Effect of frequency on plasma electrolytic oxidation of zirconium in pulsed unipolar mode

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Effect of frequency on plasma electrolytic oxidation of zirconium in pulsed unipolar mode

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Abstract. Using the method of *in situ* impedance spectroscopy, an optimization of plasma electrolytic oxidation (PEO) was performed, and the influence of the pulse frequency was evaluated for the coating of Zr-1Nb alloy. It was shown that the *in situ* impedance modulus decreased with increasing the pulse frequency in a pulsed unipolar mode. Also, the protective properties of the coating improved with frequency; this was attributed to the increase in the uniform distribution of the microdischarges over the sample surface. As a result, the optimal frequency range of PEO was justified based on the impedance spectroscopy studies.

1. Introduction

Zirconium alloys are widely used in the nuclear power industry in the active part of the reactor due to their neutron transparency and good corrosion properties. Also, Zr alloys gain attention as an alternative to Ti alloys for medical implant applications. International research teams focus mainly on two types of zirconium alloys: (i) alloyed with niobium (e.g. Zr-1Nb, the Russian alloy E-110, produced in accordance with the Russian Standard - GOST), (ii) alloyed with tin (e.g. Zr-1.5Sn, Zircaloy-2) [1-3]. These zirconium alloys used for fuel cladding, in superheated water (also containing LiOH) and water vapor, are subject to waterside corrosion, accompanied by oxygen and hydrogen release, which penetrates into the alloy and causes embrittlement, which can lead to the fuel cladding failure [4, 5]. Fretting corrosion is also a serious problem due to excessive vibration in a nuclear reactor [6]. Therefore, severe operating conditions in the reactor require appropriate surface modification by forming protective coatings to improve corrosion and wear resistance of the devices. Plasma electrolytic oxidation (PEO) of zirconium alloys is a promising method for increasing their performance, due to the properties of the formed protective coatings similar to anodizing, and the coatings obtained on the fuel cladding require careful process monitoring and control [7–9].

Recently, the method of impedance spectroscopy was adapted for *in situ* studies of PEO processes using frequency response estimates of the electrolyzer impedance [10, 11]. The methodology of the measurements was developed earlier [12]. After evaluation of the system linearity [13], this approach allows the use of electrochemical impedance spectroscopy (EIS) [14], including the equivalent circuit fitting. Moreover, the frequency response analysis helps to optimize the shape and frequency of the electric pulse by running a small number of experiments. Therefore, this paper is devoted to monitoring

the plasma electrolytic oxidation process and optimizing the frequency of the PEO of the Zr-1Nb alloy in the pulsed unipolar mode.

2. Experimental

2.1. Plasma electrolytic oxidation

The samples were cut from a sheet of the Zr-1Nb alloy in the form of plates 15×11×0.8 mm in size. PEO was carried out in a pulsed unipolar (PUP) mode under voltage control. The sample was used as the anode, the electrolyzer was connected as the cathode. The processing was carried out in the frequency scanning mode in the range from 28 to 10457 Hz, with 14 experimental points equally separated on a log scale; the exposure at every frequency was 2 s. The PEO process was also carried out at individual frequencies of 62, 713 and 3137 Hz. Other PEO parameters are given in table 1.

Table 1. Parameters of plasma electrolytic oxidation of the Zr-1Nb alloy in PUP mode.

Sample No.	Frequency (Hz)	Electrolyte (g/L)	Temperature (°C)	Voltage pulse amplitude (V)	Duty cycle (%)	Electrolyte volume (L)	Time (min)
1	62	1 g/L KOH+2 g/L Na_2SiO_3+2 g/L $Na_4P_2O_7$	20	570	50	5	7
2	713						
3	3137						

2.2. Surface characterization

The surface morphology was investigated using a Gemini SEM300 scanning electron microscope (SEM) (Carl Zeiss, Germany). The phase composition of the coating was investigated using an X-ray diffractometer (XRD) Ultima IV, (Rigaku, Japan) equipped with a Cu-Kα X-ray source; scanning was performed from 10 to 80 degrees 2θ, with 0.02 degrees 2θ step, and measurement time at each step of 1 s. The phase composition of the surface was studied for the uncoated alloy, and for all the coatings obtained. Phase identification and semiquantitative analysis was performed using Philips X'Pert HighScore Plus software with the PDF2 databank.

Electrochemical studies were carried out using a P-5X potentiostat (Elins, Russia) in a 0.1 M LiOH solution using an 80-ml three-electrode cell with a silver chloride reference electrode and a platinum counter-electrode. The electrode potential was measured for 2 h until a steady state was achieved. To obtain polarization curves, after establishing the stationary state, a potential sweep was performed in the range from –600 mV to +600 mV with respect to the open circuit potential with a scan rate of 0.25 mV/s. The potential and corrosion current were calculated by the Tafel method from the polarization curves.

3. Results and discussion

3.1. In situ impedance spectroscopy

As a result of the in-situ impedance spectroscopy, the characteristics of the frequency response of the PEO process were obtained. Figure 1 shows the impedance modulus during the treatment. Estimates of the frequency response corresponding to different PEO time moments (1, 2, 4, 6 min) are shown in figure 1 by solid lines. The impedance for all the frequencies tends to increase over the PEO time due to the coating growth and the associated growth of coating resistance. For the PUP mode, there is a gradual decrease in the impedance modulus with increasing frequency. This can be attributed to the shunting effect of the coating capacitance connected in parallel with the coating resistance represented during the PEO process by the microdischarge action.

The markers in figure 1 show the impedance modulus during the PEO processing at single frequencies of 62, 713, 3137 Hz. As follows from this figure, the single frequency experiments show

similar values of the impedance modulus; this signifies the efficiency of the frequency response method for the process optimization via one step experiment.

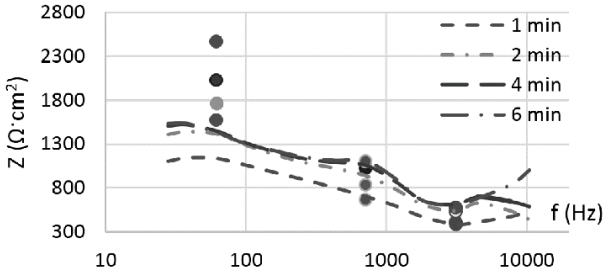
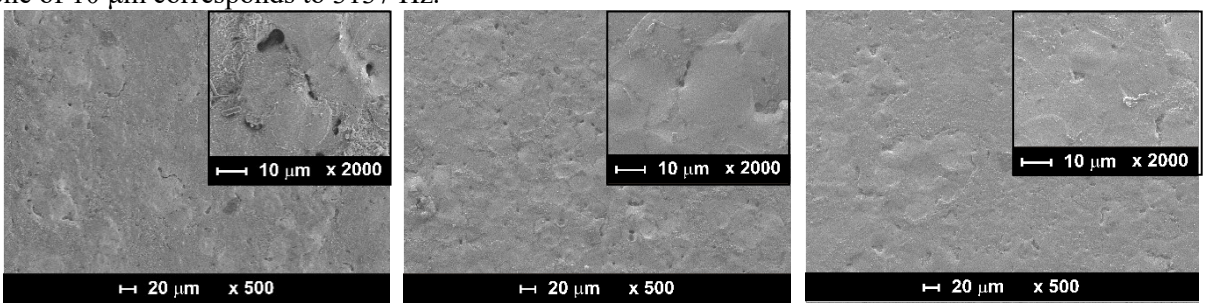


Figure 1. In situ frequency response impedance modulus for the PEO of Zr-1Nb in PUP mode.

However, some quantitative changes can be seen at the lowest frequencies: the single frequency impedance is higher than that for the frequency scan. As follows form further discussion, these treatment conditions provide the worst coating; other frequencies contribute to more uniform and protective coatings; therefore, the impact of higher frequencies during the PUP scan provided somewhat better coating than the single frequency treatment. At lower frequencies, the impedance modulus has maximal values, and as a result, it has the minimal current in the system, providing the lowest protective properties to the coating. For the minimal current, the distribution density of microdischarges decreases, which is confirmed by the video recording.

3.2. Pulse frequency effect on the coating properties

Figure 2 shows a top view of the PEO coatings obtained at different frequencies. The coatings have a porous structure, which is associated with the effect of microdischarges, and small cracks arising from the mechanical stresses as a result of rapid solidification of the oxide by the surrounding electrolyte during PEO. The coating, formed at a frequency of 3137 Hz, has the most uniform and smooth morphology. The largest coating thickness of 15 μm corresponds to a frequency of 62 Hz, the smallest one of 10 μm corresponds to 3137 Hz.



62 Hz 713 Hz 3137 Hz

Figure 2. Morphology (top view) of the coatings obtained at different frequencies of PEO.

As a result of the electrochemical tests, the corrosion properties of the samples were evaluated - free corrosion potential and corrosion current; the results are presented in table 2.

With an frequency increase, the PEO coating more and more passivates the surface, the free corrosion potential increases, and the corrosion current decreases. The highest corrosion current was found for the sample processed at the lowest PUP frequency of 62 Hz; however, it is still lower than that for the uncoated sample. The sample obtained at the frequency of 3137 Hz has the best corrosion resistance.

X-ray diffractometry analysis (table 2) shows that the substrate is characterized by α-Zr lines, and the coating contains crystalline phases of monoclinic and tetragonal modifications of ZrO_2. No other crystalline phases were detected. As follows from table 2, the predominant phase in the coating structure is m-ZrO_2. The percentage of high temperature modification of the t-ZrO_2 phase does not exceed 6%,

and it reaches the maximal value at a PEO frequency of 3137 Hz. Therefore, this electrical mode seems to be the most promising to obtain protective PEO coatings.

Table 2. Results of electrochemical corrosion tests and XRD analysis.

Frequency (Hz)	Corrosion properties		XRD analysis results		
	E_{corr} (V)	$i_{corr} \cdot 10^{-4}$ (A/m^2)	α-Zr	m-ZrO_2	t-ZrO_2
no coating	-0.1497	29.0	100 %	-	-
62	-0.1121	13.0	-	97 %	3 %
713	-0.1105	4.5	-	95 %	5 %
3137	-0.0809	4.0	-	94 %	6 %

4. Conclusion

This work demonstrates the efficiency of *in situ* impedance spectroscopy application in optimizing the frequency of the pulsed unipolar PEO processing of Zr-1Nb alloy. It has been established that at a frequency of 3137 Hz, the *in situ* impedance of the system is close to minimal value; this leads to the highest average current density due to the uniform distribution of the PEO microdischarges, over the sample surface. This uniform treatment provides coatings with the best protective properties in this study; this is supported by SEM photographs, corrosion tests and X-ray diffractometry analysis.

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References

[1] Lin J *et al.* 2004 *Materials Science and Engineering* A **381** 104
[2] Cheng Y *et al.* 2012 *Surface and Coatings Technology* **206** 3230
[3] Jeong Y H, Lee K O and Kim H G 2002 *J. Nucl. Mater*. **302** p 9
[4] Motta A T *et al.* 2007 *J. Nucl. Mater*. **37** 61
[5] Theaker J R *et al.* 1994 *Zirconium in the Nuclear Industry (Proceedings of Tenth International Symposium)* (ASTM) pp 221–242
[6] Fisher N J, Weckwerth M K, Grandison D A E and Cotnam B M 2002 *Nuclear Engineering and Design* **213** 79
[7] Borisov A M, Vostrikov V G, Romanovsky E A, Tkachenko N V, Vinogradov A V, Krit B L, Savushkina S V and Polyansky M N 2013 *Journal of Surface Investigation: X-Ray, Synchrotron and Neutron Techniques* **4** 366
[8] Klapkiv M D, Povstyana N Yu and Nykyforchyn H M 2006 *Mater Sci.* **42** 277
[9] Zhang D *et al.* 2003 *Rare Metal Materials and Engineering* **32** 658
[10] Parfenov E V, Yerokhin A L and Matthews A 2007 *Surface and Coatings Technology* **201** 8661
[11] Parfenov E V, Yerokhin A and Matthews A 2009 *Surface and Coatings Technology* **203** 2896
[12] Parfenov E V and Yerokhin A 2011 Methodology of data acquisition and signal processing for frequency response evaluation during plasma electrolytic surface treatments *Process Control: Problems, Techniques and Applications* ed S P Werther (Nova Science Pub. Inc.) pp 63–96
[13] Yerokhin A, Parfenov E V, Liang C J, Mukaeva V R and Matthews A 2013 *Electrochemistry Communications* **27** 137
[14] Barsukov E and Macdonald J R 2005 *Impedance Spectroscopy: Theory, Experiment, and Applications* (Hoboken: John Willey & Sons, Inc.)