)	O-N (16-18/-18-16)
N-d(-14-15)	NO (-18-16)	Op (-16-18/18-16)	Op-N (-14-15)
	NO (-14-15)		Op-N (-18-16/-16-18)
	NdO		OdNd (-18-16/-16-18/-14-15)
			OdpNd

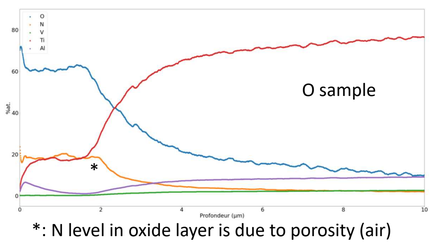
NRA : $^{15}N(p;\alpha)^{12}C$ $E_{beam\text{-}max}$=1050 keV $^{18}O(p\ \alpha)^{15}N$ $E_{beam\text{-}max}$=850 keV scanning beam size (3.5 x 6.5 µm²) on the cross section (13x100 µm²).

Plasma Nitriding/Oxydizing



XRD (θ/2θ) and GDOES profiles of N and O samples

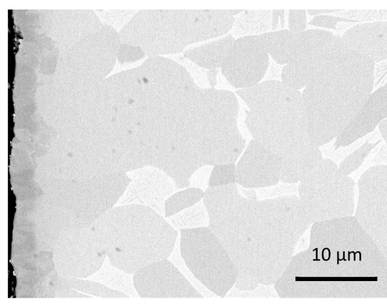




*: N level in oxide layer is due to porosity (air)

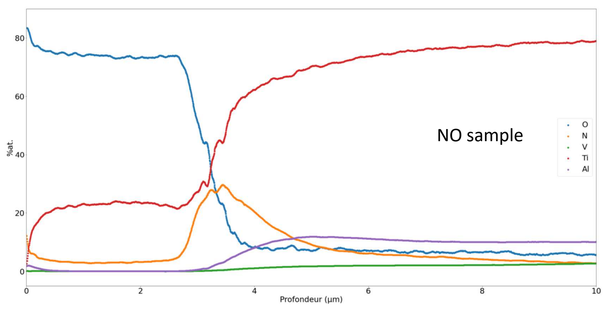
Cells parameters (a,c) of the different hexagonal α-Ti(N) detected by XRD

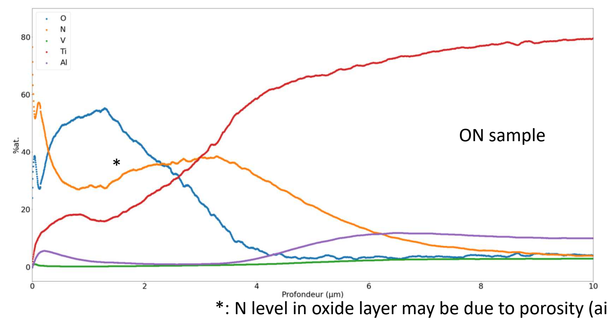
	a_1	c_1	a_2	c_2	a_3	c_3
Ti6Al4V	2.925 (0)	4.670 (0.04)	—	—	—	—
N	2.930 (0.07)	4.732* (1.07)	2.910 (0.04)	4.696* (0.24)	—	—
N-14-15	2.930 (0.01)	4.726* (0.68)	2.905 (0.08)	4.692* (0.08)	—	—
Nd	2.955 (0.02)	4.764 (0.18)	2.935 (0.04)	4.718 (0.02)	2.902 (0.02)	4.696 (0.02)
Nd-14-15	2.953 (0)	4.749 (0.11)	2.932 (0.03)	4.722 (0.03)	2.897 (0.02)	4.685 (0.02)

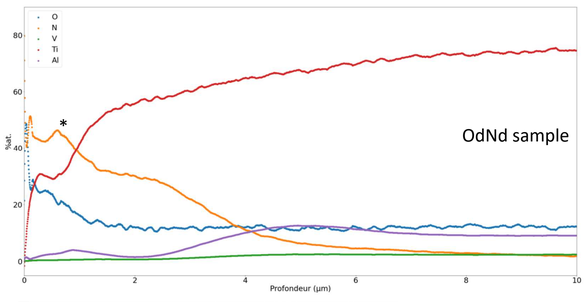


SEM cross section of sample N.
Small Ti_2N (ε phase) elongated grains in the surface layer. Short underlying Ti(N) depleted in β-Ti phase

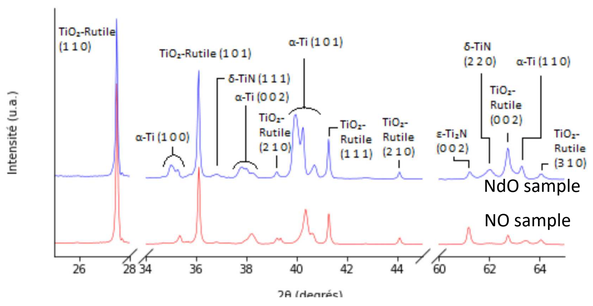
Sequential NO or ON treatments

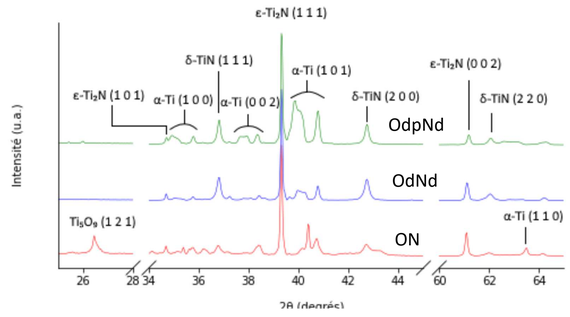


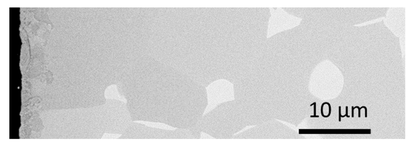


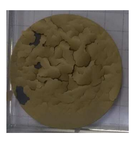


*: N level in oxide layer may be due to porosity (air)

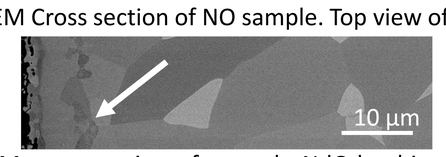






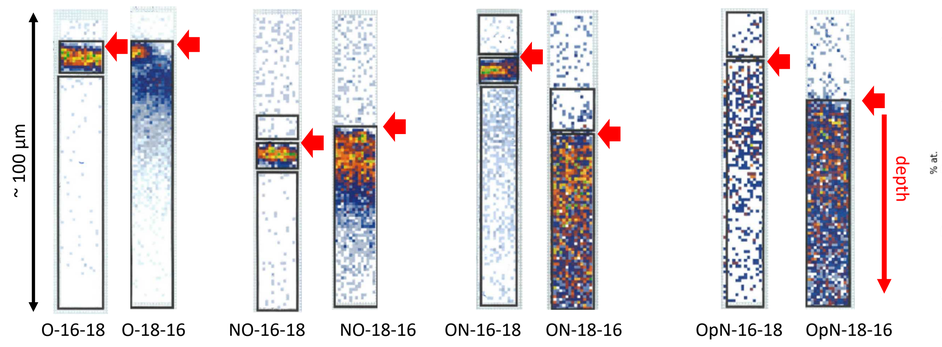


SEM Cross section of NO sample. Top view of the delaminated TiON layer

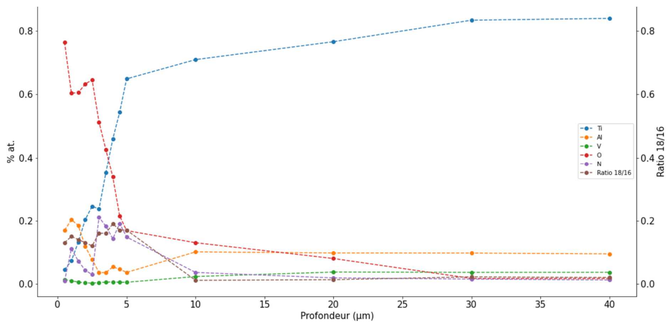


SEM cross section of sample NdOd, white arrow indicates small grains enriched in the aluminium.

NRA investigations

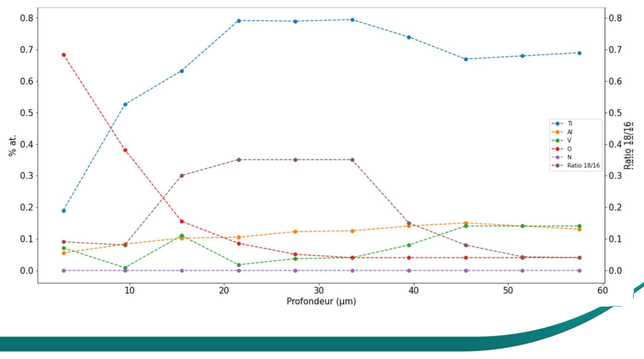


NRA ^{18}O counts maps ; RED arrow: surface position ATTENTION : color scales are not the same within all the map



NRA normalized detected reaction counts

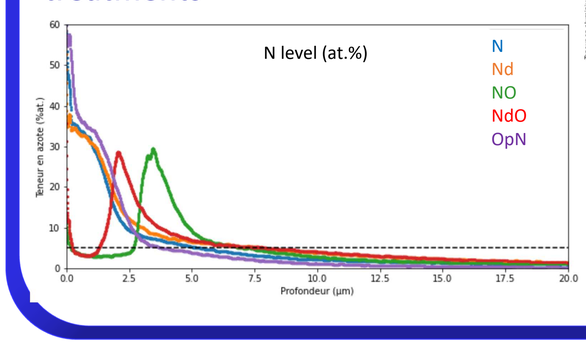
Sample	Layer	Diffusion zone
O-16-18	140	2
NO-16-18	160	8
ON-16-18	180	50
OpN-16-18	—	45

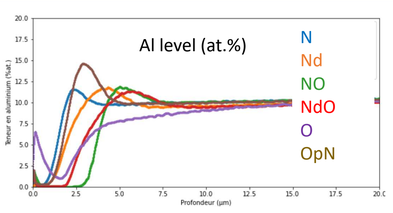


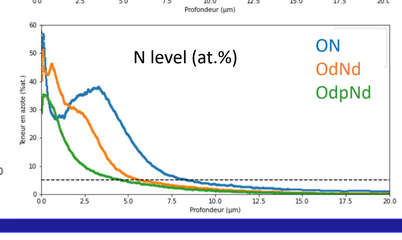
Oxidation is performed by:
- O adsorption at surface
- diffusion by replacement O cascade till oxide/Ti6Al4V interface
- Ti short diffusion at the oxide/Ti6Al4V to react and form oxide

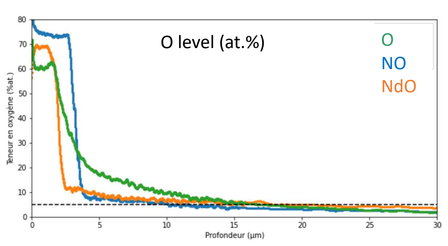
Previous nitriding does not modify the O diffusion mechanism

Influence of multi-interstitials treatments









Conclusion

- NRA $^{18}O/^{16}O$ analysis enables to determine that O is not diffusing through the oxide layer; the TiO2 layer is growing by a simple "cascade" mechanism of O till the interface.
- The Al profiles indicates the Ti diffusion from the bulk to the oxide/Ti6Al4V interface.
- Previous Nitriding, leading to TiN/Ti_2N/Ti(N), limits the deep O diffusion in solid solution.
- Influence of previous oxidizing leading to TiO_2/Ti(O) on the Nitrogen diffusion in solid solution has to be clarified (GDOES profiles are unclear due to porosity in TiO_2 layer).