

SPECTRAL-LUMINESCENT AND ELECTROPHYSICAL STUDY OF RADIATION OXIDATION OF BERYLLIUM IN WATER

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The radiation oxidation of Be in water at room temperature in the absorbed dose range $D_\gamma = 0.5 \dots 180$ kGy was studied by radiothermoluminescence (RTL), infrared reflection-adsorption spectroscopy (IRRAS), and electrical conductivity. The participation and role of surface relaxing intermediate-active particles in the dynamics of changes in the oxidation process are considered. Using the RTL method, the role of surface oxygen hole centers generated by γ -irradiation and chemisorbed oxygen in the formation of nanooxide films was experimentally established. The formation of nanooxide films on the surface of Be in water was traced in the IR reflection spectra. The kinetics of radiation oxidation of beryllium has been studied and its radiation passivation has been established. According to the logarithmic dose dependence of the surface resistivity Be, two stages of the oxidation process were revealed. It is shown that the formation of nano oxide films leads to a decrease in the surface electrical conductivity of beryllium by 2 orders of magnitude and an increase in the thickness of oxide films by 1.6 times.

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INTRODUCTION

The surface layer of metals is in a special physical and chemical state. It is largely saturated with structural defects (vacancies, dislocations, impurities) and its properties differ from bulk properties. Therefore, the special state of the surface layers can affect the kinetics of various processes, including diffusion, adsorption, and radiolysis of water molecules. The contact and interaction of water with the surface of metals leads to their change and is accompanied by the formation of an oxide layer. At the same time, a new Me-MeO nano-heterosystem is formed on the surface. The formation of a nanosystem plays a decisive role in the radiation-stimulated processes of water on the surface of metals. The study of the initial stage of the formation of a nanosized oxide film and the formation of an oxide layer is of fundamental importance for solving the problems of surface passivation and predetermines the course of the corrosion process.

The effect of the state of near-surface layers of metals on the adsorption process (shape, kinetics, mechanism) is most pronounced during their radiation modification. Since, gamma irradiation of metals leads to a change in the charge state of the surface. Therefore, it seems interesting to study the adsorption and radiation-chemical decomposition (radiolysis) of water on the radiation-modified surface of metallic beryllium. At the same time, the study of the process of radiation oxidation of the surface of metals is of fundamental importance in radiation materials science from the point of view of the safety of atomic and nuclear reactors. Despite the fact that numerous experimental and theoretical works have been devoted to its study, some questions still remain open and unresolved [1–5].

This work is devoted to a comprehensive (spectral-luminescent and electrophysical) study of the radiation

oxidation of the surface of beryllium in water at room temperature.

EXPERIMENTAL PART

The objects of study were ground and polished metal beryllium plates with $R = 0.80 \dots 0.85$ in the mid-IR wavelength region. Twenty samples with the same R values were prepared for parallel experiments of radiation oxidation in the beryllium-adsorbed water system by radiothermoluminescence (RTL), Infrared reflection-absorption spectroscopy (IRRAS) and electrical conductivity methods.

Radiation oxidation of the surface of beryllium plates in contact with water was carried out at $T = 300$ K under the action of γ -quanta. The samples were irradiated on a ^{60}Co source with a dose rate of $dD_\gamma/dt = 1.03 \text{ Gy}\cdot\text{s}^{-1}$.

Measurement of resistivity of beryllium plates before and after radiation oxidation was carried out according to the procedure [6]. The thicknesses of oxide films were determined by ellipsometric and gravimetric methods. The RTL curves were obtained in the temperature range $80 \dots 500$ K on a TLG-69 M thermoluminograph at a sample heating rate of 0.08 K/s . Fourier IR reflectance spectra were obtained by the incidence of linearly polarized radiation on the sample at an angle $\varphi = 88^\circ$ on a Varian 640 FTIR spectrometer in the frequency range $\nu = 1200 \dots 800 \text{ cm}^{-1}$.

THE DISCUSSION OF THE RESULTS

When radiation-oxidized beryllium plates are irradiated with γ -quanta ($T = 77 \text{ K}$) in contact with water, RTL peaks appear at temperatures $T = 90, 190,$ and 310 K (Fig. 1, curve 1). Low temperature peak at $T = 90 \text{ K}$ with activation energy $E_a = 0.14 \text{ eV}$ can be associated with thermally stimulated luminescence of

adsorbed molecular oxygen on electronic centers [6]. The intensity of this peak strongly depends on the contact time of beryllium (or on the thickness of the radiation-oxidized film) with water during γ -irradiation in the Be-H₂O system. An increase in the thickness of the T = 90 K peak by an order of magnitude (from 8 to 130 nm), its intensity increases by a factor of ~ 2, and a new peak appears at T = 120 K with E_a = 0.26 eV (see Fig. 1, curve 2). Apparently, the peak at T = 120 K is associated with the adsorption luminescence of

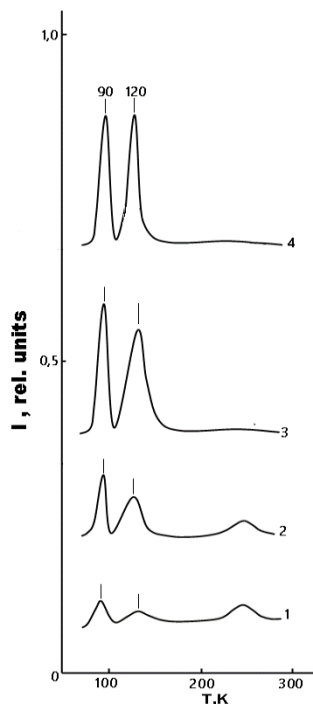


Fig. 1. Changes in the RTL curves of oxide films depending on the contact time of beryllium with water during Be radiation oxidation: 30 min (1); 5 (2); 20 (3), and 30 h (4). ($T = 300$ K, $dD_{\gamma}/dt = 1.03$ Gy/s)

The manifestation of the multicomponent structure of the RTL oxygen peak in the region of $T \sim 90 \dots 350$ K with relatively thick oxide films is associated both with the inhomogeneity of the hole centers themselves and the presence of radiation-adsorbed oxygen on the surface in various states (O_2^- ads, O^{2-} ads, OH^- ads etc.)

It should be noted that the increase in the intensity of the RTL oxygen peak at 120 K with an increase in the thickness of the oxide film is associated with an increase in the density of surface states in the near-surface BeO nanooxide layer and, hence, the probability of oxygen adsorption on these centers. (see Fig. 1, curves 3, 4).

The formation of a surface oxide film was traced from the IR reflection spectra in the range $\nu \sim 1200 \dots 800$ cm⁻¹. The change in the band of the Be-O stretching vibration depending on the contact time of beryllium with water (τ) during the radiation oxidation of Be is shown in Fig. 2. A thin nano film ($d = 8$ nm) in the spectrum leads to the appearance of a band with a maximum at 1100 cm⁻¹, which characterizes the Be-O stretching vibration [8]. The thickening of the nano oxide film from 8 to 130 nm is accompanied by an increase in intensity by ~ 2 and its broadening by a factor of ~ 2.5 irradiation in metal [8].

molecular oxygen, a product of the radiation decomposition of water, on surface localized hole centers of the O⁻ type [6, 7]. The peak at $T = 190$ K with the activation energy E_a = 0.38 eV refers to beryllium hydroxide. The diffuse peak at $T \sim 310$ K, with E_a = 0.8 eV, is associated with thermally stimulated luminescence of chemisorbed oxygen and other oxygen-containing groups (OH^-) on the surface electronic F+ and F-centers [7].

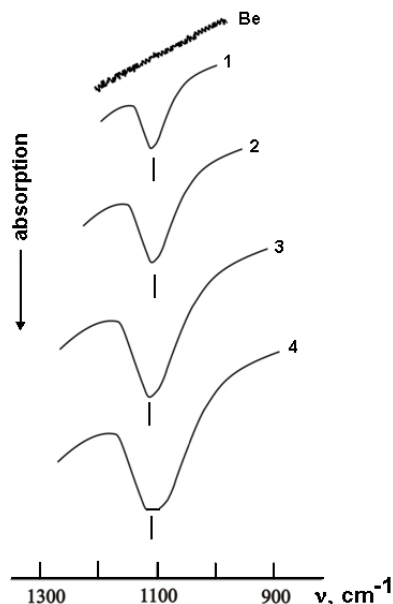


Fig. 2. Change in the absorption band of the stretching vibration of the Be-O bond depending on the contact time of beryllium with water during radiation oxidation of Be: $\tau = 30$ min (1); 5 (2), 20 (3), and 30 h (4) ($T = 300$ K, $dD_{\gamma}/dt = 1.03$ Gy/s)

Fig. 3 shows the kinetic curve of the radiation oxidation of Be in water. For this purpose, the dependence of the optical density of the absorption band of the Be-O stretching vibration with a maximum at 1100 cm⁻¹ on the contact time of beryllium with water under the influence of γ -irradiation in the Be-H₂O system was obtained.

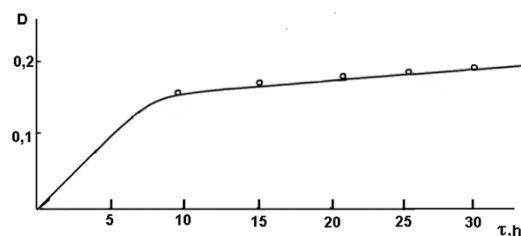


Fig. 3. Dependence of the optical density of the absorption band of the Be-O vibration on the contact time of beryllium with water under radiation exposure ($T = 300$ K, $dD_{\gamma}/dt = 1.03$ Gy/s)

As can be seen from the figure, the oxidation kinetics is close to the parabolic law ($n = 2$) and is determined by the classical diffusion of oxygen through the protective oxide film. In this case, one of the main conditions to slow down the further oxidation of the

metal is the continuity of the oxide film [6, 8]. The oxide film will prevent the penetration of intermediate relaxing products of H₂O radiolysis into the reaction space and thus inhibit its further growth.

A comparative analysis of the RTL and IRRAS data shows that the oxidation of beryllium in an water medium at room temperature results in nanostructuring of the surface of this metal, which accompanies the formation and formation of nanooxide films. The Table lists the spectroluminescent parameters of beryllium nanooxide films.

The radiation oxidation of beryllium in water was also studied by the electrical conductivity method. For this purpose, a logarithmic dependence of the surface resistivity on the absorbed dose of gamma irradiation was obtained (Fig. 4).

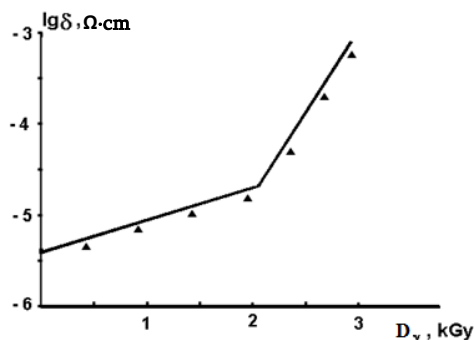


Fig. 4. Logarithmic dependence of the change in surface resistivity on the absorbed dose of irradiation during oxidation beryllium

Spectroluminescent parameters of beryllium nanooxide films

Sample	Temperature RTL peaks, K	Activation energy of RTL peaks (E _a), eV	IR maxima AB stretching vibration Me-O, cm ⁻¹	Half-width (v _{1/2}), AB stretching vibration Me-O, cm ⁻¹	Thickness of nanooxide films d, nm
Nanooxide films beryllium	90	0.14	1100 (hv ~ 0.14eV)	45...110	8...130
	120	0.26			
	190	0.38			
	310	0.8			

An analysis of this dependence shows that it is characterized by the presence of two linear stages. The transition from the first stage to the second is accompanied by the formation of a continuous nanooxide layer, as a result of the introduction of oxygen atoms and the migration of oxygen hole centers into the volume both from the defective surface and from internal traps along the grain boundaries. In this case, the surface resistivity value increases by 2 orders of magnitude, and the thickness of the oxide layer is 1.6 times (from 8 to 130 nm).

CONCLUSIONS

Radiation-stimulated Be oxidation in contact with water at room temperature in the absorbed dose range D_γ = 0.5...180 kGy was studied by RTL, IRRAS and electrical conductivity methods. According to RTL spectra at T = 80...300 K with E_a = 0.14...0.80 eV, peaks associated with thermally stimulated adsorption and chemiluminescence of oxygen and oxygen-containing groups on surface-localized centers under γ-irradiation were recorded. It has been experimentally established that surface oxygen hole centers generated by γ-irradiation and chemisorbed oxygen play the main role in the formation of nanooxide films.

The formation of nanooxide films on the Be surface in water was traced from the IR reflection spectra. The kinetics of radiation oxidation of beryllium has been studied and its radiation passivation has been established. It is shown that the classical process of passivation by native oxide is controlled by diffusion and oxidation proceeds according to a parabolic mechanism.

The kinetics of radiation oxidation of beryllium in water was studied by the electrical conductivity method. According to the logarithmic dose dependence of the resistivity Be, a two-stage nature of the oxidation

process was revealed. It is shown that the transition from the first stage to the second is accompanied by a decrease in the electrical conductivity of beryllium by 2 orders of magnitude and an increase in the thickness of the oxide layer by 1.6 times. The participation and role of surface relaxing intermediate-active particles in the dynamics of changes in the oxidation process are considered.

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СПЕКТРАЛЬНО-ЛЮМІНЕСЦЕНТНЕ ТА ЕЛЕКТРОФІЗИЧНЕ ДОСЛІДЖЕННЯ РАДІАЦІЙНОГО ОКИСНЕННЯ БЕРИЛІУ У ВОДІ

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Методами радіотермомлюмінесценції (РТЛ), інфрачервоної відбивно-адсорбційної спектроскопії (IRRAS) та електропровідності досліджено радіаційне окиснення Be у воді кімнатної температури у діапазоні поглинених доз $D\gamma = 0,5 \dots 180$ кГр. Розглянуто участь і роль поверхневих релаксуючих проміжно-активних частинок у динаміці змін процесу окиснення. Методом РТЛ експериментально встановлено роль поверхневих кисневих дірок, генерованих γ -опроміненням та хемосорбованим киснем, у формуванні нанооксидних плівок. Формування нанооксидних плівок на поверхні Be у воді простежено за ІЧ-спектрами відбиття. Досліджено кінетику радіаційного окиснення берилію та встановлено його радіаційну пасивацію. За логарифмічною дозовою залежністю питомого поверхневого опору Be виявлено дві стадії процесу окиснення. Показано, що утворення нанооксидних плівок призводить до зменшення поверхневої електропровідності берилію на два порядки та збільшення товщини оксидних плівок у 1,6 рази.