ESRF	**Experiment title:** Laser surface gas reactions: nitriding, carburising and silicide formation	**Experiment number**: HS-1951
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Report:

Nitriding is a common technique to enhance the hardness and the corrosion-wear resistance of metallic surfaces. For this purpose, pure titanium substrate have been irradiated with an infrared (3.1 µm) Free Electron Laser (Thomas Jefferson Labs., Newport News, VA, U.S.A.) in nitrogen atmosphere. The peculiarity of this laser is its time structure: each *macropulse* is made by a series of 2 ps pulses with repetition rate of 37.4 MHz and overall duration ranging from 50 to 1000 µs. Several samples have been irradiated with different laser parameters (macropulse duration, laser fluence, spot overlap), and a strong crystallographic texture have been observed, depending mainly on the laser spot overlap. Although the long range order investigated by XRD has shown the formation of fcc TiN, the local atomic order and the exact stoichiometry on the surface were unknown.

The XANES spectra at the Ti K-edge (E=4966 eV) of some selected samples irradiated under different conditions (see Table I) are shown in Fig. 1. The parameters t_m, ϕ_m, σ refer to the macropulse duration, the laser fluence and the spot overlap (the higher its value, the stronger the overlap), respectively.

Table I. Irradiation parameters of the samples shown in Fig. 1.

Sample	t_m (µs)	σ	ϕ_m (J/cm^2)
Ti18	250	0.6	125
Ti19	500	0.3	250
Ti20	750	0.3	375
Ti22	1000	0.1	500
Ti23	1000	0.05	500

The XANES edges are re-normalized for the sake of the viewer and compared with the fingerprints of pure Ti (dash) and the TiN standard (dot). Dispite of the large range of experimental parameters, it is evident how the spectra of the irradiated samples look extremely similar, suggesting that the resulting chemical structures are rather insensitive to the experimental conditions. The “white line” of TiN (E = 4983 eV) is visible in all samples, although it is shifted (~1 eV) to lower energy compared to the TiN standard. Besides, the resonant peak of Ti at E=4966 eV seems to appear, to lower extent, in all spectra except the TiN standard, suggesting a small presence of non-reacted Ti on the surface.

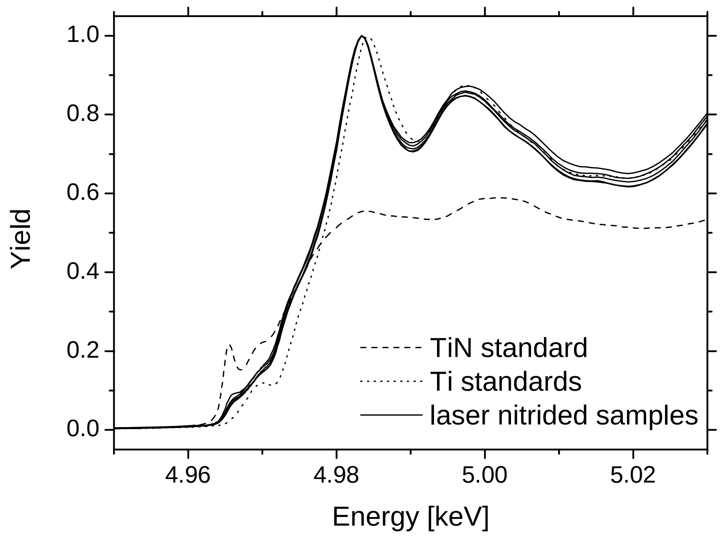

Fig. 1. XANES spectra of some laser-irradiated Ti samples (Ti K-edge at E=4966 eV): the dash line is the spectrum of pure Ti, while the dotted line is the spectrum of the TiN standard.

Also the EXAFS oscillations of the treated samples reveal a remarkable resemblance, as shown in Fig. 2, confirming the weak dependence of the local atomic ordering (especially the surface stoichiometry) on the laser parameters.

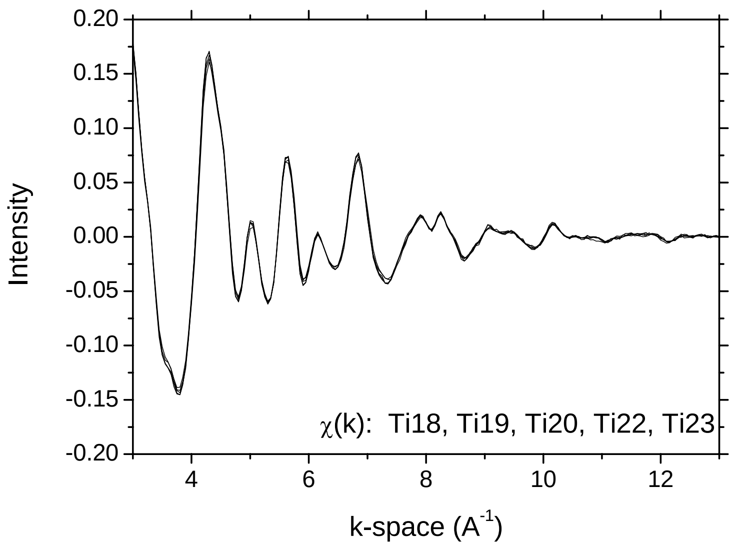

Fig. 2. EXAFS oscillations of some laser-irradiated Ti samples.

The results of this analysis has reveald that Free Electron Laser nitriding is a very successful method to incorporate nitrogen in the irradiated metal. Variations of (i) the spot overlap (and therefore the speed of the treatment) of a factor of 10 and (ii) the laser fluence of a factor of 4 (see Table I), lead to no significant changes in the morphology of the short range order, allowing us to optimize the processing parameters in order to achieve the best results with the lowest energy and the shortest time, that is the final goal of our research.