

Article

Formation of Alpha- Al_2O_3 Coatings on Tungsten Substrate by Plasma Electrolytic Oxidation

Stevan Stojadinović^{1,2,*}  and Pedro Nelson¹
¹ Faculty of Physics, University of Belgrade, Studentskitrg 12-16, 11000 Belgrade, Serbia; nelson2021jair@gmail.com

² Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, 11000 Belgrade, Serbia

* Correspondence: sstevan@ff.bg.ac.rs; Tel.: +381-11-7158161

Abstract: Oxide coatings formed by plasma electrolytic oxidation (PEO) of tungsten substrate for 10 min in a phosphate alkaline electrolyte (PAE, 2 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) with an addition of 2 g/L, 3 g/L, and 4 g/L NaAlO_2 were investigated by SEM/EDS and XRD. In PAE + 2 g/L NaAlO_2 , a weakly crystalline coating is formed, consisting of amorphous Al_2O_3 , the triclinic phase of WO_3 , the cristobalite phase of AlPO_4 and the gamma and alpha phases of Al_2O_3 . Strong micro-discharges during PEO in PAE with the addition of 3 g/L and 4 g/L NaAlO_2 lead to the crystallization of amorphous Al_2O_3 into gamma- Al_2O_3 and alpha- Al_2O_3 phases. The coating formed in PAE + 4 g/L NaAlO_2 is well crystallized and rich in alpha- Al_2O_3 , which makes it suitable for high-temperature applications. To explain the composition of the formed coatings and the transformation of the amorphous Al_2O_3 into gamma and alpha phases, we followed the change in morphology, thickness, chemical and phase composition of the coatings during PEO in PAE + 4 g/L NaAlO_2 .

Keywords: tungsten; plasma electrolytic oxidation; coatings; alpha- Al_2O_3 ; WO_3

1. Introduction

Tungsten is a transition metal with many special properties, including a high melting point (3420 °C), excellent thermal conductivity, strong mechanical performance, a low coefficient of thermal expansion, low vapor pressure, excellent corrosion resistance, and a relatively large thermal neutron absorption cross-section [1]. Due to these properties, it is used in numerous fields, such as high-temperature applications, high vacuum engineering, nuclear and medical X-ray radiation shielding, aerospace and military industries, etc. [2].

The anodization of tungsten is a simple, affordable, and highly effective method of creating an oxide structure on tungsten substrates, mainly WO_3 . The development of porous WO_3 layers in fluoride-containing electrolytes (NaF and NH_4F), which are often unavoidable in the synthetic process of conventional anodization, has been the main focus of research on tungsten anodization [3,4] due to their numerous applications in photoelectrochemistry [5], photocatalysis [6], water splitting [7], hydrogen and ethanol sensors [8], lithium-ion batteries [9], supercapacitors [10], and other areas. Also, structures with tungsten oxides can be produced by plasma electrolytic oxidation (PEO) [11] and cathodic PEO [12].

The formation of WO_3 -rich coatings was our original motivation for investigating PEO for tungsten. The electrolytes commonly used in this technology, such as water solutions containing potassium or sodium hydroxide, sodium phosphate, sodium silicate, sodium tungstate, sodium aluminate, and some acidic solutions, were not able to provide the high voltages required for micro-discharges, so our attempts to apply PEO on tungsten in these



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electrolytes failed. Micro-discharges were only generated by anodization of tungsten at sufficiently high voltages when we used electrolytes containing 2 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ + 2 g/L NaAlO_2 [11]. However, the main component of the oxide coatings formed in this electrolyte is Al_2O_3 .

Due to the high-wear resistance, chemical inertness, hot-hardness, and thermal stability, there are numerous applications for crystalline Al_2O_3 coatings. The thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ with corundum structure is the optimum oxidation coating for high-temperature applications [13]. Aluminum substrates can be coated with $\alpha\text{-Al}_2\text{O}_3$ using PEO [14], but these coatings are unsuitable for high-temperature applications because aluminum has a low melting point ($\sim 660^\circ\text{C}$). On the other hand, the $\alpha\text{-Al}_2\text{O}_3$ coating on a tungsten substrate has the potential for high-temperature applications as tungsten has the highest melting point of all metals.

In this work, we have shown that a phosphate alkaline electrolyte (PAE, 2 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) containing NaAlO_2 can easily form $\alpha\text{-Al}_2\text{O}_3$ coatings on a tungsten substrate by a PEO process. The effects of NaAlO_2 concentration in the PAE on the morphology, chemical, and phase composition properties of the formed coatings were investigated.

2. Materials and Methods

The PEO experimental setup is described in Ref. [15]. Samples of tungsten with a purity of 99.9% were used as the working electrode (anode) in a double-walled glass cell with water cooling, which was surrounded by a tubular cathode made of stainless steel. PEO was performed at a current density of 400 mA/cm^2 for 10 min using a DC source (Consort EV261) in a water solution containing 2 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ with the addition of NaAlO_2 in concentrations of 2 g/L, 3 g/L, and 4 g/L. A magnetic stirrer was used to mix the electrolyte in the electrolytic cell. The electrolyte temperature was maintained at $(22 \pm 2)^\circ\text{C}$. To avoid the build-up of electrolyte components during the drying process, the samples were rinsed with distilled water after the PEO procedure.

The anodization potential was recorded over time using an Agilent 34970 A Data Acquisition Switch Unit. The surface morphology and elemental composition of the PEO coatings were examined using a scanning electron microscope (SEM, JEOL 840A, Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscopy detector (EDS, Oxford INCA, Abingdon, UK). The crystalline structures of the coatings were investigated by X-ray diffraction (XRD, Rigaku Ultima IV, Tokyo, Japan). The XRD data in the 2θ range from 20° to 55° were acquired in a scanning mode with a step size of 0.05° and a scanning rate of $0.25^\circ/\text{min}$.

3. Results

Figure 1 summarizes the potential-time characteristics during the anodization of tungsten in PAE with the addition of NaAlO_2 at different concentrations, as well as the pH value and conductivity of the electrolytes. The potentials show a similar change trend during PEO in the electrolytes used. The almost linear increase in voltage characterizes the relatively uniform growth of a compact barrier oxide layer. Supported by a strong electric field ($\sim 10^7\text{ V/cm}$), the migration of $\text{O}^{2-}/\text{OH}^-$ anions and substrate cations through the oxide results in the formation of the oxide layer at the metal/oxide and oxide/electrolyte interfaces [16]. Furthermore, during anodization, anionic electrolyte components are integrated into the oxide at the oxide/electrolyte interface. Deflection from linearity starts from so-called sparking (breakdown) voltage, and a large number of small-size micro-discharges emerge, evenly distributed over the whole sample surface. Various physical and chemical processes are induced at micro-discharging sites due to increased local

temperature and pressure, thus modifying the structure, composition and morphology of formed coatings. Crystalline and amorphous phases with components originating from both the metal and the electrolyte are typically found in the oxide layers formed by the PEO [11]. The pH value and the conductivity of the electrolyte influence the breakdown and final voltages, which decrease with increasing concentration of NaAlO_2 in PAE, which is in agreement with theory and experimental results [17,18]. Visually, the micro-discharges intensify as the concentration of NaAlO_2 in PAE increases.

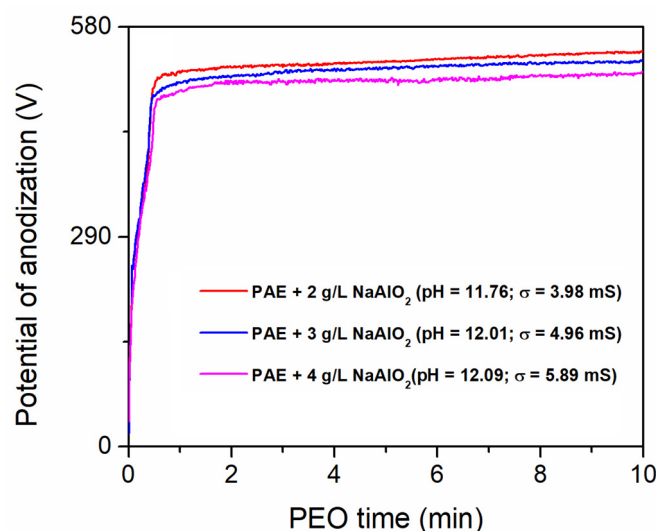


Figure 1. Potential–time curves during the anodization of tungsten in PAE with the addition of NaAlO_2 at different concentrations.

The increasing tendency of the potential during anodization is related to the current density distribution. The total current density is the sum of the ion and electron current densities [17]. At the beginning of anodization, the electric field strength remains constant at a certain current density, while the ion current is two to three orders of magnitude greater than the electronic component. In order to keep a constant electric field strength, the anodizing voltage must increase linearly with increasing layer thickness. In addition, during anodization, electrons are injected into the conduction band of the anodic oxide and accelerated by the electric field, which leads to avalanches via an impact ionization mechanism [17]. When the electronic current of the avalanche reaches a critical level, breakdown occurs [18]. Thereafter, a low voltage is required to maintain the same total current density, since the electron current density is independent of the thickness of the anodic oxide layer. Finally, the electron current density component dominates the total current density. The total current density is almost independent of the thickness of the anodic oxide layer, and the voltage–time slope is almost zero.

Figure 2 shows the morphologies of the formed coatings in the top view and the cross-section. A dense, thick, and slightly porous structure with numerous molten areas, formed by the rapid cooling of the molten material, adorns the surface of the coatings. Table 1 shows the results of the integral EDS analyses of the surface coatings shown in Figure 2a (the relative errors are less than 5%) and the thickness of coatings according to Figure 2b. The coatings consist of W from the substrate and Al, O, and P from the electrolyte. The Al content in the coatings is high and increases with the concentration of NaAlO_2 in PAE, while the W content is very low. The thickness of the coatings increases with increasing NaAlO_2 concentration in the PAE, as more intense micro-discharges cause a larger amount of molten oxidized material to be ejected from the micro-discharge channels onto the coating surface and solidify rapidly in contact with the electrolyte.

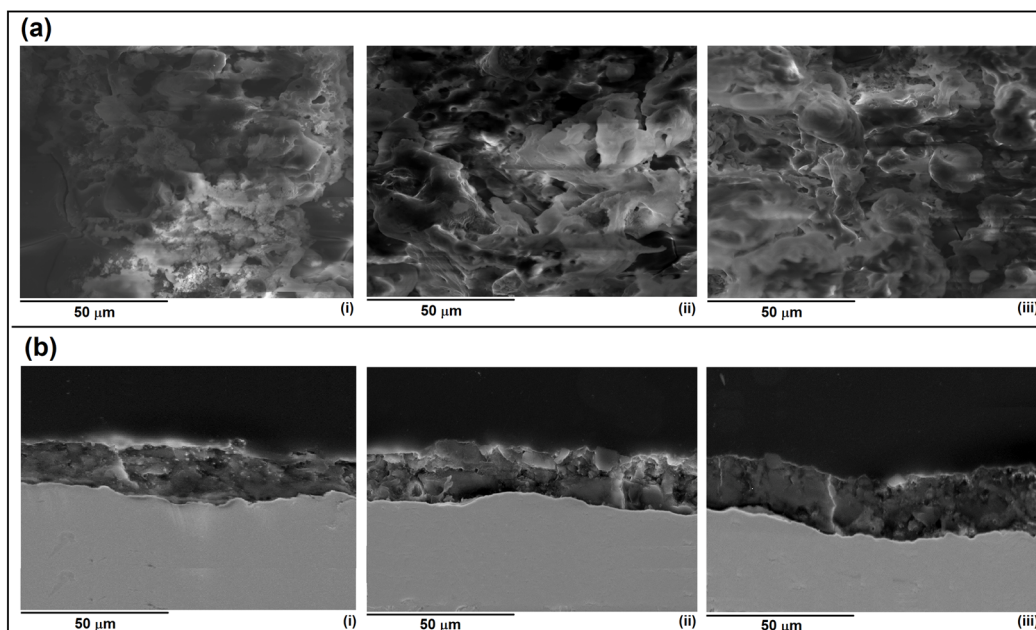


Figure 2. (a) Top view; (b) cross-section; images of coatings formed in PAE with the addition of NaAlO₂ in different concentrations: (i) 2 g/L; (ii) 3 g/L; (iii) 4 g/L.

Table 1. EDS elemental analysis and thickness of coatings in Figure 2.

NaAlO ₂ (g/L)	Thickness (μm)	Atomic (%)			
		O	Al	P	W
2	16.2 ± 1.9	74.21	20.15	5.22	0.42
3	19.1 ± 1.8	69.34	27.92	2.39	0.36
4	21.8 ± 1.6	67.14	31.41	1.19	0.26

The XRD patterns of the coatings formed are shown in Figure 3. In PAE + 2 g/L NaAlO₂, a poorly crystalline coating is formed, which produces broad and low-intensity diffraction peaks. XRD pattern consists of no well-defined diffraction peaks of the triclinic phase of WO₃ (PDF Card No.: 1010618), peaks assigned to the cristobalite phase of AlPO₄ (JCPDS Card No.: 011-0500) and the gamma-Al₂O₃ (JCPDS Card No.: 010-0425) and alpha-Al₂O₃ (JCPDS Card No.: 010-0173) phases. In addition, an amorphous halo can be observed in the 2θ range from 15° to 40°, which is typical for amorphous Al₂O₃ [19]. The XRD pattern of the coating formed in PAE + 3 g/L NaAlO₂ consists of well-defined diffraction peaks assigned to the gamma-Al₂O₃ and alpha-Al₂O₃ phases, indicating the crystallization of amorphous Al₂O₃. The alpha-Al₂O₃ phase becomes the predominant crystalline form of the coating formed in PAE with the addition of 4 g/L NaAlO₂. Sharp and intense XRD peaks of alpha-Al₂O₃ show the good crystallinity of the formed coating in PAE + 4 g/L NaAlO₂. The phase ratio of alpha and gamma Al₂O₃ in the coatings formed in PAE with the addition of 4 g/L NaAlO₂ is about 87:13, based on the comparison of the integrated intensities of alpha and gamma diffraction peaks.

To explain the growth mechanism of the oxide coatings and the transformation of amorphous Al₂O₃ into gamma and alpha phases, we investigated the change in morphology, thickness, chemical, and phase composition of the coatings formed in PAE + 4 g/L NaAlO₂ at various stages of PEO. The top view and cross-sectional morphology of the coatings formed are shown in Figure 4. Relatively flat coatings are formed before PEO (0.5 min) and short PEO times (1, 3 and 5 min). The results of the integral EDS analyses of the surface coatings, shown in Figure 4a and the coating thickness according to Figure 4b are shown in Table 2. The coatings are composed also of W, Al, O, and P. The content of Al

increases with PEO time. The content of tungsten in coatings is low and weakly depends on time PEO.

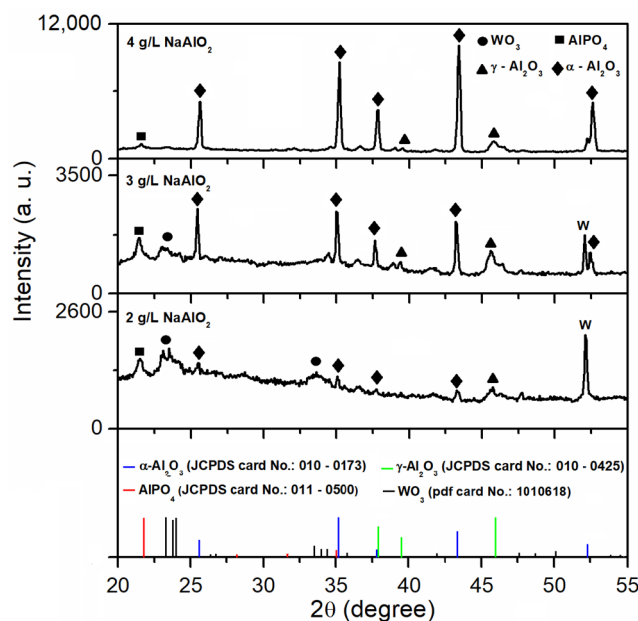


Figure 3. XRD patterns of coatings formed in PAE with the addition of NaAlO₂ in different concentrations.

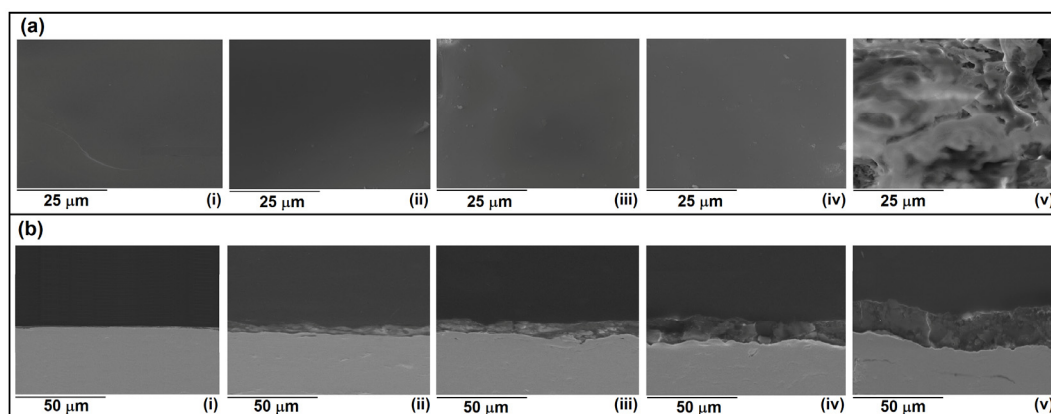
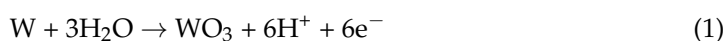


Figure 4. (a) Top view; (b) cross-section; images of coatings formed in PAE + 4 g/L NaAlO₂ at various stages of PEO: (i) 0.5 min; (ii) 1 min; (iii) 3 min; (iv) 5 min; (v) 10 min.

Table 2. EDS elemental analysis and thickness of coatings in Figure 4.

PEO Time (min)	Thickness (μm)	Atomic (%)			
		O	Al	P	W
0.5	1.2 ± 0.2	75.05	18.88	5.23	0.84
1	6.3 ± 0.4	75.72	19.06	4.92	0.30
3	9.7 ± 0.7	75.59	19.87	4.25	0.29
5	13.9 ± 1.1	74.60	20.88	4.17	0.35
10	21.8 ± 1.6	67.14	31.41	1.19	0.26

The XRD patterns of coatings in Figure 4 are shown in Figure 5. The peaks observed in the XRD pattern of the coating formed after 0.5 min were indexed to the triclinic phase of WO₃. The formation of WO₃ results from the high electric field-assisted opposite migration of W⁶⁺ from the substrate and O₂[−] from the electrolyte according to the following reaction [20]:



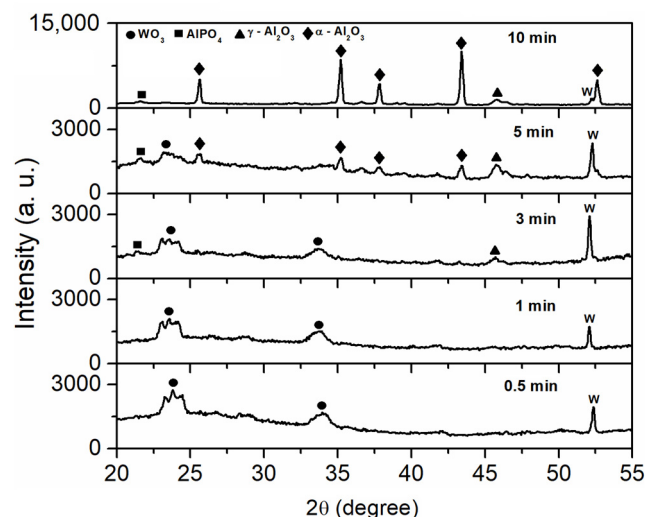
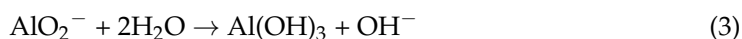


Figure 5. XRD patterns of coatings formed in PAE + 4 g/L NaAlO₂ at various stage of PEO.

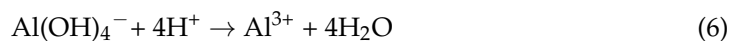
Although the Al content is high in the coating formed after 0.5 min, the diffraction peaks originating from the crystalline phases of Al₂O₃ are not visible in the XRD patterns, indicating the amorphous structure of Al₂O₃ [5]. The following reactions lead to the formation of amorphous Al₂O₃ [21]:



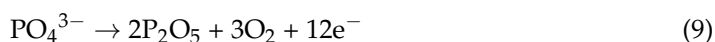
The content of phosphorus is also high in the coating, but any diffraction peaks related to phosphorus species are not observed in the XRD pattern.

The content of Al increases with PEO time. The content of tungsten in coatings is low (~0.3% atomic). This indicates that due to the high melting point of tungsten, micro-discharges do not have sufficient energy to cause evaporation of the substrate that would be oxidized in the micro-discharge channels. WO₃ phases can be noticed on XRD patterns of coatings formed after 1 min, 3 min, and 5 min, which indicates that they are formed electrochemically (Equation (1)).

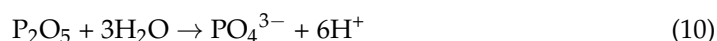
High temperatures at the micro-discharge sites enable the formation of the high-temperature AlPO₄ phase, which occurs at temperatures above 1024 °C [22]. The cristobalite phase of AlPO₄ can be observed in the XRD patterns of the coatings formed for PEO times of 3 min, 5 min, and 10 min. The formation of AlPO₄ is the result of the following chemical reactions:



It is also possible that PO₄^{3−} was ionized to P₂O₅ in the molten oxide [23]:



but P_2O_5 can be easily hydrolyzed to PO_4^{3-} [23]:



After 3 min, amorphous alumina becomes moderately crystallized and the gamma phase of Al_2O_3 can be noticed on the XRD pattern. The XRD patterns of the coatings formed after 5 min and 10 min of PEO clearly show the gamma and alpha phases of Al_2O_3 . It is well known that amorphous Al_2O_3 transforms into metastable gamma- Al_2O_3 at temperatures between 800 °C and 950 °C, and gamma- Al_2O_3 converts into alpha- Al_2O_3 at temperatures above 1000 °C [24]. The alpha- Al_2O_3 phase becomes the predominant crystalline form of the coatings, which are formed after 10 min in PAE with the addition of 4 g/L $NaAlO_2$.

The amorphous $\rightarrow$ gamma $\rightarrow$ alpha Al_2O_3 transformation is related to the property of PEO [25]. At the beginning of PEO (1 min and 3 min), the micro-discharges are small and evenly distributed, and the energy of micro-discharges is not enough to transform amorphous Al_2O_3 into gamma and alpha phases. As the PEO time increases (5 min and 10 min), the number of micro-discharges decreases and their size increases as the micro-discharge sites through which a high anodic current can flow decrease. Intense micro-discharges now have enough energy to convert amorphous Al_2O_3 into gamma and alpha phases.

The formation of Al_2O_3 films or coatings on a tungsten substrate has not been extensively studied in the literature [11,26], but these films or coatings can most likely be formed using various techniques such as sol-gel, atomic layer deposition (ALD), chemical vapor deposition (CVD), etc. The PEO process offers a number of advantages over alternative methods of creating alpha- Al_2O_3 films/coatings on a tungsten substrate. PEO forms alpha- Al_2O_3 coatings on a tungsten substrate in a short time, skipping the process of annealing at high temperatures required to convert amorphous Al_2O_3 into a crystalline phase, as is the case with other techniques. The process is also simple, cost-effective and environmentally friendly.

Al_2O_3 coatings formed by PEO on aluminum and its alloys substrates exhibit excellent mechanical and thermal properties, depending on the substrate and electrolyte used [27–31]. This indicates that alpha- Al_2O_3 coatings on tungsten substrate can be used wherever a high degree of hardness, thermal stability, and wear resistance is required. These coatings can also serve as protective coatings for tungsten, as tungsten has poor oxidation resistance at high temperatures (especially above 800 °C) [32]. Alpha- Al_2O_3 coatings on tungsten are promising candidates for high-temperature luminescence thermometry due to their high refractive index and high transparency from the ultraviolet to the near-infrared region, which makes them suitable hosts for rare earths and transition metal ions [33,34].

4. Conclusions

We presented the effects of $NaAlO_2$ concentration in alkaline phosphate electrolyte (PAE, 2 g/L $Na_3PO_4 \cdot 12H_2O$) on the morphology, chemical, and phase composition of the formed coatings on tungsten substrate in this work. The most important result is the creation of rich alpha- Al_2O_3 coatings in PAE + 4g/L $NaAlO_2$ for 10 min, which are suitable for high-temperature W/ Al_2O_3 coating applications. The use of alpha- Al_2O_3 coatings on tungsten for high-temperature applications, especially for the luminescence thermometry method for measuring high temperatures, will be the focus of the upcoming study.

Author Contributions: Conceptualization, S.S. methodology, S.S.; validation, S.S. and P.N.; formal analysis, P.N.; investigation, S.S. and P.N.; data curation, P.N.; writing—original draft preparation, S.S.; writing—review and editing, S.S.; visualization, S.S. and P.N.; supervision, S.S.; project administration, S.S. All authors have read and agreed to the published version of the manuscript.

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