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Initial stages of oxide formation on titanium surfaces during oxygen bombardment at room temperature: An XPS study

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INTRODUCTION & AIM

Titanium is widely used in aerospace, biomedical, and energy applications due to its excellent mechanical properties and corrosion resistance. The surface oxidation of titanium plays a critical role in its performance, particularly in thin film applications and surface treatments. Understanding the early stages of oxidation at the atomic level is essential for controlling oxide layer growth and improving surface functionality.

This study investigates the oxidation of metallic titanium induced by low-energy O_2^+ ion bombardment under ultra-high vacuum conditions. The main goal is to monitor the evolution of titanium oxide states using X-ray Photoelectron Spectroscopy (XPS), enabling identification of oxide phases and analysis of the oxidation mechanism. By deconvoluting photoemission spectra with fitting functions such as Gaussian-Lorentzian and Doniach-Šunjić, we aim to follow the formation and progression of TiO, Ti_2O_3, and TiO_2 states over time.

METHOD

Prior to oxidation, the polycrystalline titanium sample was mechanically polished and cleaned in an ultrasonic bath with acetone. Surface cleaning and oxidation were performed **in situ** in an ultra-high vacuum (UHV) XPS chamber at room temperature (25 °C).

Initial surface preparation involved several cycles of **Ar^+ ion sputtering** (2 keV) to remove contaminants. Oxidation was carried out by bombarding the clean surface with **O_2^+ ions** at 1 keV, at various time intervals ranging from 15 seconds to 180 minutes. Each O_2^+ ion dissociates upon surface impact into two oxygen atoms of 500 eV each. The ion beam was directed at a 25° angle relative to the surface normal, with a current density of 2 μA/cm².

XPS measurements were acquired under UHV conditions (≈10^{-7} Pa) using a **SPECS XPS system** equipped with a Phoibos MCD 100 energy analyzer and a monochromatic **Al Kα X-ray source** (1486.74 eV). Spectra were analyzed using **UNIFIT** software, applying Gaussian-Lorentzian and **Doniach–Šunjić** line shapes to fit Ti 2p core levels and valence band spectra. Background subtraction was performed using the Shirley method, with particular attention to the asymmetric shape of metallic Ti peaks.

Figure 1. Experimental setup – XPS device

RESULTS & DISCUSSION

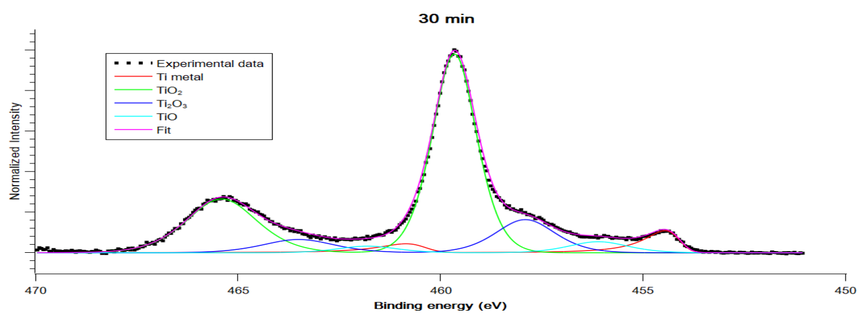

Figure 2. Ti 2p XPS spectrum after 30 min oxidation - experimental spectrum (black dots) and fitted components for metallic Ti (red), TiO (cyan), Ti_2O_3 (blue), and TiO_2 (green). The total fit is shown in magenta

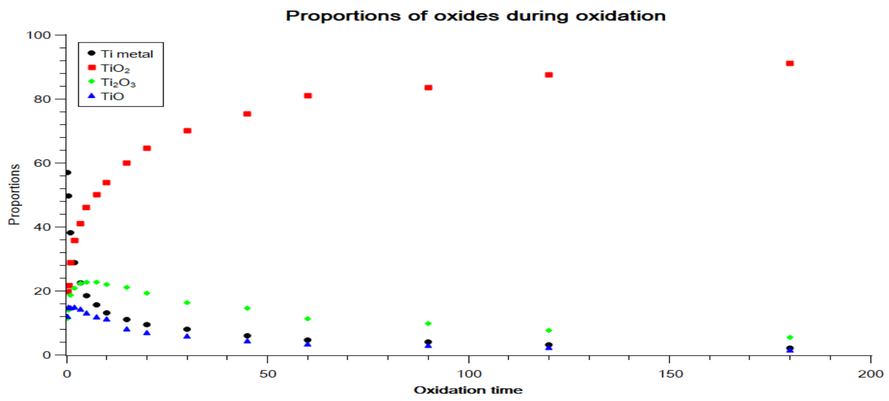

Figure 3. Evolution of Ti, TiO, Ti_2O_3, and TiO_2 components obtained from Ti 2p spectral deconvolution. TiO_2 fraction increases with time, becoming the dominant phase after 180 min

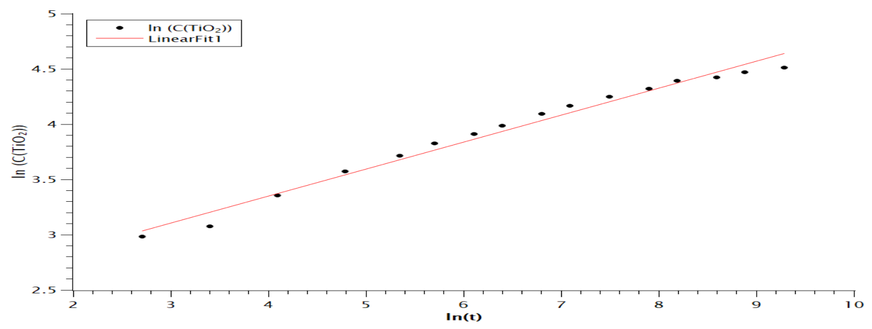

Figure 4. Log–log plot of TiO_2 concentration versus oxidation time. Linear correlation between ln(C_TiO_2) and ln(t) with slope ≈ 0.25 indicates diffusion-controlled oxidation kinetics in agreement with Wagner's theory

XPS analysis of the Ti 2p region revealed progressive oxidation during O_2^+ ion implantation. After 30 minutes, deconvolution showed coexisting metallic Ti, TiO, Ti_2O_3, and TiO_2. With time, **TiO_2 became the dominant species**, confirming surface oxidation. The **log–log plot of TiO_2 concentration vs. time** showed a slope of 0.25, consistent with **Wagner's diffusion-limited growth** via **singly charged cation vacancies**. The resulting TiO_2 behaves as a **p-type semiconductor**, and growth slows as the oxide layer thickens and diffusion pathways become restricted.

CONCLUSION

Controlled O_2^+ ion implantation induces progressive oxidation of Ti, leading to the formation of TiO_2 as the dominant surface oxide. XPS analysis confirms a **diffusion-controlled growth** mechanism consistent with **Wagner's theory**, with a **$t^{1/4}$ dependence** and **p-type semiconducting behavior** of TiO_2. These findings highlight the potential of ion implantation as a **precise method for engineering ultrathin oxide layers**, relevant for applications in **biocompatible coatings**, **corrosion-resistant surfaces**, and **semiconductor devices**.

FUTURE WORK / REFERENCES

Pupavac, P. *Oxidation of Metallic Titanium Studied by X-ray Photoelectron Spectroscopy (XPS)*. Master's Thesis, Faculty of Physics, University of Rijeka, 2023.