PLASMA ELECTROLYTIC OXIDATION OF TITANIUM AND ITS SURFACE CHEMISTRY INVESTIGATION

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Abstract

In the field of structural materials, the research to improve their properties is of real interest and continuously evolving. Titanium belongs to an advanced clad materials category having the technology readiness level (TRL) 1. Thus, a significant level of further development of this material is required before becoming commercially used. In this context, the development of environmentally friendly surface engineering techniques is still a great challenge. Plasma Electrolytic Oxidation (PEO) is an environmentally friendly technique used with great benefits to improve the surface properties of light alloys (Al, Mg, Ti, and Zr). The present study focuses on the development of titanium oxide/phosphate films on commercially pure titanium substrate by plasma electrolytic oxidation, and assessment of their surface chemistry at the metal-electrolyte interface. Post-deposition, the X-ray photoelectron spectroscopy analysis of the samples highlighted the successful formation of a surface coating consisting of a mixed oxide, containing both titanium oxide and titanium phosphate, as a result of an applied potentiostatic regime in NaH_2PO_4 electrolyte during the PEO process. These results, obtained in the first layers of the surface, are of great interest for understanding the chemical behaviour of titanium-based materials in oxidizing environments, important aspect for the Generation IV nuclear energy systems.

Keywords: *PEO, XPS, titanium oxide, titanium phosphate*

Introduction

Studies have shown that titanium and its alloys can be used for the primary circuit components of a pressurized water reactor due to their low neutron activation level and good mechanical properties [1]. However, the corrosion resistance is a major concern for nuclear and industrial applications, as metals have to face the harsh chemical and physical environment in a nuclear reactor [1-3]. Thus, heat-exchange tubes, steam generators, condensers, feed pipes are manufactured from titanium and designed to operate under high temperature, high pressure and radiation environmental conditions [2-4].

On the other hand, fuel-cladding chemical interaction between metallic fuel and cladding material was predicted for the next generation nuclear power reactors (Gen IV) during high temperature operation [5, 6]. As a consequence, this chemical process reduces the effective cladding thickness, which further reduces the mechanical integrity and the lifetime of the fuel element [7].

In this regard, a possible approach suggested in the literature is to develop a diffusion barrier coating consisting of titanium oxides for fuel cladding applications [7, 8] of interest for both, present and next generation nuclear reactors. The main engineering challenge for the coating process of a tubular fuel cladding material lies in the deposition of an oxide layer grown on the inside surfaces of tubular geometries [7].

For this reason, plasma electrolytic oxidation (PEO) is a suitable method for growing oxides of multiple thicknesses with tailored structural and surface properties by controlling film deposition conditions. PEO process involves electrochemical oxidation of a metal in an electrolyte solution and the ability to coat the inner and outer surfaces of tubular components. Therefore, the first aim of this study was to prepare and characterize titanium oxides and phosphates on titanium substrates as a confirmation test platform which could be further extended in the future for zirconium based alloys, such as Zy-4 and Al-Cr-Zr.

Experimental

Plasma electrolytic oxidation method was employed to obtain titanium dioxide on pure titanium substrate. This process was performed using a single-pole and pulsed, direct-current power source, at a frequency of 150 Hz. The duty cycle was fixed at 40%. The electrolytic solution containing sodium hydrogen phosphate (NaH_2PO_4) was prepared using pure reagents and distilled water.

The samples were made of grade 2 commercially pure titanium sheet which was shaped into square pieces of 10x10x0.5 mm^3 in size. The chemical composition of the titanium substrates is as follows: 0.105 % Fe; 0.011 % C; 0.175 % O; 0.006 % N; 0.0005 % H and balanced Ti.

After a mechanical polishing with sandpaper of grit size 200-1400, the samples were degreased and cleaned with ethyl alcohol and distilled water before plasma treatment. During the PEO process, the voltage was raised to 50V and held for 2 min until spark discharges occur. At this point, the voltage was increased rapidly to 200V and was kept constant throughout the process (10 min), after which the voltage was abruptly reduced to 0V, when the experiment ended.

The surface composition of the PEO films was determined with an Escalab 250 electron spectrometer using monochromatic AlKα radiation at 1486.6 eV. A base pressure of 10^{-8} Pa was maintained in the ultra-high vacuum chamber during the X-ray photoelectron spectroscopy (XPS) measurements. The acquired binding energies were referenced to the C1s line at 284.8 eV of the surface adventitious carbon

Results and discussion

PEO deposited oxide layers on titanium were studied by XPS before and after 30 sec in-situ Ar^+-ion etching to investigate the chemical composition at the surface and near-surface region of the coated substrates. For this study, the argon-ion bombardment was performed at 1 keV with an ion current density of 0.5μA/cm^2 and a raster size of 3x3 mm^2 in order to avoid altering the chemical information of the surface.

The XPS wide spectra before and after Ar^+ sputtering show the main XPS core-level peaks associated with Ti2p, Na1s and P2p (Fig.1 and Fig. 2). After 0.5 min ion etching, carbon (the main surface contaminant) was significantly reduced, from ~ 62% to ~ 42%, confirming its contaminant nature, without being incorporated into the sample matrix (Table 1). At the same time, there is an increase of titanium content together with phosphorus and sodium, the latter two corresponding to electrolyte constituents (Table 1). Although initially detected on the surface, silicon was also removed after sputter-cleaning. Calcium has a constant behaviour, its presence being noticed on the surface regardless of ion bombardment. A possible cause can lead to the reagents used for the preparation of the electrolytic solution. Additionally, magnesium can be found after the carbon removal.

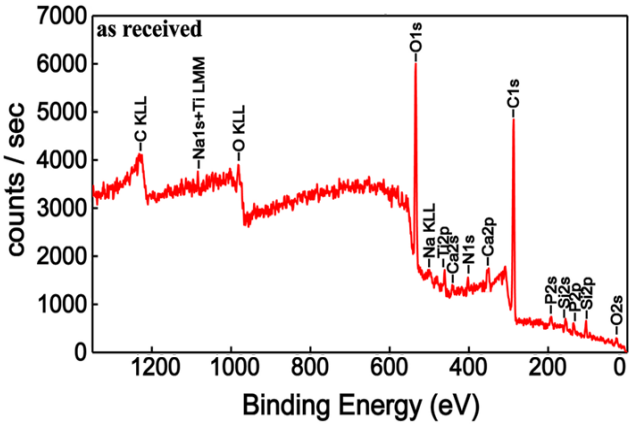


Fig. 1. XPS general spectrum (survey) of the PEO-coated titanium substrate before Ar^+ ion etching

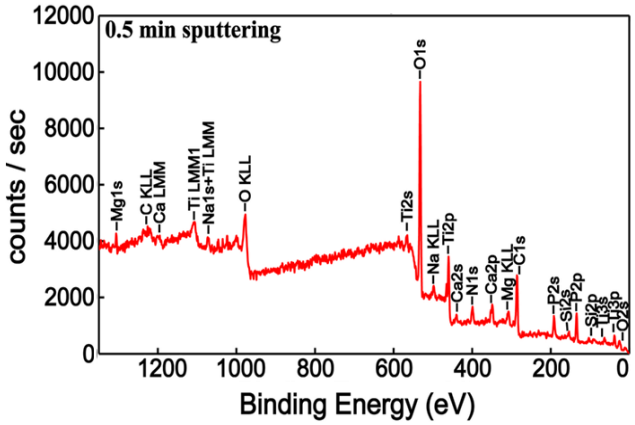


Fig. 2. XPS general spectrum (survey) of the PEO-coated titanium substrate after 30s Ar+ ion etching

Table 1. Element relative concentrations (at.%)

Sample	C1s	O1s	Na1s	Si2p	P2p	Ti2p
0.0 min Ar^+ ion etching	62.6	29.0	-	3.9	3.0	1.5
0.5 min Ar^+ ion etching	42.0	41.7	2.5	-	8.2	5.6

As depicted in Fig. 2, at large strains (short life) the plastic strain component is predominant, while at the small strains (longer life) the elastic strain component is predominant. Strain line fatigue curve is plotted on a log-log scale.

On the other hand, the appearance of oxygen, titanium, phosphorus and sodium on the sample surface confirms the formation of the PEO coating layer through the oxidation and chemical interaction between the metal substrate and sodium hydrogen phosphate solution.

The curve fitting of O1s peak (Fig.3) shows P-O/P=O and P-O-H chemical bondings located at 530.9 eV and 532.5 eV, respectively, [9-11]. Thus, on one hand, the fingerprint of phosphorus is much stronger than that of titanium in the oxygen spectrum, the latter being normally peaked at a lower binding energy (~ 529.8 eV). On the other hand, a very low amount of titanium (< 5%) is found on the surface (according to Table 1). This is normal because titanium acts as a substrate.

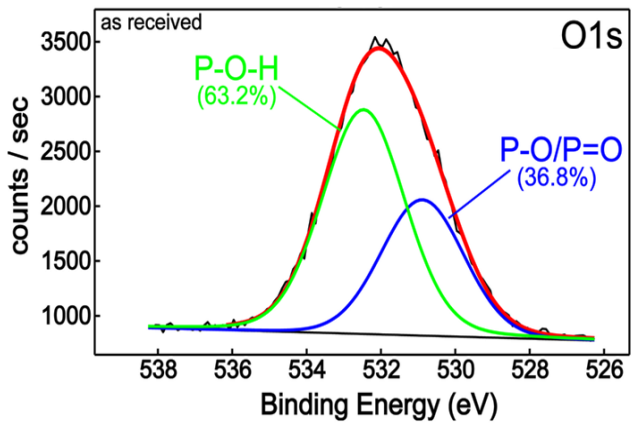


Fig. 3. O1s XPS deconvoluted spectrum of the PEO-coated titanium substrate before Ar^+ ion etching

The O1s spectrum recorded following the Ar^+ ion sputtering (Fig.4) indicates an increase of the P-O/P=O contribution, from ~36% to ~70% accompanied by a decrease of the P-O-H feature, from ~63% to ~28% (Fig. 3 and Fig. 4), which is in good agreement with titanium chemistry through the increase of titanium phosphate (see Fig. 7 and Fig. 8). In addition, these qualitative observations are consistent with quantitative determinations of increased titanium and phosphorus concentrations after cleaning the surface with argon ions (Table 1). Furthermore, the quantitative analysis shows a P/Ti ratio of 1.46, in close agreement with the nominal value of 1.33 for titanium phosphate, $Ti_3(PO_4)_4$, while at the same time confirming the qualitative results on titanium phosphate.

Peak-fitting the P2p spectra resulted in two components as shown in Fig. 5 and Fig. 6. The features located at 132.1 eV and 133.3 eV can be associated to $(PO_4)^{3-}$ and $(H_2PO_4)^-$, respectively, [9, 11-13]. The chemical states concentration labelled on the spectra reveals an increase of $(H_2PO_4)^-$ ion, from ~ 27% to ~ 90% followed by the dramatic decrease of $(PO_4)^{3-}$ ion, from ~ 73% to ~ 9%.

For the current paper, fatigue behavior simulations of Zy-4 C43 samples were performed, in which the number of finite elements was varied with the purpose of highlighting the quality and precision of computations. For the selected thick and thin samples two cases were taken into account. In the first case (*case 1*) the sample thickness was divided in 4 sections, and the element dimension of 0.4 mm was imposed. For the second case (*case 2*), the sample thickness was divided in 6 sections, and the element dimension of 0.2 mm was taken into account.

Figs. 4 and 5 show the number of nodes and elements for each case. The finite element discretization for the two cases is illustrated in Fig. 6.

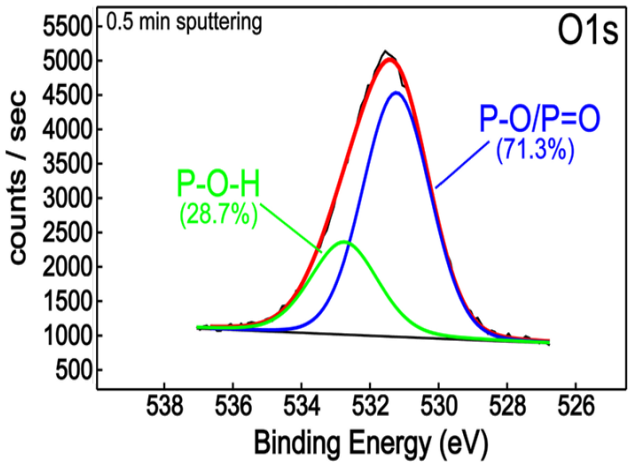


Fig. 4. O1s XPS deconvoluted spectrum of the PEO-coated titanium substrate after 30s Ar^+ ion etching

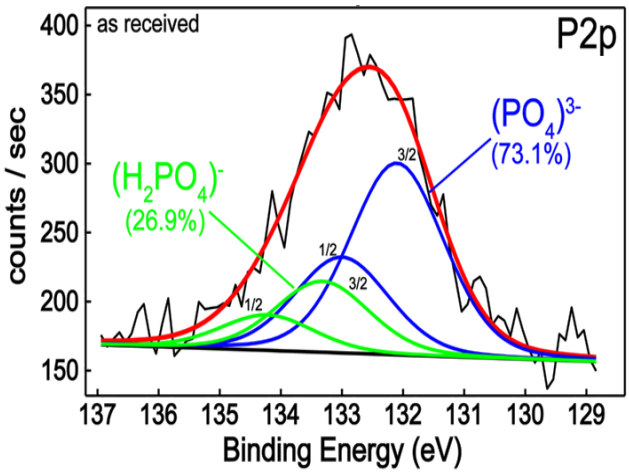


Fig. 5. P2p XPS deconvoluted spectrum of the PEO-coated titanium substrate before Ar^+ ion etching

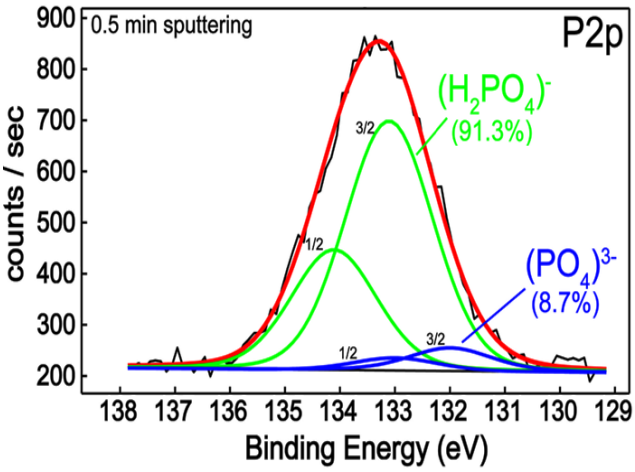


Fig. 6. XPS deconvoluted spectrum of the PEO-coated titanium substrate after 30s Ar^+ ion etching

Moreover, the chemical tendency of titanium is perfectly correlated with phosphorus and hence, the amount of titanium phosphate increases with the increase of $(H_2PO_4)^-$ ion, as presented in Fig. 7 and Fig. 8.

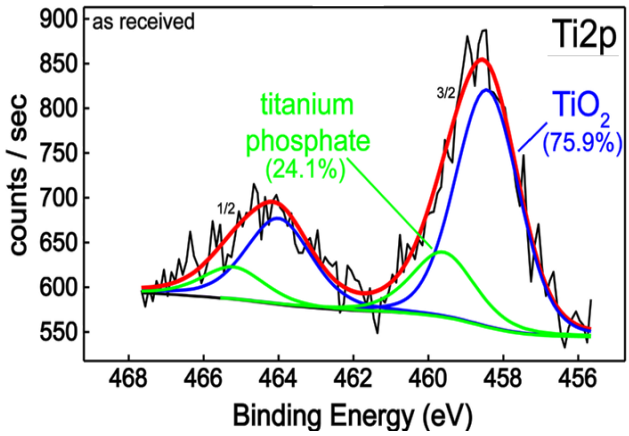


Fig. 7. Ti2p XPS deconvoluted spectrum of the PEO-coated titanium substrate before Ar^+ ion etching

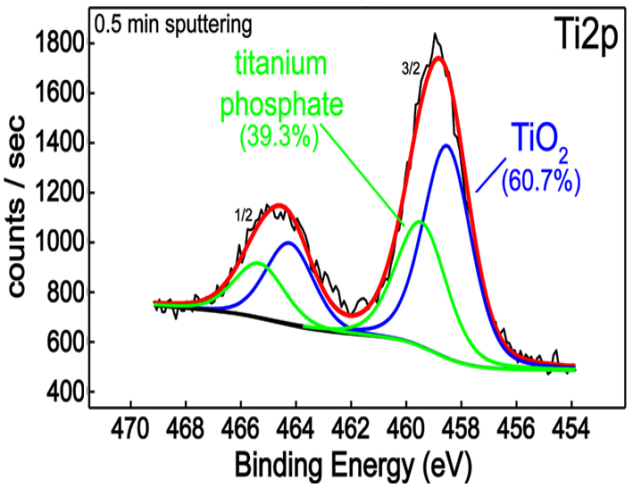


Fig. 8. Ti2p XPS deconvoluted spectrum of the PEO-coated titanium substrate after 30s Ar^+ ion etching

Surface chemistry of titanium (Fig. 7 and Fig. 8) shows a mixture of titanium chemical states, namely fully oxidized titanium and titanium phosphate, and located at 458.4 eV and 459.5 eV, respectively, [9, 11-13]. Additionally, titanium phosphate increases from ~ 24% to ~ 40% after Ar^+ etching, whilst this chemical trend was observed also in oxygen behaviour (Fig.4) as P-O/P=O feature increases.

The sodium presence was detected only when the surface was etched (see Fig. 9, Table 1).

Using the deconvolution procedure, it was possible to distinguish between the overlapping signals of Ti Auger transitions and sodium chemical states. Therefore, sodium was found in the form of Na_3PO_4 located at 1070.8 eV (~21%) and NaH_2PO_4 (~40%) located at 1072.2 eV, respectively, [11, 14], according to phosphorus chemistry which shows a quantitative increase of the acid phosphate ion (Fig. 6).

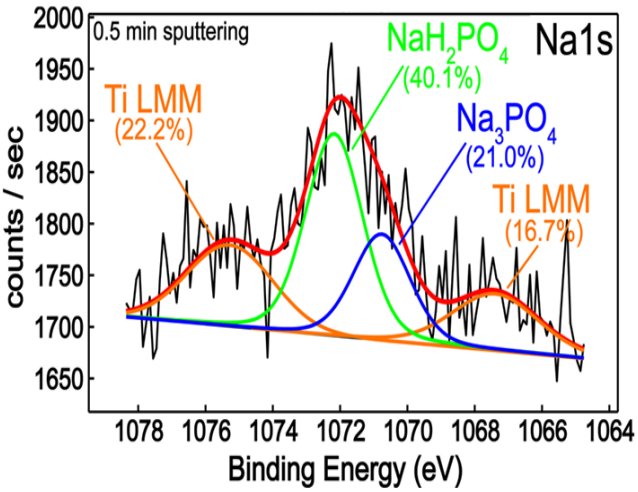


Fig. 9. Na1s XPS deconvoluted spectrum of the PEO-coated titanium substrate after 30s Ar^+ ion etching

Conclusions

The present work aimed to assess the surface chemistry at the metal-electrolyte interface for the titanium oxide/ phosphate films obtained on commercially pure titanium substrate by using Plasma Electrolytic Oxidation (PEO) technique.

Coatings were developed on commercially pure titanium substrates by PEO in an electrolytic solution containing NaH_2PO_4 under an applied potentiostatic regime. Formation of the PEO films was confirmed by X-ray photoelectron spectroscopy.

The atomic concentrations of titanium and phosphorus were highlighted, before and after Ar^+ ion etching, Ti^{4+} (TiO_2) being identified as the oxidation state of titanium.

The successful incorporation of phosphorus into the coating, its chemical interaction with the metal substrate and the occurrence of titanium phosphate has been demonstrated.

The results obtained in the outermost surface layer can be of great interest to the corrosion science community as the corrosion process begins and ends at the surface.

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