Formation of plasma electrolytic oxidation coatings on pure niobium in different electrolytes

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ABSTRACT

The development of PEO surface treatments for Nb (niobium) provides a possibility to produce functionalized coatings with a combination of new compositions and phases. In the frame of this work, PEO coatings on pure Nb are produced in three electrolytes containing aluminate, phosphate and silicate. Furthermore, the influence of the electrolyte composition on the PEO process and the microstructure, composition and properties of the coatings were studied. It was observed that most of the coating forming species did not participate in the plasma reactions directly, while the chemical-, electrochemical- and thermal stimulated reactions are dominating the coating formation. The results show that all the coatings are mainly composed of the Nb oxide layer on pure Nb is necessary in terms of the microstructure and corrosion resistance. Nevertheless, modification of the native oxide layer on pure Nb is necessary in terms of the microstructure and composition for further applications.

1. Introduction

Niobium (Nb) based materials are of great interest in various applications, strikingly for the fields of catalysis [1–4] and biomedicine [5–9] relying upon their catalytic activity and bio functionality. Nb oxide’s combination with redox property, acidic property and photosensitivity has been used especially in catalytic reactions where it can remarkably promote the processes [10–12]. As biomedical implants, the intriguing properties of biocompatibility, corrosion resistance and specific strength also render Nb materials practical to reconstruct the failed tissue in the body [13–16]. A thin oxide layer of Nb₂O₅ is deposited on the surface of pure Nb immediately through spontaneous oxidation, isolating it from the corrosive environment. Nevertheless, modification of the native oxide layer on pure Nb is necessary in terms of the microstructure and composition for further applications.

Plasma electrolytic oxidation (PEO) is an advanced surface modification process. It has been widely performed on light metals such as Al [17,18], Mg [19,20] and Ti [21,22] to form ceramic-like coatings. The PEO coatings are primarily composed of the metal oxides of the substrate metals [23–25], such as, Al₂O₃, MgO and TiO₂. PEO technology is also a promising candidate to produce functional coatings on pure Nb. The semiconducting Nb oxides in combination with the inherent porosity of PEO layer are potentially interesting for the catalytic efficiency as well as for the osseointegration of bio-implants.
According to the intensive studies of PEO processing on Al, Mg and Ti, the process is generally made up of few stages including the conventional anodization, discharging and sparking [26]. With the assistance of plasma, the electrochemical-driven process enables the formation of coatings with excellent corrosion and wear resistance. Most studies of plasma electrolytic oxidation involving Nb were focused on metallic substrates alloyed with Nb, such as Ti-Nb, Zr-Nb and Ti-Nb-Zr alloys [27–29]. Only a limited number of studies are available for pure Nb substrates [30–38]. Stojadinovic et al. [30,32] studied the luminescence during PEO processing of pure Nb in acidic electrolyte before and after reaching the breakdown voltage. The sparking emissions were only composed of signals from oxygen and hydrogen atoms, originating from the electrolyte. The absent spectral line of Nb resulted from the high melting point of Nb (2447 °C) hindering its evaporation during the processing. PEO coatings on pure Nb were composed of Nb oxides and complex compounds deriving from the electrolytes. A study [34] has claimed hydroxyapatite formation in the coating on pure Nb during PEO processing after doping with calcium acetate in the phosphoric acid electrolyte. Furthermore, SiC particles, added to the electrolyte, were revealed partly buried in the coating on pure Nb [36].

With respect to the extensive reports of PEO processing on Mg, Al and Ti alloys [39–41], the insight of PEO process on pure Nb is also necessary considering the complexity of possible reaction mechanisms with the electrolytes. This work was focused on the formation of PEO coatings on pure Nb in three different types of PEO electrolytes, containing phosphate, silicate and aluminate, respectively. The evolution of the coating formation process in different electrolyte composition was studied during the treatment as a function of processing time. For comparison reasons, the microstructure and composition of the resultant PEO coatings were also characterized by a combination of analytical techniques, correlated with the evaluation of photocatalytic activity and degradation resistance.

2. Materials and methods

A pulsed DC power source was used to carry out the PEO processing on the pure Nb for 600 s under a constant current density of 10 A/dm². A duty cycle of 10 % and a frequency of 100 Hz were selected. Rectangular specimens of pure Nb with dimensions of 15 × 15 × 4 mm were used as anode and processed in three different aqueous electrolytes, containing (1) NaAlO₂ 20 g/L and KOH 1 g/L (pH 12.49, conductivity 520 µS/cm), (2) Na₂SiO₃ 20 g/L and KOH 1 g/L (pH 12.29, conductivity 496 µS/cm) and (3) Na₃PO₄ 20 g/L and KOH 1 g/L (pH 12.72, conductivity 529 µS/cm), respectively. A stainless steel tube cathode was integrated in the cooling system to keep the temperature of the electrolyte at 20 ± 2 °C. A mechanical stirring system was used to agitate the electrolyte keeping it homogeneous and avoid temperature gradients. The specimens were labeled as PEO-Al, PEO-P and PEO-Si after treatment in aluminate-, phosphate- and silicate-based electrolyte, respectively. The voltage response as a function of processing time was recorded using a data acquisition system (SignaSoft 6000 software package, Gantner, Germany). The spectral emission of the plasma was monitored during PEO processing, using an Emicon OES system (PLASUS, Germany). The following data acquisition system (DESY, Hamburg, Germany) using the nano focus end station of the beamline P03 at PETRAIII storage ring [42]. The X-ray beam energy was 19.7 keV with a beam size of 1.5 by 1.5 µm. An Eiger 9 M detector was employed with a pixel size of 75 µm by 75 µm. The beam was scanned across the surface in steps of 2 µm and 4 µm in vertical and horizontal direction respectively, covering a measured area of 80 µm × 80 µm. Each XRD pattern was recorded with an acquisition time of 0.5 s. Data reduction was done by employing in-house developed Matlab® code and the PyFAI [43] routine. The scattering angle 2θ of the diffraction pattern was converted to Cu K-alpha radiation with the wavelength of 1.5406 Å. The spatial distribution of the phases in the coating was reconstructed, in order to reveal the phase distribution across the coating thickness. A lab-made script in Python programming language was operated in the “Snyder” software package environment included with Anaconda Navigator, to analyze and generate two-dimensional phase map graphics.

The photocatalytic properties of the PEO coatings on pure Nb were investigated by measuring photodegradation of methyl orange (MO) at room temperature. The temperature in the photoreactor was kept constant by a water recirculation system. The specimen surface, placed on a perforated holder, was immersed in a 10 ml aqueous solution containing 8 mg/L of MO, under constant stirring conditions (300 rpm) and positioned under the irradiation source. Prior to irradiation, the catalyst and solution were stirred in the dark for 30 min to achieve adsorption–desorption equilibrium. Then, the solar radiation was simulated using a lamp (Osram Vitalux 300 W), fixed at 25 cm above the surface of the solution providing 16,000 lx intensity. The total irradiation duration was selected to be 6 h. A fixed quantity of 1 ml MO solution was taken every hour to measure the MO concentration at the maximum of the absorption spectra (λ = 464 nm) by Agilent Cary 60 UV–vis spectrophotometer. The absorption was converted to concentration according to a standard curve showing the linear dependence between MO concentration and absorption at 464 nm wavelength. Similarly, the MO adsorption in darkness with the presence of photocatalyst was also recorded every hour during 6 h. After each measurement, the solution was returned to the photocatalytic reactor. Prior to the measurement, MO solution was tested for photocatalysis in the absence of the photocatalyst to confirm its stability. The absence of change in MO concentration after 6 h of irradiation indicated its stability under the applied conditions and its degradation resulted only from the presence of a photocatalyst. The adsorption and degradation percentage of MO was given as ((C₀/Cₜ)/C₀), where C₀ was the initial MO concentration and Cₜ was the MO concentration before and after exposure.

The corrosion resistance of the PEO coated specimens and bare Nb was evaluated by performing potentiodynamic polarization and electrochemical impedance spectroscopy experiments, with a computer controlled Gamry potentiostat Interface 1010E. A classical three-electrode cell system was used and the specimens were acting as a working electrode. The counter and the reference electrode were a Pt wire and a saturated Ag/AgCl electrode, respectively. A specimen surface area of 0.5 cm² was exposed to Ringer’s solution (8.6 g/L NaCl, 0.3 g/L KCl and 0.56 g/L CaCl₂⋅2H₂O). After 1000 s immersion at open circuit potential, potentiodynamic polarization scan started from +1.0 V vs reference electrode at a scan rate of 0.5 mV/s and terminated at 10 V. EIS (electrochemical impedance) tests were carried out at open circuit potential with AC amplitude of 10 mV RMS over the frequency range of 100 kHz - 0.01 Hz. The measurements were performed after subsequent immersion durations of 5 min, 1 h, 3 h, 6 h, 12 h, 24 h, 48 h, and 72 h, respectively. The same measurement was reproduced on three specimens for each PEO coating for repeatability.
3. Results

3.1. Voltage evolution

The voltage as a function of processing time in three different electrolytes containing aluminate, phosphate and silicate is shown in Fig. 1, respectively. The voltage response is typical for the current-controlled PEO processing [44–46] and two stages are obviously revealed. At the initial conventional anodization, the primary oxide layer from air and electrolyte passivation facilitates the rising of the voltage. The continuous voltage increase, resulting from the coating formation and increasing electrical resistance, maintains the pre-set current density. The voltage ramp shows average growth rates of 27.8 V/s, 13.8 V/s and 27.1 V/s in aluminate-, phosphate- and silicate-based electrolytes, respectively. Subsequently, the voltage ramp experiences a transition due to the development of discharges on the specimen surface. The presence of discharges manifests the commencement of the second stage. It takes 20 s and by reaching ca. 350 V, the discharges become visible in the aluminate-based electrolyte. However, it only takes around 10 s in phosphate- and silicate-based electrolytes to reach the breakdown voltage of ca. 240 V and ca. 260 V, respectively. Afterwards, the voltage increase declines further, at average rates of 0.13 V/s, 0.30 V/s and of 0.29 V/s for PEO-Al, PEO-P and PEO-Si specimens, respectively. The final voltage of PEO-Al specimen is 489 V after 600 s of processing, much higher than that of PEO-P (402 V) and PEO-Si (418 V) specimens.

3.2. Optical emission

At the beginning of the process, anodic luminescence is observed with color evolution on the specimen surface. It is associated with the collision-radiative recombination of electrons and bremsstrahlung radiation at the conventional oxidation stage [20,30,47]. Once the discharges appear, they rapidly cover the entire specimen surface. The discharges are firstly tiny, short living and fast moving, and then their size and lifetime increase, accompanied by a color change. Their motion slows down with time. At the end of the process, the discharge number dwindles obviously and they become large-sized and long-lasting. It seems that the appearance of static large-sized discharges at certain regions is due to the rapid creating and extinguishing of a cluster of discharges [47]. Furthermore, the process is always accompanied by gas evolution on the surface due to the oxygen production and electrolyte evaporation under the high temperature of the discharges.

The characteristics of the discharges have a great influence on the PEO coatings, such as its growth, composition and morphology [26].
stability. This was also observed in an investigation using phosphoric acid [30]. With increasing processing time, the emission intensity for all specimens rises. A broad halo was observed in the visible wavelength range between 450 nm and 650 nm at 374 V after 20 s of treatment in the aluminate-based electrolyte (Fig. 2(a)). It confirms the first observation of the white shining at the voltage up to 350 V. Subsequently, the color of the discharges changes immediately from white to orange-yellow. At that moment, a surge of discharging intensity at 598 nm (Na I) is found to reach the technical saturation limit of the detector under 415 V (30 s). Thus, the color change of the discharges is ascribed to the dominant Na species in the plasma discharges. In addition, it can be seen that the spectral lines of H I, K I, Al I and OH band are also present with further increasing voltage. In the silicate-based electrolyte, the discharge emission shows similar patterns under a lower voltage (Fig. 2(c)). The strong line of Na I appears already at 273 V (10 s). The spectral lines of other species, including H I, OH and K I, are starting to be seen under a voltage of 397 V (220 s). For the treatment in the phosphate-based electrolyte, the emission intensity is revealed to be the lowest (Fig. 2(b)). Even at the end of the process, the spectrum still shows continuous emission and only the spectral lines of Na I at 598 nm, Hα at 486 nm and Hβ at 656 nm are recognized at low intensity. It seems that the voltage influences the emission intensity. The final voltage (402 V) in phosphate electrolyte is lower compared to the other two electrolytes, possibly resulting in the lower energy of the discharges and thus the lowest emission intensity.

3.3. Surface characterization

The surface morphology of the coatings is visible in the three-dimensional view of the surfaces and the extracted profile curves (Fig. 3). Similar surface roughness Ra (arithmetical mean height, μm) values are revealed for PEO-Al and PEO-P coatings, which are 3.24 ± 0.30 μm and 3.04 ± 0.25 μm, respectively, while PEO-Si coating has a lower Ra of 2.53 ± 0.21 μm. The results also indicate the highest and the lowest RSm (mean width of the profile, mm) values (Gaussian filter, 0.8 mm) of PEO-Al and PEO-P coatings, 0.039 ± 0.011 mm and 0.018 ± 0.002 mm, respectively. Between them, RSm of PEO-Si coating is with a value equal 0.024 ± 0.003 mm. The higher Ra combined with lower RSm gives an impression of a larger coating surface area to a certain degree, demonstrating that PEO-P coating probably has the largest surface area. One should notice that the surface laser scanning measurement conducted at 20 × magnitude can not fully consider the contribution of the detailed surface morphology to the surface area at the micrometer or nanometer scales.

Fig. 4 illustrates surface morphologies of the coatings on the PEO-Al, PEO-P and PEO-Si specimens, respectively. Discriminable local morphologies can be easily found on each coating surface. Typical regions are marked by rectangles in Fig. 4 and the composition was determined there as well (Table 1). It is clearly revealed in Fig. 4(a) that the coating surface of PEO-Al specimen appears as the network of crater-centered islands. The crater morphology is constructed from the discharge channels, where the discharges generate and extinguish (Fig. 4(c)). The yellow-circled (Fig. 4(a)) present as molten morphology near the crater mostly resulted from the fast solidification of melts, which are ejected from the discharge channel. Between the sintered islands, there are many tiny particles and micro-pores appearing within the transition regions (Fig. 4(b)). The main element content shows a mass of Al incorporated into the coating, of up to 32.4 at.% on the sintered islands and 27.4 at.% within the transition regions. Nb content rises from 5.5 to 11.2 at.% at different regions. The higher content of Nb is more likely involved at the locations closer to the centered pores (discharge channels), in which large and strong discharges are formed.

As shown in Fig. 4(d), open micro-pores of ca. 8 μm in diameter spread on the entire PEO-P coating surface. What is visible in Fig. 4(e) is that the micro-pores are connected from the coating surface ending up to the inner coating towards the substrate. The large number and size of micro-pores indicate the intensive gas release during the processing, thus confirming the melting of coating materials during coating formation process. In addition, some relatively large sintered-discs are appearing sporadically (Fig. 4(f)), which is speculated to correlate with the discharges that have the lowest emission intensity. The PEO-P coating has the highest Nb content with respect to PEO-Al and PEO-Si coatings, reaching 29.0 at.% at the more porous regions, as exhibited in Fig. 4(e). The coating seems mainly composed of Nb oxide. In spite of some discharges, it seems that the coating formation process is not typical with mixed oxides from substrate and electrolyte, however, is more a conventional anodization.

The PEO-Si specimen Fig. 4(g) has the most compact morphology, characterized by the highly sintered surface. Similar to PEO-Al coating, the coating surface consists of relatively low Nb content, but higher Si concentration originated from the electrolyte. The high brightness regions around the micro-pore shown at a higher magnitude in Fig. 4(i)
contains a relatively high Nb concentration of 7.9 at.% compared to the other regions (1.8 at.%). It shows that the melted material was ejected through the discharge channel and solidified on the surface. Thus, it should be rich in Nb as it originated from the interface region of coating/substrate. Furthermore, the different brightness might indicate a not complete mixing of the coating materials since the image is taken under the BSE (backscattered electron) mode.

### 3.4. Cross-sectional characterization

Fig. 5 displays the cross-sectional morphologies of different coatings, as well as the EDS line scan across coating thickness, respectively. The observations confirm that PEO-Al coating has the highest thickness of 24.9 ± 5.5 μm, similar to 22.9 ± 4.1 μm of PEO-P coating, and the lowest coating thickness, 16.6 ± 4.0 μm, is revealed for PEO-Si coating. All the coatings show porous cross-sectional morphology and a layered structure, with a thin barrier layer of a few hundred nanometers thickness at the interface of substrate/coating typically [48–50]. Pore bands parallel to the coating surface are found in the PEO-Al coating (Fig. 5(a)), between the more porous outer layer and the inner barrier layer. EDS line scan shows the uniform distribution of Na and K across the coating thickness, having a concentration lower than 10 wt%. As expected, fluctuations of Nb, O and Al signals were detected along the micro-pores. The concentration of Nb is higher than Al since Nb is 3.4 times the atomic mass of Al. Near the coating/substrate interface there is a small decrease of Al concentration while the O concentration increases slightly towards the substrate. For PEO-P coating, open micro-pores stretch from the coating surface to the inner layer (Fig. 5(b)), agreeing with the surface observation. The EDS line scan shows that almost all of the main coating composition elements are distributed uniformly across coating thickness. Nb is dominant reaching 70 wt% and the O concentration is about 20 wt%. One could observe a slight increase of P concentration to 10 wt% near the pore band, suggesting a preferred P accumulation at this region. As seen in Fig. 5(c), it is obvious that PEO-Si coating shows the most compact cross-sectional morphology and only relatively small-sized micro-pores are present near the coating/substrate interface. Nevertheless, the local morphology at a high magnitude should be responsible for the absence of large-sized micro-pores/pore bands, which could be seen in Fig. 6(c). The elemental distribution across the coating seems not uniform. The concentration of Nb initially decreases from 70 wt% to 40 wt%, starting at the coating surface to a distance of 6 μm towards the coating/substrate interface, in contrast, the concentration of O and Si show a reverse change. Before reaching stable value, there is a bump and a hollow for the concentration of Nb and Si, respectively, at the blue-marked area with high brightness in BSE image (Fig. 5c). Interestingly, a track with higher brightness (highlighted by red dash line) compared to the surrounding was found to extend across almost the entire coating thickness. According to the BSE result, this track contains a high accumulation of Nb, which indicates the outward transport of coating formation species from the substrate to the coating/electrolyte interface. These observations are also supported by the EDS

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**Table 1**

Content of main elements (at. %) at different regions (Fig. 4) of coating surface in different electrolytes.

|   | Nb  | O   | Al  | P   | Si  | Na  | K   |
|---|-----|-----|-----|-----|-----|-----|-----|
| 1 | 5.5 | 57.6| 32.4| –   | –   | 4.1 | 0.4 |
| 2 | 11.2| 59.2| 27.4| –   | –   | 2.1 | 0.1 |
| 3 | 29.0| 62.7| 5.6 | –   | –   | 2.5 | 0.2 |
| 4 | 24.4| 64.7| 7.2 | –   | –   | 3.5 | 0.2 |
| 5 | 1.8 | 58.6| –   | 33.1| 5.7 | 0.8 |
| 6 | 7.9 | 63.5| –   | 26.0| 2.3 | 0.3 |

Fig. 4. Surface morphologies of PEO-Al coating (a), PEO-P coating (d) and PEO-Si coating (g), with local high magnitude (b) and (c) for region 1 and 2, (e) and (f) for region 3 and 4, (h) and (i) for region 5 and 6.
mapping results in Fig. 6. Al and Si have slightly stronger signals in PEO-Al (Fig. 6(a)) and PEO-Si coatings (Fig. 6(c)), respectively. As a result, Nb signals are diluted in the coatings. Especially at the region of micropores and pore bands, PEO-Al coating shows a more intensive signal, indicating that these regions are enriched with the species from the electrolyte. The open porosity of the coating is obviously the preferential place for the penetration of electrolytes. Similar observations are found for P in PEO-P coating although the overall signal is quite low compared to Nb and O (Fig. 6(b)).

3.5. Phase composition

The XRD patterns in Fig. 7 show a large, broad bump at the two theta range between 15° - 35° for all the coatings, suggesting the presence of amorphous phases. The crystalline Nb$_2$O$_5$ phase is visible in all the coatings, especially for the PEO-Si coating it looks like the main phase. It can be inferred that the large amount of Si in the PEO-Si coating is responsible for the large halo since Si can form a glassy phase [51]. Additionally, Nb peaks are shown in all the coatings due to the X-rays penetrating the coating and reaching the Nb substrate. The PEO-Al coating contains additional crystalline phases of Al$_2$O$_3$, and a mixed oxide AlNbO$_3$ formed between Nb$_2$O$_5$ and Al$_2$O$_3$. Thus, the formation of Al$_2$O$_3$/AlNbO$_3$ can also explain the high Al concentration in the coating. It has been previously reported that Al$_2$O$_3$ can be produced in PEO coatings in aluminate-containing electrolytes [52]. Besides amorphous phosphate and Nb$_2$O$_5$, additional crystalline Nb$_2$(PO$_4$)$_3$ is also observed in PEO-P coating, however, at a lower intensity with respect to Nb$_2$O$_5$, in accordance with the much lower P concentration in the coating.

High-resolved localized XRD measurement was conducted in order to unveil the spatial phase distribution in the PEO coatings. Fig. 8 and Fig. 10 display the XRD patterns across the coating moving from the air above the surface via the coating towards the substrate for the PEO-P and PEO-Al specimens, respectively. It shows the identical phase composition of the coatings as depicted in Fig. 7. It is evident that Nb$_2$O$_5$ is dominant in the PEO-P coating (Fig. 8). The spatial Nb$_2$O$_5$ distribution (Fig. 9(a)) separated from the high contrast of Nb substrate (Fig. 9(b)) can be easily distinguished, crossing the entire coating thickness. The well-defined region of Nb$_2$O$_5$ appears to be thicker in comparison to the thickness measurements and cross-sectional observation. This could have resulted from the rough coating surface and interface of coating/substrate. Additionally, the spatial distribution of Nb$_2$(PO$_4$)$_3$ phase in Fig. 9(c)) suggests a thickness of ca. 15 μm near the coating/air interface.

Fig. 5. Cross-sectional morphologies of (a) PEO-Al, (b) PEO-P and (c) PEO-Si coatings with EDS line scan across coating thickness.
A well-defined interface of coating/substrate for PEO-Al specimen is visible in Fig. 11. At the substrate side (Fig. 11(b)), the intensity of Nb shows an intensity reduction towards the inner substrate. The limited transmission of the synchrotron X-ray beam due to the strong absorption of photons through the Nb substrate [53] is responsible for this absence. The coating thickness is estimated to be at 30 µm, also slightly higher than the observation from the cross-section. The spatial intensity shows the highest concentration of AlNbO$_4$ in the center of the coating, perpendicular to the coating/substrate interface. Compared with the

**Fig. 6.** Cross-sectional morphologies and elemental distributions of (a) PEO-Al, (b) PEO-P and (c) PEO-Si coatings.
3.6. Photocatalytic activity

Fig. 12 shows the efficiency of MO photodegradation for the different coatings in a photocatalytic activity test as a function of time. While the bare substrate does not show photocatalytic activity, thus there are only comparisons between different coatings. All coatings have shown considerable photocatalytic activity, with MO degradation increasing gradually with time. The best photocatalytic activity has demonstrated for the PEO-Si specimens showing a MO degradation of ca. 39.3% within 6 h. The MO degradation of the PEO-P specimens is ca. 35.7% and the lowest MO degradation rate of ca. 32.9% is revealed for the PEO-Al specimens. Additionally, all coatings also show obvious MO adsorption in the dark. This could be related to the surface morphology of the coatings, where the excess of micro-pores increases the surface area for the adsorption of MO to the internal surface area.

3.7. Corrosion performance

3.7.1. Potentiodynamic polarization

Fig. 13 (a) reveals an obvious increase of open circuit potential of specimens after PEO processing and the most significant enhancement is found for PEO-Al coating, stabilizing at a value of 0.015 V. The potentiodynamic polarization profiles of PEO coatings and bare Nb are presented in Fig. 13(b). It can be seen that the corrosion potentials for PEO coated specimens are similar and show negative shift, which could be attributed to the decreased cathodic current [54]. While no visible change for that of bare Nb is found, which is slightly nobler than the cases after PEO processing. During anodic polarization, bare Nb shows a stable corrosion current density about $2.62 \times 10^{-6}$ A/cm$^2$, indicating the passive behavior. Nevertheless, the corrosion current densities for all PEO coated specimens are lower compared to bare Nb, especially for PEO-Si coating having the lowest corrosion current density of $5.695 \times 10^{-8}$ A/cm$^2$, while for PEO-Al coating showing a higher current density of $8.578 \times 10^{-10}$ A/cm$^2$. For PEO-P coated specimen, the corrosion current density experiences a remarkable scattering at the potential range of 2-5 V and then remains at $1.876 \times 10^{-7}$ A/cm$^2$ before an obvious breakdown of the passive film. It can be expected that PEO-P coating is less stable than the other two coatings during the polarization.

3.7.2. EIS measurement

The long-term degradation of PEO coated specimens and bare Nb in Ringer’s solution after different immersion duration up to 72 h is evaluated by EIS technique and the results are presented in Fig. 14. It can be seen that one well-defined time constant is detected on the Bode plots of bare Nb for all measurements (Fig. 14(a)). This time constant is the electrochemical response of the native oxide layer, indicating the capacitance of the barrier passive film. With immersion time, the resistive response at the low frequency (0.01 Hz) is disappearing and a near pure capacitive response is illustrated by the phase angle close to -90°. Meanwhile, the impedance loop expands, indicating that the native oxide layer is becoming more protective.

Fig. 7. XRD patterns of PEO-Al, PEO-P and PEO-Si coatings at grazing angle of 3°.

Fig. 8. XRD patterns crossing the thickness of PEO-P coating on Ti6Al4V.
It has been known that anodic niobium oxide is a $n$-type semiconductor [55], therefore, the influence of the space charge layer due to the well defined semiconductive behavior could be noticed on the electrochemical impedance spectra [54,56]. Fig. 14(b)-(d) shows the respective impedance spectra of the three PEO coated specimens. For the measurement of PEO-Al specimen (Fig. 14(b)), two time constants can be recognized. Although the porous outer layer is observed from cross-section, however, the fast infiltration of corrosive solution makes it not possible to show any clear electrochemical response from it. As a result, the first time constant at the high frequency ($10^3$–$10^4$ Hz) is assigned to the capacitance of inner barrier layer, combined with the subtle influence of the outer layer that is disappearing with immersion time. At the low frequency around 0.1 Hz, a second time constant appears, related to the space charge region formed at the layer-electrolyte interface. Similar for PEO-P specimen (Fig. 14(c)), two time constants can be also observed at high and medium frequencies of $10^4$ Hz and $10^2$ Hz, attributed to the capacitance of the inner layer and the space charge region respectively. As for the PEO-Si coating (Fig. 14(d)), the first time

Fig. 9. Two-dimensional distribution of (a) $\text{Nb}_2\text{O}_5$, (b) $\text{Nb}$ and (c) $\text{Nb}_2(\text{PO}_4)_3$ crossing the thickness of PEO-P coating on Ti6Al4V.

Fig. 10. XRD patterns crossing the thickness of PEO-Al coating on Ti6Al4V.
constant related to inner layer at $10^4$ Hz is well-defined and always present for all measurements during the immersion. Nevertheless, it can be seen that the second time constant at low frequencies is shifting to lower frequencies with immersion time, indicating the relaxation process regulated by the space charge layer response. The impedance value at the lowest frequency of 0.01 Hz is shown in Fig. 15 used to evaluate the total impedance of the pure Nb and PEO coatings. All cases show a slight fluctuation for the first 24 h immersion and then reaches a stable value for the remaining immersion time. It is obvious that the total impedance for PEO coated specimens is better than bare Nb and especially the PEO-Si coating shows the highest total impedance value.

4. Discussion

It is obvious that the different electrolyte composition influences the PEO processing, the coating formation, chemical and phase composition and morphology, as well as the coating performance. In previous studies, the PEO coatings on pure Nb were composed of Nb$_2$O$_5$ oxide phase [30,31,57], which we also find in the present work. It is known that the coating phase composition during PEO process is greatly connected to the change of discharges [26,58]. According to the OES results, the coating forming element Nb is absent in the discharging emission, which indicates that the formation of Nb$_2$O$_5$ is not produced directly from the plasma interactions. This is easy to understand in terms of the high melting temperature ($2477\, ^\circ\text{C}$) and chemical stability. In the aluminate-based electrolyte, the coating forming element Al is found to be involved in the discharging emission. However, it does not mean that the formation of crystalline Al$_2$O$_3$ and mixed oxide AlNbO$_4$ in the coating happens directly in the plasma of the discharges. One can expect that the coating formation and deposition are not favored in the plasmas, estimated of an electron temperature up to $10^4\, \text{K}$ [59]. The possibilities are the interactions of plasma and liquid/solid states [47] and the thermally assisted combination of the species at the end of discharges and the cooling of plasmas [26]. For PEO-Si coating, neither the production of a solid solution or the presence of silica phases is found. Only a wide halo associated with an amorphous phase could be attributed to a large amount of Si. It can be expected that the energy released from discharges enables to sinter an amorphous silica phase. For the coating of Nb, one could notice that this sintering process is similar to the calcination of the SiO$_2$/Nb$_2$O$_5$ binary oxides, which were used to modify the catalytic activity for environment protection [60,61]. There is only 5-7 at.% of P in PEO-P coating, some is incorporated in Nb$_2$(PO$_4$)$_3$ and the rest is assigned to the amorphous phosphate. It is
known that P also has the ability to form the amorphous phase during PEO processing [33, 62]. However, the lowest emission intensity of the discharges and the more porous coating morphology are responsible for the low P content in the PEO-P coating [59]. The continuous emission is present in the entire processing duration in the phosphate-based electrolyte. Only moderate Na I and H I emission lines derived from the species of the electrolyte are visible. Since the emission intensity shows a dependence on the voltage, it can be speculated that the efficient temperature of discharges could not stimulate the formation of more species of the electrolyte are visible. Since the emission intensity shows a dependence on the voltage, it can be speculated that the efficient temperature of discharges and the more porous coating morphology are responsible for the lowest emission intensity of the coating is greatly dependent on the photogenerated hole/electron pairs and the recombination rate of photo-excited electrons and holes [30]. It was reported that higher catalytic activity of silica-supported/Nb2O5-supported catalysts was demonstrated by the addition of Nb2O5/silica [61]. The PEO-Si coating with the combined composition of Nb2O5 and silica could be the case containing higher concentration of charge carriers. Furthermore, the significantly distinct coating surface morphology, resulting from the different discharge behavior appears to influence the photocatalytic activity. The distribution of tiny sintered particles on the entire PEO-Si coating surface may effectively increase the active surface area for MO degradation. The open micro-pores extending into the inner layer on the PEO-P coating can additionally expand the surface area, however, does not make visible contribution to the active surface area for the degradation process.

All of the PEO coatings present a significant improvement of corrosion resistance, around one or two magnitudes of total impedance value higher than that of the bare substrate. PEO-Si coating shows the best corrosion performance compared to the other two coatings due to the most uniform and compact morphology. The space charge layer originated from the semi-conductive property of Nb2O5 is disclosed, which is similar to the anodic TiO2 film [66]. The lowest corrosion resistance of PEO-P coatings is attributed to the large amount of open micro-pores on the coating surface and their connection to the inner layer. Nevertheless, even after 72 h immersion duration, the stable total impedance values can be seen for all coatings, indicating the slow degradation of the coatings. Therefore, the PEO coatings provide evidently additional protective properties and functionality to pure Nb.

5. Conclusions

Different PEO coatings were produced on pure Nb successfully. The coating formation process on Nb involves a combination of various interactions, including electrochemical/chemical conversions, and the thermal assisted sintering process. The Nb substrate and the electrolyte composition are highly effective in controlling the morphology and composition (elements and phases) of the coatings, by influencing the characteristics of the discharges during PEO processing. Nb2O5 and Nb2(PO3)3 are formed in the phosphate-based electrolyte with additional amorphous phosphate. Amorphous silicon phase can be produced in the coating in the silicate-based electrolyte. Furthermore, the electrolyte containing aluminate tends to form a composite coating with a mixture of oxides (Nb2O5, Al2O3 and AlNbO4).

The photocatalytic activity is determined by the coating composition and active surface area of the coatings. The large active surface area of

![Fig. 13. Open circuit potential (a) and potentiodynamic polarization behavior (b) of PEO-Al, PEO-P and PEO-Si specimens and Nb substrate.](image-url)
the coating can obviously increases the degradation rate of methyl orange. PEO-Si coating, containing an amorphous silica phase that also improves the photocatalytic activity. The order of the photocatalytic activity of the three coatings is PEO-Al < PEO-P < PEO-Si.

The coating morphology also has an evident influence on the degradation of the coating in Ringer’s solution, by influencing the paths of infiltration of the corrosive solution. The corrosion resistance of the coatings and bare substrate follows the order Nb < PEO-P < PEO-Al < PEO-Si.

Due to the respectable photocatalytic activity and the high corrosion
resistance, the environmentally friendly PEO coatings on Nb, could potentially attract great interests for the environmental protection of photocatalysis and biomedical degradation of implants.

CRediT authorship contribution statement

Ting Wu: Visualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. Carsten Blawert: Conceptualization, Supervision, Writing – review & editing. Maria Serdechnova: Formal analysis, Visualization, Writing – review & editing. Polina Karlova: Investigation, Visualization, Writing – review & editing. Gleb Dovzhenko: Investigation, Visualization, Writing – review & editing. D. C. Florian Wieland: Investigation, Writing – review & editing. Mikhail L. Zheludkevich: Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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