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The electrophysical properties of the surface of radiation: Thermal oxidized beryllium in water medium

N. N. Gadzhieva, A. A. Garibov, Sh. S. Ismailov, F. N. Nurmamedova

Institute of Radiation Problems of Azerbaijan National Academy of Sciences, Baku city, Azerbaijan

Email address:
nushaba6@mail.ru (N. N. Gadzhieva)

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Abstract: The electrophysical properties of the surface of metallic beryllium were studied before and after radiation-thermal treatment in water medium at temperatures 473 –773K under the influence of gamma quanta. On the features of the curves current-voltage characteristics it is established that radiation-thermal modification of the surface of beryllium is accompanied by the formation of oxide structures, defects which are determined by the temperature and time of irradiation. It is shown, that the formation of continuous oxide layer with dielectric properties leads to the increase of the surface resistivity by order. It was a comparative study the kinetics of changes in the values of surface resistivity of contact time for radiation - thermal and thermal oxidized beryllium samples. It was revealed stimulating role of radiation at relatively low temperatures in the oxidation process.

Keywords: Beryllium, Gamma-Irradiation, Thermal and Radiation-Thermal Oxidation, Oxide Layer, Surface Resistivity, Current-Voltage Characteristics, Water

1. Introduction

Beryllium is widely used as nuclear reactor materials [1, 2]. The study of radiation-heterogeneous processes of these materials with water heat carrier contact in a wide range of temperatures is necessary basis for assessing the safety of nuclear power plants, including fusion reactors [3, 4]. These processes usually lead to oxidation reactor materials, which is accompanied by a change in their surface states (condition). Change in the surface state, in turn, strongly influences the course of radiolysis of water and the rate of formation of molecular hydrogen [3, 5]. Therefore, the study of surface properties of the radiation - thermal treated beryllium plates in water medium is of particular interest. Spectral-luminescent properties and morphology of the surface topography of radiation - thermally oxidized beryllium in water medium at temperatures of 473–673K and exposed to gamma - quanta studied in our papers [5-8].

The present work is a continuation of these studies and devoted to the study of the electrophysical properties of radiation - thermal treated beryllium plates in water medium at temperatures of 473–773K and exposed to gamma - quanta. For this purpose it was investigated current - voltage characteristics and measured the values of surface resistivity of radiation - thermal and thermal oxidized beryllium samples at room temperature. The kinetics of changes of the surface resistivity (ρ_s) radiation - thermal and thermal treated samples Be depending on contact time (τ) were studied and comparative analysis was carried out.

2. Experimental

We used ground and polished beryllium metal plates 20 × 10 × 0.2 mm, having a smooth surface. Samples were treated with solvents (ethanol and acetone) and pre-dried at room temperature under argon. For surface dehydroxylation and complete cleaning of organic contamination samples were placed in quartz cells and carried out additional heat treatment at 673K in vacuum P = 10^{-6} Pa for 6h. H_2O adsorption was studied as described in [9].

Radiation thermal oxidation of the surface of the beryllium plates in contact with water was carried out at temperatures of T = 473 – 773K at a pressure of 2 atm. under the influence of γ - quanta. Samples were irradiated by ^{60}Co isotopic source at dose rate dD_γ/dt = 0.54 Gy/s.

Measurement of surface resistivity ρ_s beryllium plates before and after radiation-thermal and thermal oxidation was

carried out by four probe compensation method at constant current at room temperature [10]. In the calculations we used the average values ρ_s, which account for the effect of geometrical sizes of plates.

3. Results and Discussion

In this paper we obtained and studied peculiarities of current - voltage curves (CVC) and measured values of surface resistivity of beryllium metal plates before and after radiation-thermal processing of these samples in water medium at temperatures of 473–773K and exposed to gamma - quanta depending on the time of contact or exposure. To identify the stimulating role of radiation at relatively low temperatures in the oxidation process it was carried out a comparative study of the kinetics of changes of values ρ_s on the contact time for radiation – thermal (RT) and thermal (T) processes.

As an example, in Fig. 1 it is shown the current - voltage curves before (curve1) and after radiation- oxidation at temperature of 673K of beryllium samples in water medium with different contact time (curves 2, 3, 4).

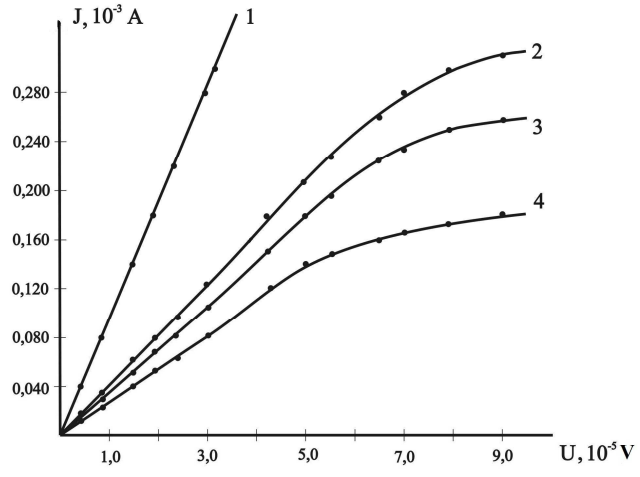

Fig. 1. *CVC curves of beryllium plates before (1) and after radiation - thermal oxidation in water medium at temperature 673K and at γ - rays action (2-4): τ = 15 (2), 30 min (3) and 1h. (4) (D_γ/dt = 0.54 Gy/s).*

As can be seen from the figure, the current-voltage dependence of J-U of initial sample described ohmic law and has a linear form, inherent in most metals. [11]. Radiation-thermal processing of beryllium plates leads to a deviation from linearity of the current-voltage curves, and with increasing contact time, these deviations are most pronounced. Since an increase in contact time or exposure to 4 times (from 15 min to 1 hour) followed by decreasing values of the slope, in the linear region is determined in ~ 2.2 times. The value of the voltage corresponding to the start area deviation from linearity shifts to $\Delta U \approx 3 \cdot 10^{-5}$ V (from 8 to $5 \cdot 10^{-5}$V). Furthermore, as can be seen from the figure, at the same voltage value at the transition from a pure sample Be (curve.1) to radiation -thermal treated samples (curves 2, 3, 4) values J decrease. For example, in the linear region when the voltage U = $10 \cdot 3^{-5}$V amperage in the treated samples as a function of contact time τ = 15,30 min. and 1 hour and relative value J of the initial sample are reduced to 2.3; 2.8 and 3.5 times, respectively. Reducing the value of the current it should be increased the value of surface resistivity ρ_s. Indeed, as shown by the measurements, the value of surface resistivity radiation - thermal treated beryllium samples relative to the initial sample is increased by an order (Fig. 2, curve RT).

The observed features of the curves current - voltage characteristics, i.e. violation of ohmic law J-U depending accompanying by decrease voltage and amperage, as well as increasing the surface resistivity values of radiation – thermal treated beryllium plates indicate the formation of oxide on their surface structures with dielectric properties. According to the results of spectral-luminescent and microscopic studies [6, 12], the radiation-thermal processing of beryllium plates in water medium at the temperature of 673K and exposed to gamma - quanta leads to the formation of oxide on their surface structures, defects of which is determined by the contact or exposure time. Increase contact time of 15 min. to 1 hour (or absorbed dose of γ- irradiation from 0.5 to 2 kGy) accompanied by the formation of thin oxide film, and continuous formation of the oxide layer. The thickness of the oxide layer on the surface of the radiation – thermal treated beryllium relatively to the thickness of oxide layer of initial sample is increased by about an order of magnitude (from 6 to 110 nm). [8] The thin oxide films are high, and the continuous oxide layers lower defect rate. According to the AFM - surface morphology studies radiation - thermal oxidized metallic beryllium, with formation of thin oxide film involving nanoparticles of one species of 150 nm, and the formation of a continuous oxide layer - equally spaced with different kinds of nanoparticles 400-600 nm in size. Apparently, these oxygen nanoclusters are the basic elements forming continuous oxide layers [12].

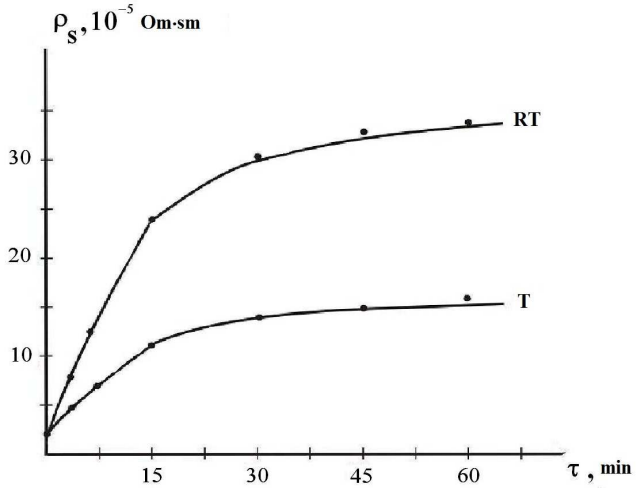

Fig. 2. *Kinetic curves of changes of surface resistivity ρ_s depending on the contact time τ of radiation - thermal (RT) and thermal (T) oxidized beryllium plates in a water medium (T = 673K, dD_γ/dt =0.54 Gy/ s).*

Formation of oxygen nanoclusters and their participation

in the process of oxidation of beryllium in water medium confirms the results of IRRAS and RTL (radio- thermo luminescence) researches. Since, on the surface radiation - thermal oxidized beryllium registered us absorption band with a maximum at $\nu = 1250$ cm^{-1} and decay curve with an activation energy $E_a = 0.15$ eV, related to the molecular oxygen ion - radical O_2^-[6]. Oxygen ion -radicals O_2^- also recorded by scanning tunneling microscopy for metals coated with thin film of oxides [13].

As it is known, in the mechanism of conductivity of metals, the major role played free electrons [11]. In the presence on metal surface the oxide layer, i.e. in a heterogeneous system Be-BeO conductivity of the oxide layer is determined emitted on metal and issued by trapped traps free charge carriers (electrons). The main charge trapping traps are generated by gamma - radiation surface-localized oxygen hole centers type O^-[10]. Free conduction electrons are trapped and usually blocked by these hole centers, whose role in the conduction mechanism becomes more noticeable as the thickness of the oxide layer increase. Since the growth of the oxide layer thickness is accompanied by both an increase in the density of surface-localized hole centers and the probability of capture of free charge carriers by these centers. Major changes in the JU dependency occurs when the value of oxide thickness under the condition $d \geq \lambda$, where λ-free path of the charge carriers in the metal beryllium and its oxide, which is 3-50nm.

In Fig. 2 it is presented the curves of changes of the surface resistivity values (ρ_s) of radiation - thermal (curve PT) and thermal treated (curve T) beryllium oxide plates at 673K in water medium depending on the contact time. As seen in Figure 2, these relationships are characterized by the presence of two regions. Comparative analysis of these curves reveals the following:

1.Values of surface resistivity of the radiation – thermal and thermal oxidized beryllium plates compared with the value ρ_s of initial samples increased in ~ 14 and 5 times, respectively.

2. Ggrowth rate of values ρ_s, defined in the linear region, depends, in the case of the radiation-thermal oxidation ~ 2.5 times higher than the growth rate ρ_s during thermal oxidation.

3. Difference of values of surface resistivity $\rho_s = \rho_s$ (RT) - ρ_s (T) defined in the second region equals (составляет) $2 \cdot 10^{-5}$ om·sm.

4. Second region of the dependence ρ_s -τ in the case of the thermal treated samples actually approaching to saturation. However, in the case of radiation – thermal treated samples, the dependence ρ_s -τ is not saturated and the surface resistivity values continue to rise.

Curves of the observed features of ρ_s -τ radiation-thermal and thermal oxidation process of beryllium plates show that in both cases, oxide layers are formed on their surface. Thus the rate of formation of the oxide layer at the initial stage of the process on the surface of the radiation – thermal treated beryllium samples occurs 2.5 times faster than the surface of the thermal treated plates. At the second stage, within the contact time range ($30 \leq \tau \leq 60$ min.) the oxidation process of radiation – thermal treated beryllium plates compared to the thermal-treated samples still continues. It indicates the stimulating role of radiation action of gamma-irradiation at relatively non-high temperatures during the oxidation process of beryllium in water medium.

Similar results were also obtained in the comparative study of the relative changes on the surface resistivity for radiation - thermal and thermal oxidized beryllium plates in water medium.

4. Conclusions

Peculiarities of current - voltage characteristics of beryllium plates radiation - thermal treated in water medium show that modification of the surface leads to the formation of oxide structures, which defectiveness is determined by the temperature and contact (or exposure) time. The main features of the observed violation of the CVC are ohmic law JU dependencies and decrease values of voltage and current with increasing irradiation time. Formation of oxide layers with dielectric properties is also confirmed by measurements of surface resistivity values of radiation – thermal and thermal treated beryllium plates. Revealed, that the value of surface resistivity of radiation -thermal and thermal oxidized samples relatively values ρs of initial plates increases by order and in ~ 4 times respectively. Based on the comparative analysis of the dependences of the surface resistivity values ρs on the contact time of radiation - thermal and thermal treated beryllium plates in water medium at the temperature of 673K it is found that radiation-thermal oxidation of Be compared with thermal oxidation occurs 2.5 times faster. This indicates the stimulating influence of radiation on the oxidation process of beryllium at relatively low temperatures.

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