

S. Aliasghari^{1,2}, P. Skeldon², R. Valizadeh¹

¹ASTeC, STFC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK.

²Corrosion and Protection Group, School of Materials, The University of Manchester, Manchester M13 9PL, UK.

Abstract

Porous structures in anodic coatings, such as those formed by plasma electrolytic oxidation (PEO), are potentially favourable for the addition of material that improves the surface properties. The PEO process results in relatively thick ceramic coatings, which are formed in aqueous electrolytes under high voltages that cause formation of microdischarges on the coating due to dielectric breakdown. In this study coatings have been formed on niobium. The coatings are being developed with the purpose of providing coated niobium substrates that can support a magnesium boride superconducting layer, with several methods of layer production being considered. The present work focuses on the processing conditions required for formation of the PEO coatings, the kinetics of coating formation, and the composition, morphology and structure of the resulting oxide layers. The study employed a silicate electrolyte, a constant rms current density, with a frequency of 50 Hz and a square waveform. A range of negative-to-positive current ratios was used to form the coatings. Voltage-time curves were recorded to monitor the coating growth. The coatings were examined by field emission analytical scanning microscopy and X-ray diffraction. The coatings, which were of thickness in the range 40 to 60 μm , are shown to be highly porous, with a relatively thick, silica-rich outer region and a thinner, niobium-rich inner region. The coatings contained Nb_2O_5 and silicon-rich amorphous material. The rate of coating growth decreased with increasing processing time, associated with a relatively drop in the voltage, and a reduction in the intensity of sparking.

1. Introduction

Plasma electrolytic oxidation (PEO) is a surface technology for producing ceramic oxide coatings on metals, particularly valve metals, such as aluminium and titanium [1]. The coatings are formed by polarizing the metal to the dielectric breakdown voltage in a suitable electrolyte under either DC or AC and pulsed condition the latter encompassing, a variety of waveforms and frequencies. The coatings contain species derived from both the substrate and the electrolyte. The coating material is generated at the sites of microdischarges where high local current densities, temperatures and pressures exist [2, 3]. The localized heating by the discharges is sufficient to melt the coating material, and possibly also the metal [4]. The coatings contain numerous pores, which are formed by the discharges and gas evolution [5]. The porous coating structure is potentially favourable for incorporation of material that further improves the surface property [6, 7].

The main aim of the present work was to produce a surface coating on niobium that could support a thin layer of MgB₂. Niobium is a valve metal and hence can be treated by PEO. It is a material favourable for biomedical applications [8], and of present relevance reveals superconducting properties at relatively high temperatures (below $T_c \sim 9.25$ K). The latter makes it a material of choice for superconducting radio frequency (SRF) cavities for accelerators [9][9]. The deposition of MgB₂ could potentially increase the temperature range in which superconducting properties could be achieved. While extensive studies have been made of growth of oxide film on niobium by conventional anodizing [10-14], very few studies have been made on growth of coatings under PEO conditions.

Sowa et al. formed PEO coatings of a few microns thickness on niobium using a potassium silicate electrolyte and employing DC conditions, with a current density of 0.1 A dm^{-2} , a treatment time of 10 min and voltages of 100, 200 and 400 V [10]. Crystalline niobium oxide was revealed in the coatings. Also incorporation of amorphous silica improved the corrosion resistance. Stojadinovic et al. used PEO to incorporate of Eu^{+3} and Sm^{+3} from the electrolyte into oxide coatings on niobium in order to obtain photoluminescent properties [11].

In the present work, PEO has been carried out on niobium under a range of current densities, waveforms and treatment times in an alkaline silicate electrolyte in order to identify whether or not these parameters have a significant influence on the composition, structure and morphology of the coatings.

2. Materials and methods

2.1. Material and PEO conditions

Commercial purity 99.6% niobium sheet, of 2.0 mm thickness, was obtained from ADVENT Research Materials Ltd., England. Rectangular specimens were cut from the sheet and ground to a 1200 SiC grade finish. They were then degreased with acetone, washed with distilled water, dried in air at 40°C and, finally, coated in lacquer (Stopper 45 MacDermid), leaving a working areas of $\sim 1.0 \text{ cm}^2$.

AC PEO treatments were carried out at a constant rms current density with a square waveform, employing different negative to positive (peak-to-peak) current ratios (i_n/i_p), using an ACS-FB power supply (ET systems electronic GmbH). The frequency was 50 Hz, with a duty cycle of 50%. An aqueous electrolyte was prepared by dissolving reagent grade sodium silicate (10.5 g l^{-1} specific gravity 1.5), phosphoric acid (3 ml l^{-1}) and sodium hydroxide (2.8 g l^{-1}) in deionized water. The electrolyte, of volume 1 dm^3 , was stirred with a magnetic stirrer during PEO. A double-walled glass cell was employed to contain the electrolyte. The temperature of the electrolyte was kept at 25°C by a flow of cold water through the cell wall. A stainless steel (type 304) plate of dimensions $7.5 \times 15 \text{ cm}$ was used as a counter electrode. The applied current density was 500 mA cm^{-2} (rms), with treatment times of up to 2000 s. Voltage-time responses were recorded electronically during anodizing, employing LabView software with a sampling time of 20 ms. The data acquisition system for monitoring of the voltage employed National Instruments (NI) SCXI high-performance signal conditioning and switching platforms. Light emission of the discharges was collected using an optical emission spectroscope (USB4000 Ocean Optics), with an optical fibre immersed in the electrolyte, and located a few centimetres from the specimen to optimize the collected light intensity and to reduce absorption from the bath. The polarisation-resistant optical fibre (ZFQ-9596, Ocean Optics), with PVDF sleeving and a PEEK ferrule, was of $1000 \mu\text{m}$

diameter, with a numerical aperture of 0.22 ± 0.22 . Emission spectra were recorded in the wavelength range 200–850 nm with a resolution of 1 nm.

2.2. Specimen examination

PEO-treated specimens were examined in plan view and cross-section using Zeiss Ultra 55 scanning electron microscopes, equipped with energy dispersive X-ray (EDX) analysis facilities. Cross-sections were ground through successive grades of SiC paper, followed by finishing with 1 μm diamond paste. Phase composition was investigated by X-ray diffraction (XRD), using a Philips X'Pert-MPD (PW 3040) instrument with copper $K\alpha$ radiation, a step size of 0.005° and a scan range from 5° to 85° (in 2θ).

3. Results and discussion

3.1 Voltage-time response

Figure 1 presents the voltage-time response during PEO of niobium for 2000 s at a constant current density of 500 mA cm^{-2} with a duty cycle of 50% and an i_n/i_p ratio of 1. The voltage first rises rapidly to $\sim 290 \text{ V}$ as a barrier anodic film is formed. Sparking then commences and the voltage subsequently remains steady up to about 180 s. It then increases to a maximum value of $\sim 325 \text{ V}$ at $\sim 700 \text{ s}$, followed by a steep drop, with superimposed increasing oscillations, to $\sim 150 \text{ V}$ at 1100 s. Thereafter, voltage oscillations of up to $\sim 120 \text{ V}$ occur with a decreasing frequency until the end of the treatments at 2000 s. The individual oscillations comprised a relatively slow voltage rise and a rapid drop.

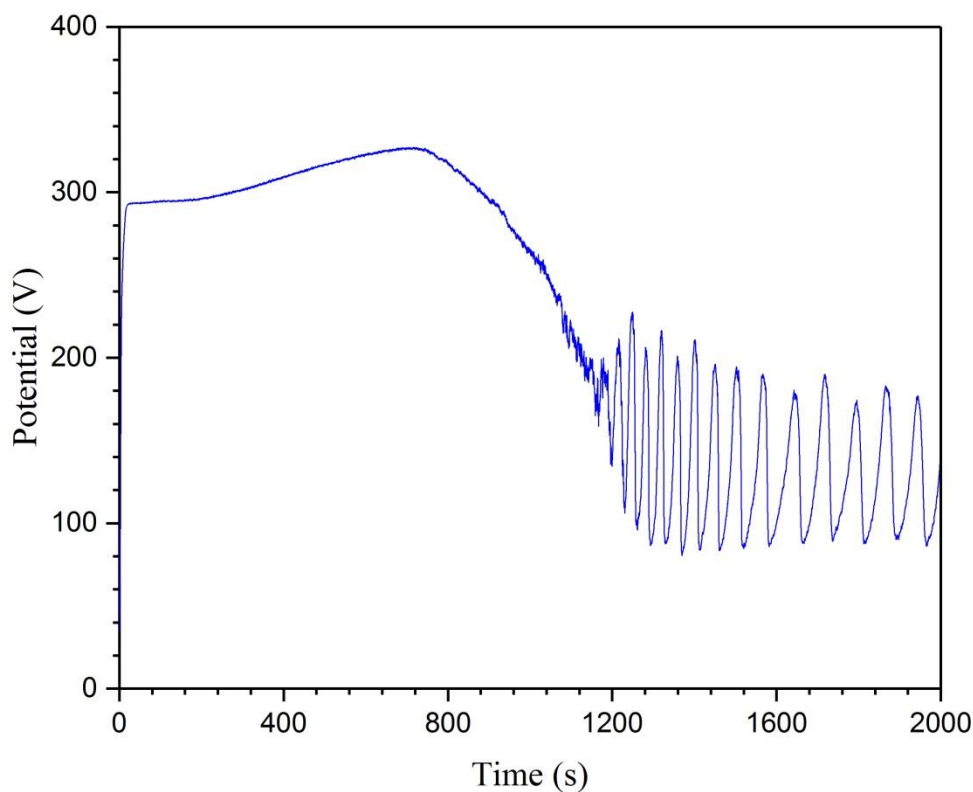


Figure 1. Voltage-time during PEO of niobium in silicate electrolyte for 2000 s at 500 mA cm^{-2} , with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive ratio of 1.

Numerous, fine, violet sparks occurred at the commencement of sparking. The sparks first appeared around the edge of the working area then rapidly spread to all regions. Their size and brightness increased with time and their colour changed from violet to white then orange. Beyond the maximum voltage, the sparks became progressively fewer and smaller. Sparks ceased during the large voltage drop. The sparking re-commenced in the period of large voltage oscillations, but sparks were fewer and smaller sparks. The sparks initiated during the rise of voltage in each voltage oscillation and extinguished as the voltage fell. Gas evolution occurred throughout the PEO process. The specimen was dark grey when sparking commenced. White coating material then formed all of working area.

The effect of changing the i_n/i_p ratio from 1 to 1.27, at a current density of 500 mA cm^{-2} and a duty cycle of 50% is shown in Figure 2. The changes had only minor influences on the voltage-time response and sparking behaviour, which were accountable for the variability observed between repeated experiments at a particular PEO condition.

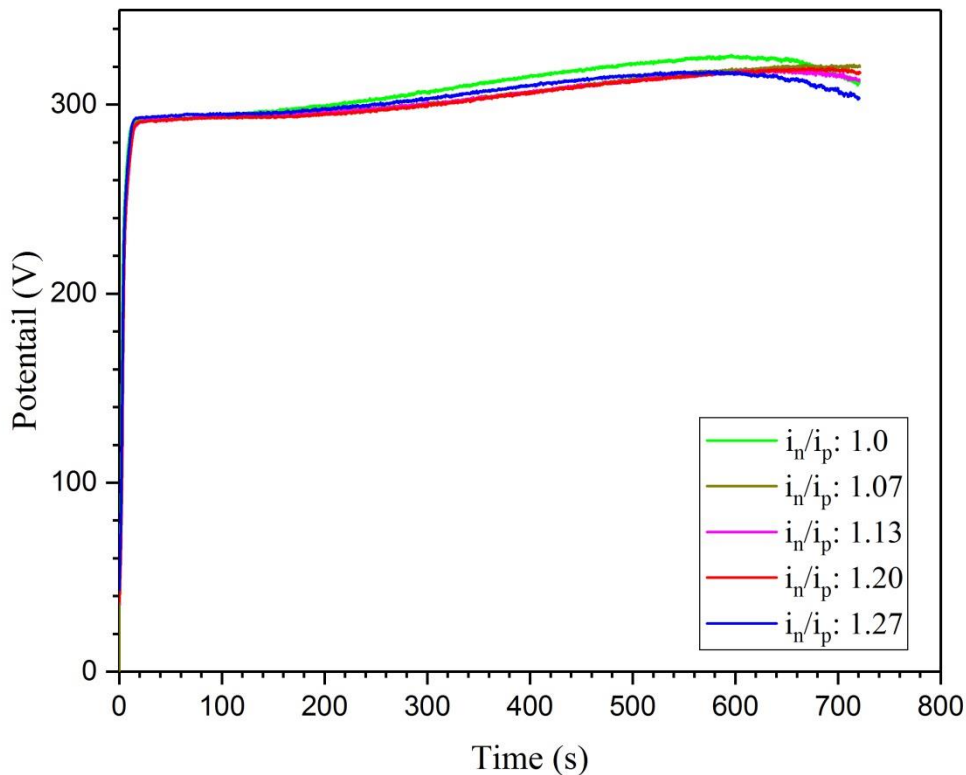
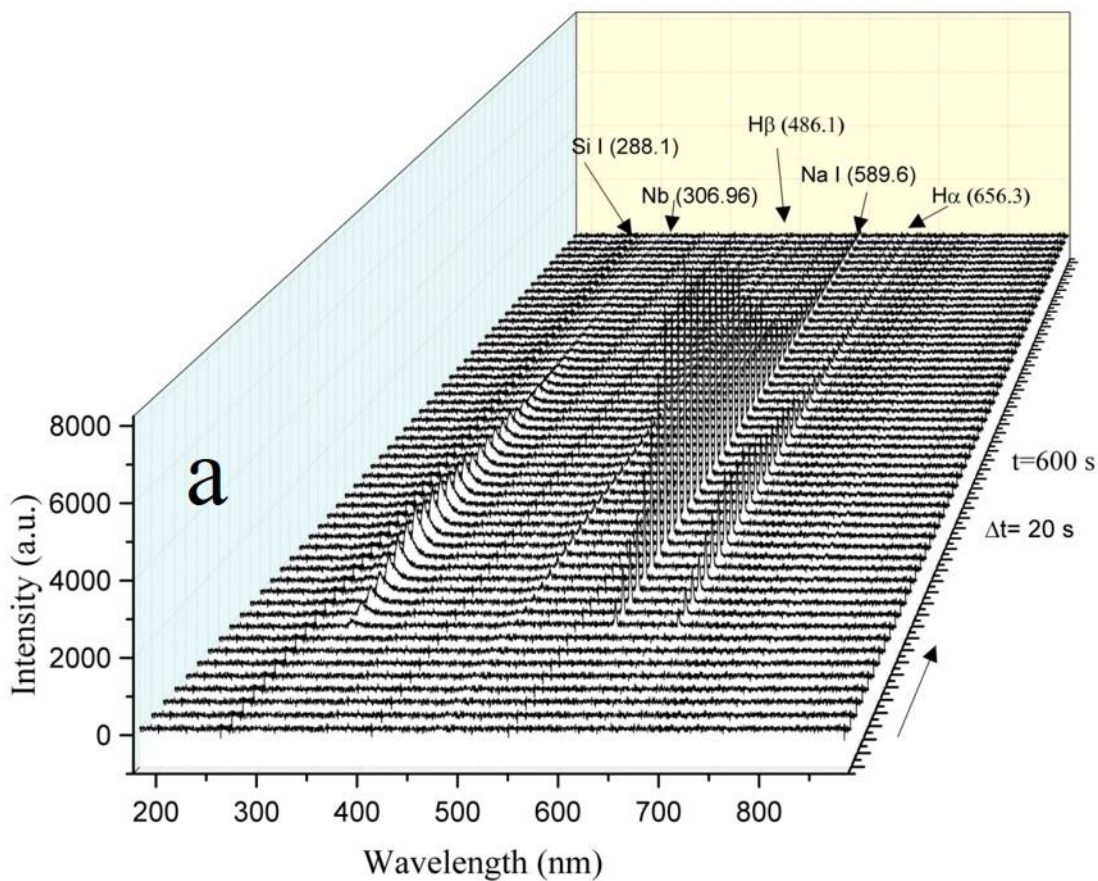


Figure 2. Voltage-time during PEO of niobium in silicate electrolyte for 720 s at 500 mA cm⁻², with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratios in the range of 1 to 1.27.

3.2 Optical emission spectroscopy

Figure 3 (a) displays the optical emission spectra recorded at intervals of 20 s during PEO for 600 s at a current density of 500 mA cm⁻², with a duty cycle of 50 % and an i_n/i_p ratio of 1. Emissions were detected from mainly sodium (Na I 589.6 nm) and hydrogen (H_α 656.3 nm) derived from the electrolyte and niobium (Nb 306.96 nm) derived from the substrate. Small peaks were also present due to hydrogen (H_β 486.1 nm) and silicon (Si I 288.1 nm) originating from electrolyte. The voltage-time response (Figure 3-b) was recorded during measurements. The peaks for niobium, sodium and hydrogen increased after 240 s, coincident with a voltage small increase from the earlier relatively constant voltage. In contrast a large reduction of these peaks occurred after ~480 s, which is close to start of drop in voltage response.



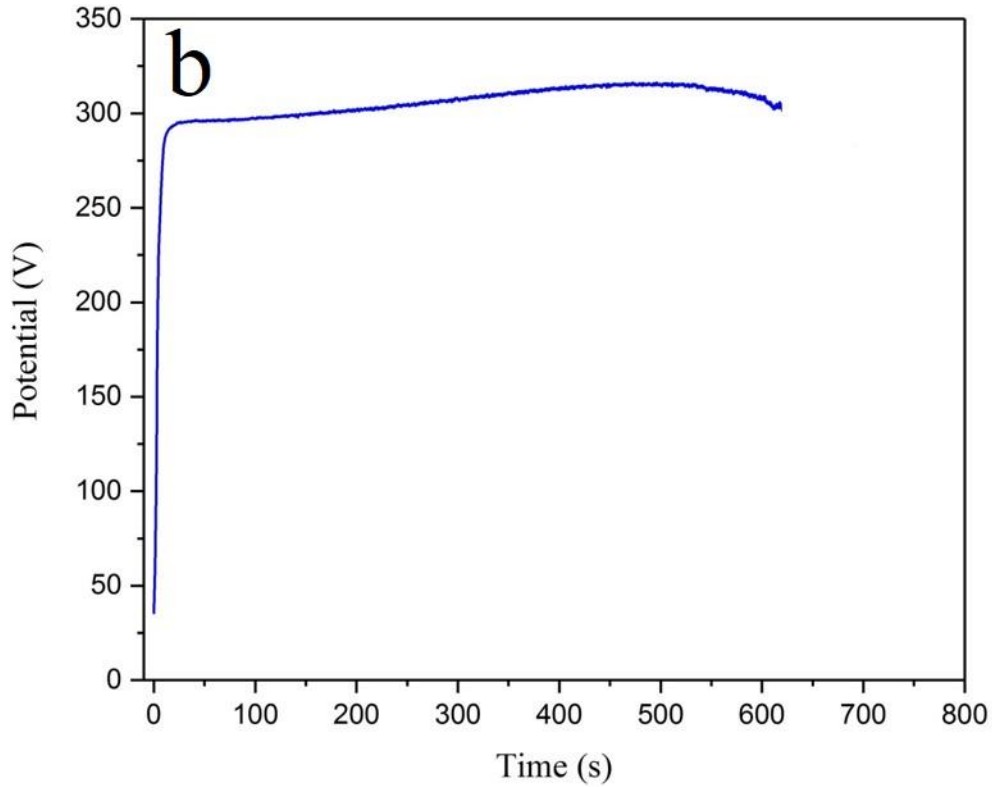


Figure 3. (a) Optical emission spectra recorded during PEO of niobium in silicate electrolyte for 720 s, with a frequency of 50 Hz, a duty cycle of 50%, a negative-to-positive current ratio 1 and at current density of 500 and 800 mA cm⁻², (b) The voltage-time response during recording of the spectra.

3.3 Kinetics of coating formation

The dependence of the coating thickness on the time of PEO at 500 mA cm⁻², with a duty cycle of 50% and i_p/i_n ratio of 1 is shown in Figure 4. The coating thickness was determined from SEM observations of coating cross-sections. The average rate of coating growth in the first 120 s was ~61 nm s⁻¹. It then increased to ~83 nm s⁻¹ up to 720 s, when a thickness of ~60 μm was attained. Thereafter, the growth rate slows to ~47 nm s⁻¹, with the final thickness after 1800 s reaching ~90 μm. The slower final growth rate correlated with a reducing voltage (Figure 1).

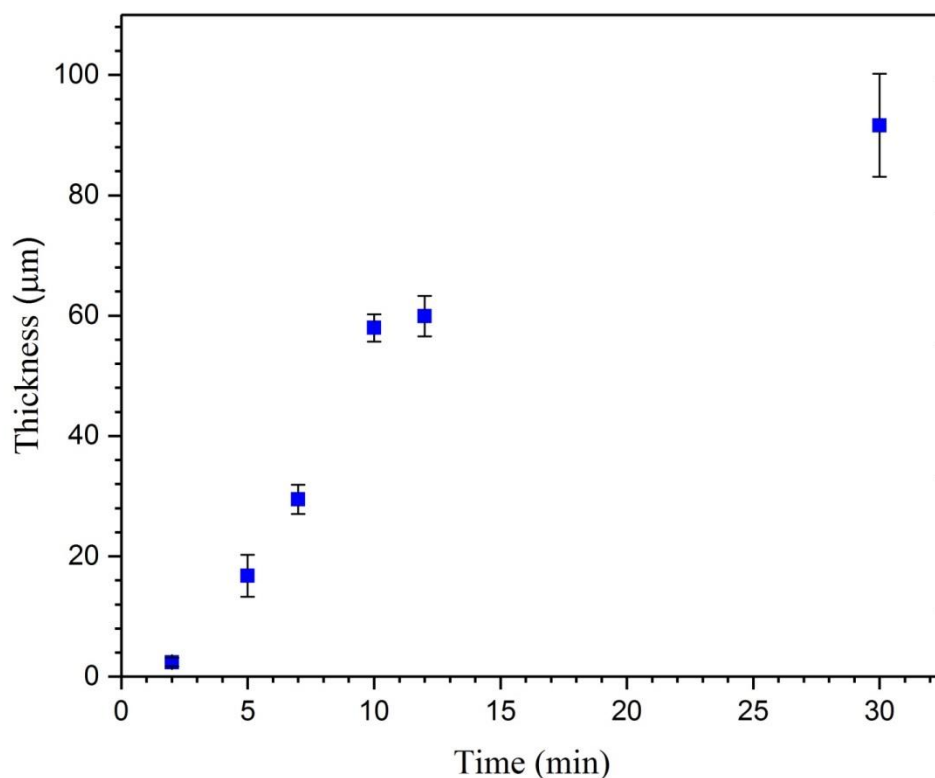


Figure 4. Dependence of the thickness of the coating on the time during PEO of niobium in silicate electrolyte for 1800 s at 500 mA cm^{-2} , with a frequency of 50 Hz, a duty cycle of 50%, and a negative-to-positive current ratio 1. The thickness of the coating was measured from the cross-sections of the coating observed by SEM.

3.4 Coating morphology and composition

Figure 5 shows a scanning electron micrograph of the surface of a coating formed for 720 s at 500 mA cm^{-2} , with a duty cycle of 50% and an i_n/i_p ratio of 1, revealing a nodular coating material, with nodules of size up to several tens of microns. Deep cavities were present between the nodules, resulting in a relatively rough coating surface. The composition of the surface region according to EDS point analysis (in at%) was 70%O, 23% Si, 3% P, 3% Nb, <1% K, <1% Na, suggesting that SiO_2 is the main constituent.

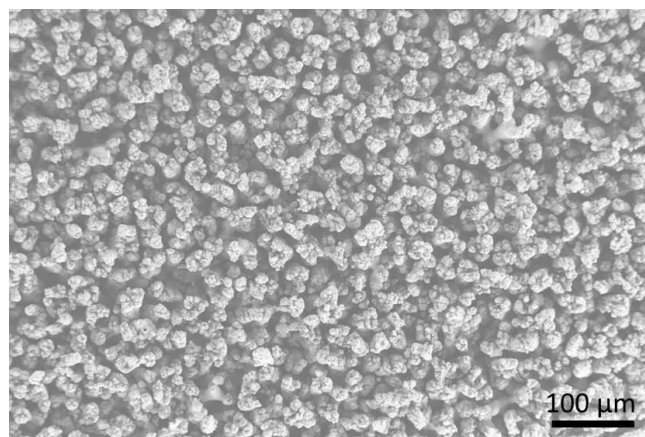


Figure 5. Scanning electron micrographs (secondary electrons) of the surface of coating formed using PEO of niobium in silicate electrolyte for 720 s, with a current density of 500 mA cm^{-2} , a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio 1.

The cross-section of Figure 6 shows that the coating thickness ranges from ~ 50 to 70 μm . Numerous pores and discharge channels are present throughout the coating. The EDS elemental maps of Figure 7 show that oxygen and silicon are present in most parts of the coating, while niobium mainly occurs in region next to the substrate. Sodium and phosphorous are negligible or minor constituents of most regions of coating.

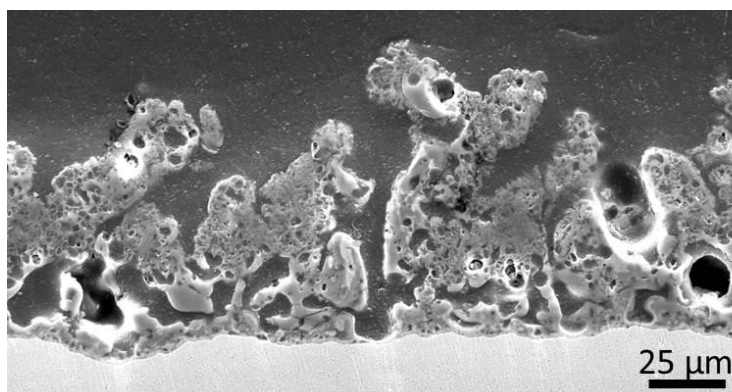


Figure 6. Scanning electron micrographs (secondary electrons) of a cross-section of coating formed using PEO of niobium in silicate electrolyte for 720 s, with a current density of 500 mA cm^{-2} , a frequency of 50 Hz, a duty cycle of 50% and negative-to-positive current ratio 1.

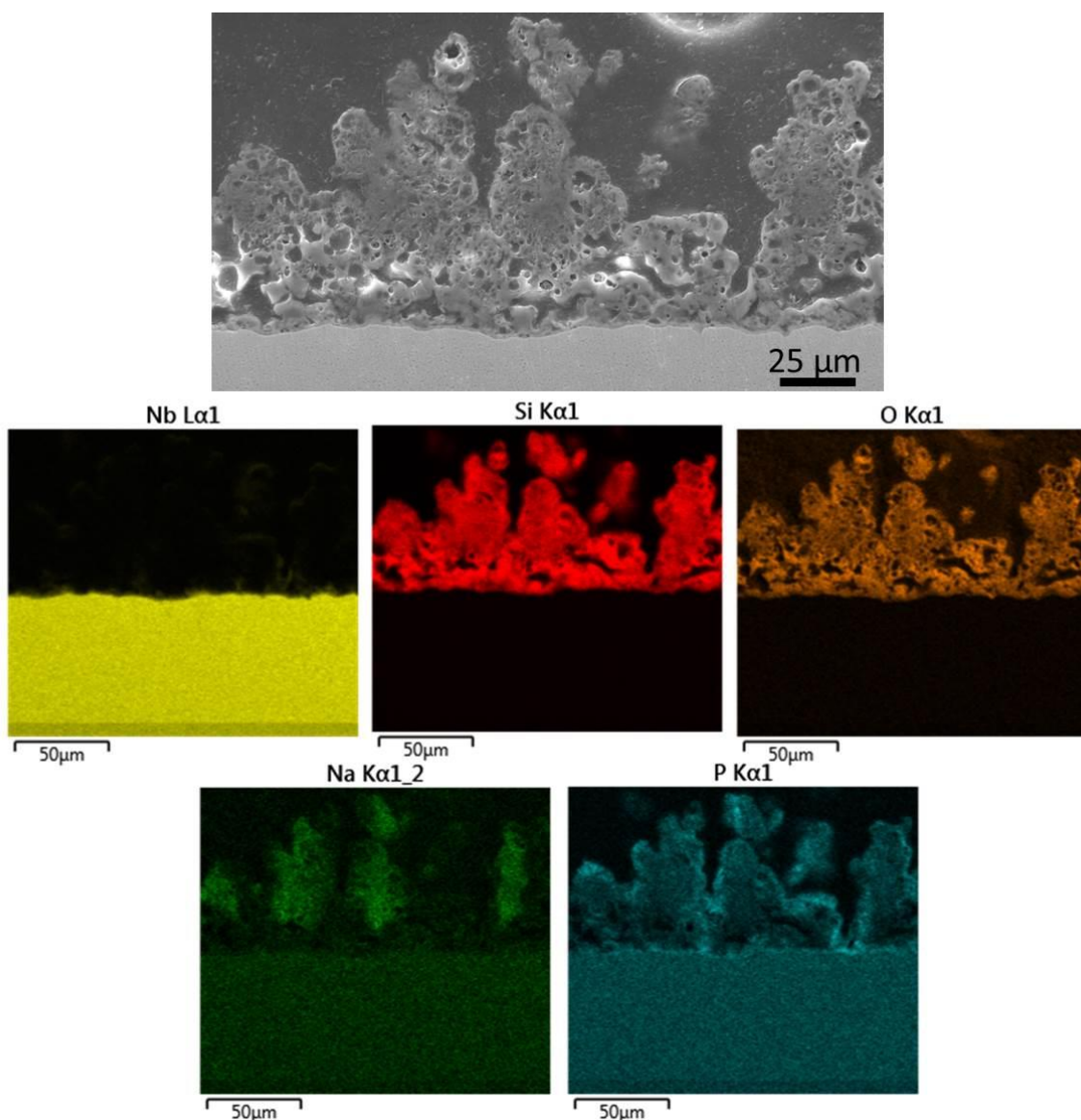


Figure 7. EDS elemental maps of a cross-section of coating formed using PEO of niobium in silicate electrolyte for 720 s, with a current density of 500 mA cm^{-2} , a frequency of 50 Hz, a duty cycle of 50% and negative-to-positive current ratio 1.

Results of XRD are shown in Figure 8 for coatings formed for 120 and 720 s at 500 mA cm^{-2} , with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of 1 and pure niobium. At both treatment times, peaks are evident due to niobium in the substrate and Nb_2O_5 and Nb_4O_5 . The main Nb_2O_5 peak increased with increasing treatment time. Amorphous material gives rise to the broad peak between $\sim 15^\circ$ to 30° . The absence of peaks for silicon-containing compounds indicates that silicon is associated with the amorphous material.

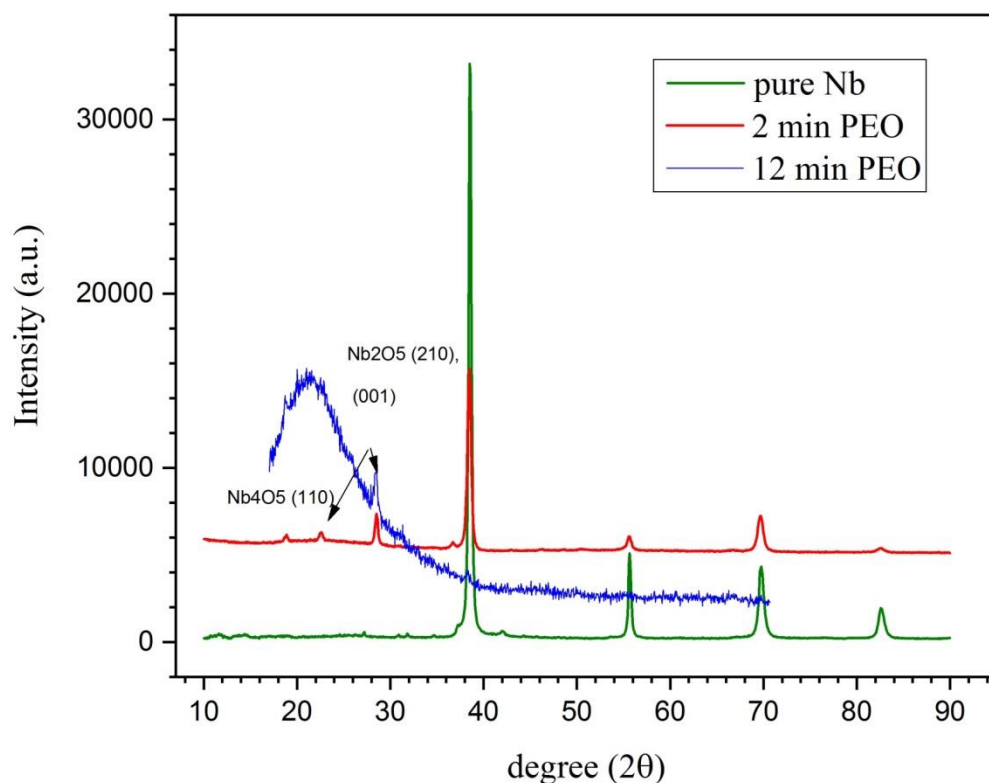


Figure 8. XRD patterns for niobium following PEO for 120 720 s in silicate electrolyte for 720 s, with a current density of 500 mA cm^{-2} , a frequency of 50 Hz, a duty cycle of 50% and negative-to-positive current ratio 1 and pure Nb.

4. Conclusions

1. PEO coatings on niobium formed at 500 mA cm^{-2} in the alkaline silicate electrolyte, with a frequency of 50 Hz, a duty cycle of 50% and a negative-to-positive current ratio of 1, are composed of amorphous silica and Nb_2O_5 . Phosphorus species and minor amounts of sodium species are also incorporated into the coating.
2. The coatings are limited in thickness to ~ 40 to $60 \text{ }\mu\text{m}$ and are highly porous, with a thick, silica-rich outer layer and a thinner and niobium rich inner region. The limitation of thickness is related to a steep drop in the voltage after $\sim 720 \text{ s}$ of PEO, with a reduction in the intensity of sparking. Similar morphologies of coatings are generated at negative-to-positive current ratios of up to 1.13.

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