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INVESTIGATION OF THE RADIATION-THERMAL OXIDATION OF BERYLLIUM IN THE SYSTEM Be-WATER BY THE METHODS OF INFRARED AND OPTICAL SPECTROSCOPY

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Radiation-thermal oxidation of beryllium in contact with water at temperatures T = 473…773 K under the combined effect of temperature and gamma radiation has been studied by methods of infrared and optical spectroscopy. The formations of an oxide layer on the surface of beryllium were traced from the infrared and optical reflection spectra. In the IR spectra, the broadening of the oxide layer on the Be surface (T = 573 K) was revealed with an increase in the absorbed dose by ~ 2.5 times, which is associated with inhomogeneities caused by gamma irradiation. According to the optical reflection spectra of the surface of radiation-thermally oxidized Be, it was revealed that in the region of the edge of short waves $\lambda \leq 250$ nm, an absorption band is observed, the intensity of which increases with increasing contact time and indicates the formation of an oxide layer.

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INTRODUCTION

Beryllium is widely used as a nuclear reactor material. The study of radiation-heterogeneous processes when these materials come into contact with an aqueous coolant is necessary to understand the patterns, mechanisms, and predict the actual course of processes in normal and emergency reactor operation modes. These processes usually lead to the oxidation of reactor materials, and its study is fundamental in solving the problems of corrosion in radiation materials science [1, 2]. The main radiation-heterogeneous processes are radiation-stimulated adsorption, conversion of water, and oxidation of the beryllium surface in the Be-H_2O heterogeneous system under the influence of gamma radiation and temperature. In this work, we consider and study the radiation-thermal oxidation of beryllium in contact with water in the average temperature range 473…773 K by spectroscopic and optical methods in order to obtain new additional information about this process.

EXPERIMENTAL PART

Ground and polished beryllium plates 20x10x2 mm in size, obtained from a Be metal ingot, were made. The resulting plates had a smooth polished surface with R = 0.80…0.85 in the mid-IR (λ = 15…2.2 μm) and with R = 0.5…0.55 in the optical (λ = 200…800 nm) wavelength ranges.

To exclude impurities, the samples were treated with ethyl alcohol and dried at room temperature in an argon atmosphere. To completely remove organic impurities and dehydroxylate the beryllium surface, the samples were placed in quartz cells and subjected to additional vacuum annealing at 673 K for 6 h at a pressure of 10^{-6} Pa. The adsorbate was unsaturated vapor of bidistilled water. H_2O adsorption was carried out at room temperature according to the procedure.

The IR reflectance spectra during the incidence of linearly polarized radiation on the samples at an angle φ = 88° were measured in the region of 4000…650 cm^{-1} at room temperature using the IR reflection-adsorption spectroscopy (IRRAS) method in the spectrometer Varian 640 FT-IR [3, 4]. Optical reflection spectra were obtained at an angle of incidence φ = 45° in the spectrophotometer Cary 50 Scan.

Irradiation of the samples was carried out on an isotope source of ^{60}Co quanta with a dose rate of dD_γ/dt = 0.54 Gy/s.

RESULTS AND DISCUSSION

The formation of an oxide layer on the surface of radiation-thermally treated beryllium in an aqueous medium at temperatures T = 473…773 K under the influence of γ-quanta was traced by the method of IRRAS. As an example (Fig. 1) shows the reflection spectra surfaces of the Be samples before (see Fig. 1, curve 1) and after oxidation in the absorption region of the oxide film (ν ~ 1300…650 cm^{-1}) (see Fig. 1, curves 2, 3). The radiation-thermal oxidation of beryllium is accompanied by the formation of absorption bands at 1100 and 720 cm^{-1} [4, 5]. According to [6], the absorption bands at 1100 and 720 cm^{-1} refer to the longitudinal (LO) and transverse (TO) vibrations of BeO lattice phonons and, accordingly, characterize the stretching and bending vibrations of the BeO bond. According to the theory of IRRAS [7], when studying thin films on a metal surface, a change in absorption upon reflection from a light sample (a decrease in reflection) occurs significantly at frequencies of longitudinal (stretching) vibrations. Therefore, the oxidation state of the Be samples was subsequently estimated from the change in the optical density of the Be–O stretching vibration band (ν ~ 1100 cm^{-1}).

Increase in contact time τ from 15 to 45 min accompanied by an increase in the intensity (optical density) of the absorption band of the stretching

vibration of the oxide film at ν = 1100 cm^{-1} by ~ 2 times (curve 2, 3). In this case, the half-width of the band increases by 60 cm^{-1} and amounts to $\Delta\nu_{1/2}$ = 150 cm^{-1}. This indicates that gamma radiation at relatively low temperatures has a stimulating effect on the formation of an oxide layer on the surface of beryllium in an aqueous medium.

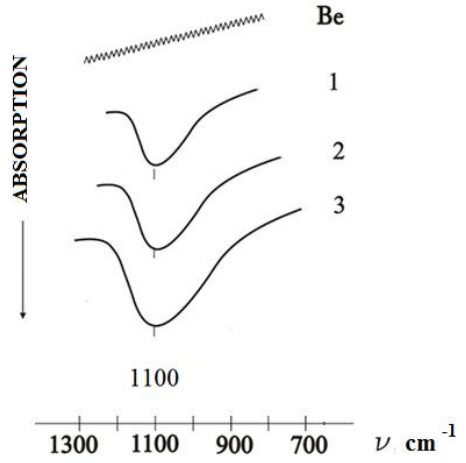

Fig. 1. IR-spectra of the absorption band of the stretching vibration of the Be–O bond before (1) and after radiation-thermal oxidation at a temperature of T = 573 K of the beryllium surface: τ = 15 (2) and 45 min (3)

Comparison of the optical density and half-width of the band of the stretching vibration of the Be–O bond of the oxide film (ν ~ 1100 cm^{-1}) during radiation-thermal and thermal oxidation under identical conditions shows that the intensity and half-width in the first case are ~ 1.5 times greater, than in the second case. The broadening of the stretching vibration band of oxide films during radiation-thermal oxidation of Be indicates the inhomogeneity of their structures, which is apparently associated with microstructural inhomogeneities caused by γ-irradiation. An increase in the treatment temperature from 473 to 773 K during the radiation-thermal oxidation of Be leads to an increase in the intensity of the Be–O stretching vibrations by a factor of ~ 2 and their broadening by a factor of ~ 2.5, while the position of the band actually remains unchanged.

Kinetic curves of radiation-thermal oxidation of beryllium with water, i. e. The dependences of the optical density of the absorption band of the stretching vibrations of the Be–O bond on the contact time of beryllium with water under the influence of γ-quanta at temperatures of 473…773 K showed that all of them obey the parabolic law, but differ in the rate of oxidation. The parabolic law of oxidation indicates that the controlling mechanism of the process is the diffusion of the metal and/or oxygen through the oxide passivation layer. According to [8], surface-adsorbed molecular oxygen in its π-form, i.e. π-O_2^-, actively participates in the formation of the oxide layer. The role of the latter was also confirmed by radiothermoluminescence (RTL) [8]. The formation and formation of oxide structures on the surface of radiation-thermally treated beryllium plates in an aqueous medium at temperatures of 473…773 K under the action of gamma rays is also confirmed by electrophysical measurements of the surface electrical conductivity of Be. As shown by these measurements, the formation of a continuous oxide layer is accompanied by a decrease in the value of the surface electrical conductivity by 4 orders of magnitude compared with the initial samples.

The optical reflectance spectra of the surface of radiation-thermally oxidized beryllium at temperatures of 473…773 K under the combined effect of temperature and gamma radiation undergo significant changes. Fig. 2 shows the changes in the optical reflection spectra of the surface of radiation-thermally oxidized Be at a temperature of 573 K depending on the time of contact with water.

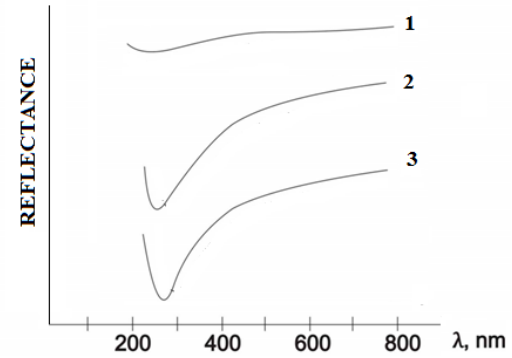

Fig. 2. Optical reflection spectra before (1) and after radiation-thermally oxidized at a temperature T = 573 K beryllium surface: τ = 15 (2) and 45 min (3)

A comparison of these spectra shows that with increasing contact time in the wavelength range λ = 350…800 nm, no changes are observed. However, in the region of the edge of short waves λ ≤ 250 nm, an absorption band is observed, the intensity of which increases with increasing contact time and indicates the formation of a new substance. The band gap of this band is E ≥ 7 eV and corresponds to the band gap of BeO (according to various sources, it is equal to E ≥ 6.8…10 eV). An increase in the contact time and temperature leads to an increase in the thickness of the oxide layer on the Be surface and, accordingly, to an increase in the band gap.

CONCLUSIONS

The radiation-thermal oxidation of beryllium in contact with water at temperatures T = 473…773 K under the combined effect of temperature and gamma radiation was studied by infrared and optical spectroscopy. According to the IR reflectance spectra, it was found that an increase in the treatment temperature from 473 to 773 K during radiation-thermal oxidation of Be leads to an increase in the intensity of the Be–O stretching vibrations by a factor of ~ 2 and their broadening by a factor of ~ 2.5. The broadening of the stretching vibration band of oxide films during radiation-thermal oxidation of Be indicates the inhomogeneity of their structures, which is apparently associated with microstructural inhomogeneities caused by γ-irradiation. According to the optical reflection spectra of the surface of radiation-thermally oxidized

Be, it was revealed that in the region of the edge of short waves $\lambda \leq 250$ nm, an absorption band is observed, the intensity of which increases with increasing contact time and indicates the formation of an oxide layer. The band gap of this band is $E \geq 7$ eV and corresponds to the band gap of BeO.

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ДОСЛІДЖЕННЯ РАДІАЦІЙНО-ТЕРМІЧНОГО ОКИСЛЕННЯ БЕРИЛІЮ В СИСТЕМІ Be–ВОДА МЕТОДАМИ ІНФРАЧЕРВОНОЇ ТА ОПТИЧНОЇ СПЕКТРОСКОПІЇ

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Методами інфрачервоної (ІЧ) та оптичної спектроскопії досліджено радіаційно-термічне окислення берилію в контакті з водою при температурах T = 473…773 К і сумісній дії температури та гамма-випромінювання. За інфрачервоним та оптичним спектрами відбиття простежено утворення оксидного шару на поверхні берилію. В ІЧ-спектрах виявлено розширення оксидного шару на поверхні Be (T = 573 K) при збільшенні поглиненої дози в ~ 2,5 рази, що пов'язано з неоднорідностями, викликаними гамма-опроміненням. За даними спектрів оптичного відбиття поверхні радіаційно-термічно окисленого Be виявлено, що в області краю коротких хвиль $\lambda \leq 250$ нм спостерігається смуга поглинання, інтенсивність якої зростає зі збільшенням часу контакту та вказує на утворення оксидного шару.