Effect of high-power ion beam irradiation modes of magnesium on the chemical composition of the surface layers at long-term storage in a surrounding atmosphere

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The composition of the surface layers of magnesium irradiated (2015) by a high power ion beam of nanosecond duration under various conditions and after long-term storage in the surrounding atmosphere (2023) was studied. It was found that multiple irradiation of magnesium, leading to an increase in the surface relief, does not lead to a noticeable increase in the concentration of oxygen and atmospheric corrosion products in the surface layer compared to a single-irradiated sample. Using X-ray photoelectron spectroscopy, an increased carbon content in the surface layer of magnesium after irradiation, as well as the formation of the Mg−O−C bond, was established. Possible mechanisms of the influence of the composition of the irradiated surface layer of magnesium on the slowing down of its atmospheric corrosion are considered.

Keywords: high power ion beam, magnesium, atmospheric corrosion.

1. Introduction

Magnesium (Mg) and its alloys, despite their good machinability and adequate mechanical properties, are of limited use in the aerospace, automotive, and medical industries due to their low corrosion resistance [1,2].

Intensive research has been conducted in the recent years to develop new compositions of magnesium alloys with improved corrosion characteristics [3,4], and to create technologies for modifying magnesium and its alloys that enhance the corrosion properties [5,6].

The surface modification is the most promising method for increasing the corrosion resistance of magnesium and its alloys (including for medical use). It can be implemented by applying various protective thin coatings to the surface, ion implantation of the surface layer and surface treatment with various pulsed energy fluxes. In the latter case, doping of the surface layer and a change of its microstructure can occur simultaneously because of high heating and cooling rates of the surface layer, which increases corrosion resistance.

An increase of the corrosion resistance of pure magnesium [7] and magnesium alloys AM60, AZ91D [8,9] was achieved by implanting carbon ions into it. This effect leads to the formation of a thin carbon-rich layer near the surface.

The treatment of magnesium by a high power proton-carbon beam with nanosecond duration significantly increases the resistance of magnesium to atmospheric corrosion [10]. The observed increase of corrosion resistance was associated with a change of the chemical composition of the magnesium surface layer after exposure to such a beam, including carbon enrichment of the thin magnesium surface layer and the formation of Mg−O−C bond. We studied in this paper the chemical composition of the surface layers of magnesium once irradiated with a high power ion beam. This mode is the easiest for interpretation of the observed changes of composition, compared with repeated irradiation. At the same time, repeated irradiation should contribute to an increase of the carbon content in the surface layer and thus improve the resistance of magnesium to atmospheric corrosion. However, it should be noted that repeated irradiation can lead to an increase of surface roughness, which can negatively affect the corrosion resistance of magnesium [11–14].

The purpose of this paper is to study the changes of the chemical composition of magnesium repeatedly irradiated with a high power ion beam during its long-term storage in the surrounding atmosphere.

2. Experimental part

Commercial magnesium discs (with Mg content ~ 99.7 wt.%) with a diameter of 12 mm and a thickness of 2 mm were mechanically polished (with diamond paste), and then washed in ethanol using ultrasound. These samples were used for study. The samples were irradiated (April 2015) in the accelerator „Temp" (Omsk State University

named after F.M. Dostoevsky, Omsk, Russia) with a proton-carbon beam $(30\%, H^+ + 70\% C^+)$ with ion energy of ~ 250 keV, with a pulse duration of 60 ns. The residual pressure in the accelerator chamber was $5 \cdot 10^{-3}$ Pa. The samples were irradiated at current densities of ~ 150 A/cm^2 with 1 and 3 irradiation pulses. The time interval between consecutive pulses is ~ 10 sec. The estimated ranges of ions in magnesium are $\sim 0.5 \mu$m for carbon ions and $\sim 3 \mu$m for protons. The initial and irradiated samples were stored in the atmosphere for 8 years (annual temperature (winter-summer) varied in the range of $15-25\,^\circ$C, humidity $45-70\%$).

Scanning electron microscopy (SEM, JSM-6610LV JEOL with an energy dispersion analyzer Inca-350) was used to study the morphology and elemental composition of irradiated Mg samples. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state of the samples. The spectra of the samples (2023) were measured using Specs laboratory spectrometer (Germany, GmbH), which is part of NANOPES station of the synchrotron radiation source „KISI−Kurchatov" (Moscow). The photoelectron spectra were excited by photons with energy of $h\nu = 1487$ eV using a monochromatic source AlK_α. The value of the transmission energy during the measurement of the survey spectra was 100 eV, it was 30 eV in case of measurement of the spectra of the main levels and the Auger transition line Mg KLL. The binding energy scale was calibrated using the Au $4f_{7/2}$ spectra at 84.0 eV, and the valence band spectrum (Fermi level) measured on a pure gold foil. The spectra were decomposed into components using a mixed Gaussian−Lorenz function. The quantitative analysis was carried out using the survey spectra, taking into account the coefficients of elemental sensitivity. Sputtering with an argon ion beam with an energy of 3 keV was used to analyze the changes in the chemical state of the elements in depth in the surface layer of the samples. The sputtering rate was estimated at ~ 0.4 nm/min.

3. Results and discussion

Magnesium samples were irradiated with a high-power ion beam (HPIB) with a current density of 150 A/cm^2 in April 2015. Such a current density was chosen due to the need to obtain a modified magnesium layer that would provide significant and reliably detectable changes in the surface layer already with a single irradiation. It should be noted that the irradiation of magnesium by HPIB with such a current density led to the formation of a developed surface morphology, probably due to the hydrodynamic movement of the melt (Figure 1, *a*). An increase of the number of irradiation pulses to 3 significantly increases the height of the surface relief (Figure 1, *b*). A more developed surface relief of a sample exposed to a triple irradiation may negatively affect the corrosion resistance of magnesium. The surface morphology of these samples after 8 years of storage in the ambient atmosphere at

Table 1. Elemental composition (at.%) of the surface of the samples of the initial and irradiated with high power ion beam (2015) according to EDA data (2023)

Sample	C	O	Mg
Initial state (2023)	37.2	27.4	35.4
Irradiated, 150 A/cm^2, 1 pulse (2023)	32.3	3.4	64.3
Irradiated, 150 A/cm^2, 3 pulses (2023)	45.9	3.6	50.5

a temperature of $15-25\,^\circ$C and humidity of $45-70\%$ is shown in Figure 1, *c* and 1, *d*, respectively. The oxygen content in the surface layer of the irradiated samples after such long-term storage is at least 7 times less than in the initial (non-irradiated) sample according to energy dispersive analysis (EDA) data (Table 1). The carbon content in the sample irradiated with 3 pulses is 1.4 times higher than in the sample irradiated with 1 pulse. This is probably attributable to both the introduction of carbon ions into the beam and the possible deposition of carbon-containing contaminants (due to the oil pumping system used) between the irradiation pulses. Since energy dispersion analysis does not allow determining which chemical compounds contain oxygen (which is important for understanding the mechanism of atmospheric corrosion of magnesium), further investigation of the surface layers was carried out using X-ray photoelectron spectroscopy (XPS).

It was shown earlier in Ref. [10] using the XPS data that the surface of the initial and irradiated samples before storage (2015) has the following differences: the surface of the „freshly irradiated" sample is more oxidized than the initial layer, however, the O/Mg ratio of the initial and irradiated samples differed slightly after 10-minute ion etching (with a slightly higher value for the irradiated sample). At the same time, it was found that the C/Mg ratio for the irradiated sample is more than two times higher both before and after ion etching, compared with the initial sample. The analysis of the chemical state indicated the formation of Mg−O−C bonds under the impact of HPIB.

Table 2 presents the results of a quantitative analysis of the initial and irradiated samples after prolonged atmospheric corrosion, conducted using XPS survey spectra (not shown in the figures). The results show that for the initial surface of the samples (before ion etching), the amount of oxygen (as well as the O/Mg ratio) markedly decreases in the series: the initial sample, sample irradiated by 1 pulse, sample irradiated by 3 pulses. The same trend is observed after ion etching. This may indicate a higher content of magnesium-containing compounds that are products of atmospheric corrosion of magnesium (oxide, hydroxide, carbonate and bicarbonate). A significantly higher carbon concentration is observed in the irradiated samples, which increases with the increase of number of irradiation pulses.
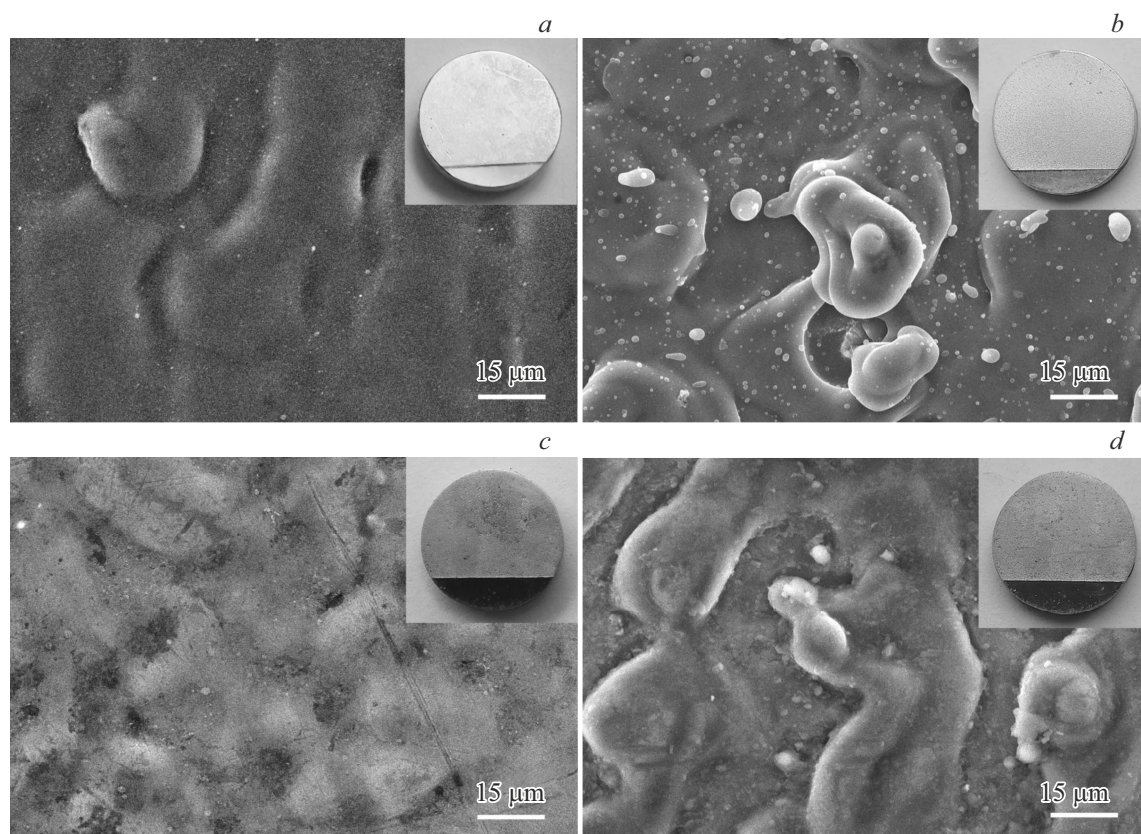
Figure 1. SEM image of the magnesium surface after irradiation by high power ion beam with a current density of 150 A/cm^2: *a, c* — 1 pulse; *b, d* — 3 pulses; *a* and *b* —2015; *c* and *d* — 2023. The corresponding optical images of the samples are shown in the inserts.

Table 2. Elemental composition of the surface of the samples (2023) according to the XPS data

Time of etching, min	Concentration, at.%			[O]/[Mg]	[C]/[Mg]
	Mg2s	O1s	C1s		
Initial sample					
0	9.8	35.0	55.2	3.57	5.63
10	23.7	46.1	30.2	1.95	1.27
Irradiated sample, 1 pulse					
0	10.8	31.5	57.7	2.92	5.34
10	23.1	29.8	47.1	1.29	2.04
Irradiated sample, 3 pulses					
0	7.9	21.0	71.1	2.65	9.00
10	21.7	18.3	59.6	0.84	2.75

The chemical state of the samples was analyzed using the XPS spectra of the carbon photoelectron line (C1s) and the magnesium auger transition line (Mg KLL) located in close energy ranges (as well as the spectra of the oxygen line O1s). The decomposition of the line C1s in the spectrum of the unirradiated sample before etching (Figure 2, *a*, curve *1*) shows that the component with the maximum binding energy has the maximum relative intensity ~ 289.3 eV, which corresponds to the carbon states in the carbonyl groups O=C−O. The relative intensity of the carbon-related components in C=O and C−O bonds (binding energies of ~ 288 and 286.9 eV, respectively) is significantly lower compared to the component O=C−O (especially in the case of component C−O). Components with maxima at binding energies of 291.2 and 292.8 eV, corresponding to carbon in the composition of magnesium carbonate and hydrated magnesium carbonate, respectively, are observed in the high-energy region of the spectrum. The presence of the latter is confirmed by the results of the spectrum decomposition O1s for this sample (Figure 3, *a*, curve *1*) — the components corresponding to oxygen in H−O−H and MgCO$_3$/C−O occupy about 60% of the total peak area. The shape and position of the main maximum of the Auger transition Mg KLL (310.1 eV) indicates its oxidized state.

After ion etching, the relative intensity of line C1s in the spectrum of the unirradiated sample noticeably drops (Figure 2, *b*, curve *1*), and its main maximum is located at the binding energy ~ 285.1 eV, which corresponds to
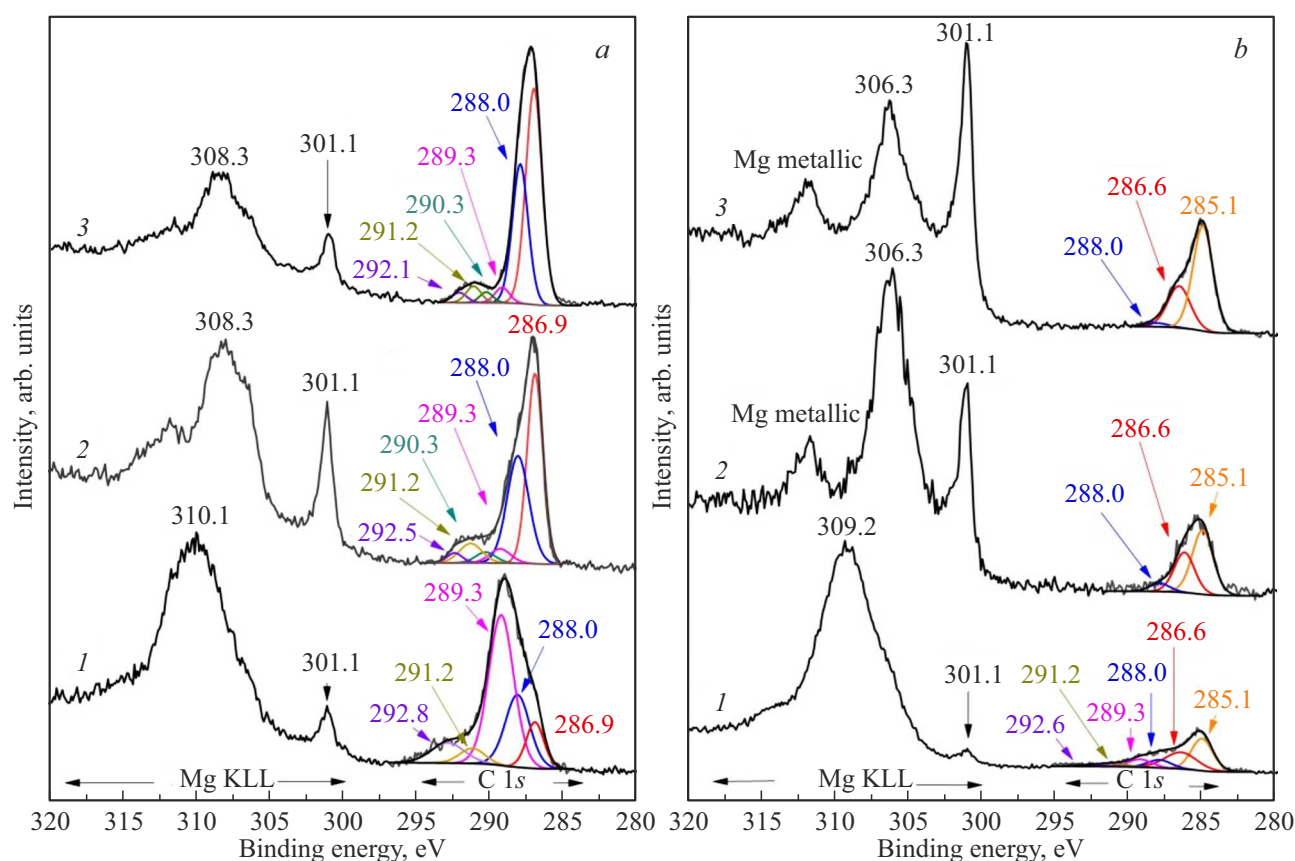
Figure 2. XPS spectra $(Mg\,KLL + C1s)$ of the initial (*a*) and etched (*b*) surfaces of the Mg samples: *1* — unirradiated; *2* — 1 pulse; *3* — 3 pulses.

carbon in $C-C/C-H$ bonds. At the same time, all the components present in the spectrum of the initial surface are observed in the spectrum, the total relative intensity of which is about 60% of the total area of line C1s. This indicates the presence of a sufficiently massive corroded layer containing magnesium carbonates and bicarbonates on the surface of the unirradiated sample. The presence of water and carbonates on the surface of the unirradiated sample after ion etching is confirmed by the results of spectrum analysis O1s (Figure 3, *b*, curve *1*). The presence of water at a sufficiently large depth from the surface (about 10 nm) suggests a high porosity of the corroded layer. At the same time, a noticeable increase of the relative intensity of the component associated with magnesium oxide (Figure 3, *b*, curve *2*) compared with the spectrum of the initial sample before etching (Figure 3, *b*, curve *1*) is observed after ion etching in the oxygen spectrum.

The spectra of $Mg\,KLL + C1s$ of the irradiated samples before ion etching (Figure 2, *a*, curves *2* and *3*) markedly differ from the spectra of the unirradiated sample. In this case, the main maximum of line C1s is located at the binding energy of 286.9 eV, which corresponds to the carbon states in $C-O$ bonds. The relative intensity of the components corresponding to magnesium carbonates and bicarbonates is noticeably lower compared to the spectrum

of the initial sample, and the maximum of the component corresponding to bicarbonates shifts towards low binding energies with the increase of the number of pulses (292.8, 292.5, and 292.1 eV for the initial samples, samples irradiated with 1 pulse and 3 pulses, respectively). According to our assumptions, this is attributable to a decrease of the degree of hydrogenation. The last two facts (a decrease of the proportion of bicarbonates and magnesium carbonates, as well as a decrease of the amount of water on the surface of the irradiated samples) are confirmed by the results of the decomposition of the spectra of O1s (see Figure 3, *a*). The relative intensity of the oxygen components in water and magnesium carbonate in the spectra of the irradiated samples is noticeably lower compared to the spectrum of the initial sample and decreases with increasing number of irradiation pulses. At the same time, the component corresponding to oxygen in the magnesium hydroxide has the maximum relative intensity in the spectra O1s of irradiated samples. In addition, there is a component at the binding energy of 290.3 eV in the C1s spectra of the irradiated samples (Figure 2, *a*, curves *2* and *3*), which may be associated with the presence of carbon in $Mg-O-C$ bonds formed under the impact of HPIB. It is possible that such compounds are the reason for the slowing down of atmospheric corrosion of magnesium [10].
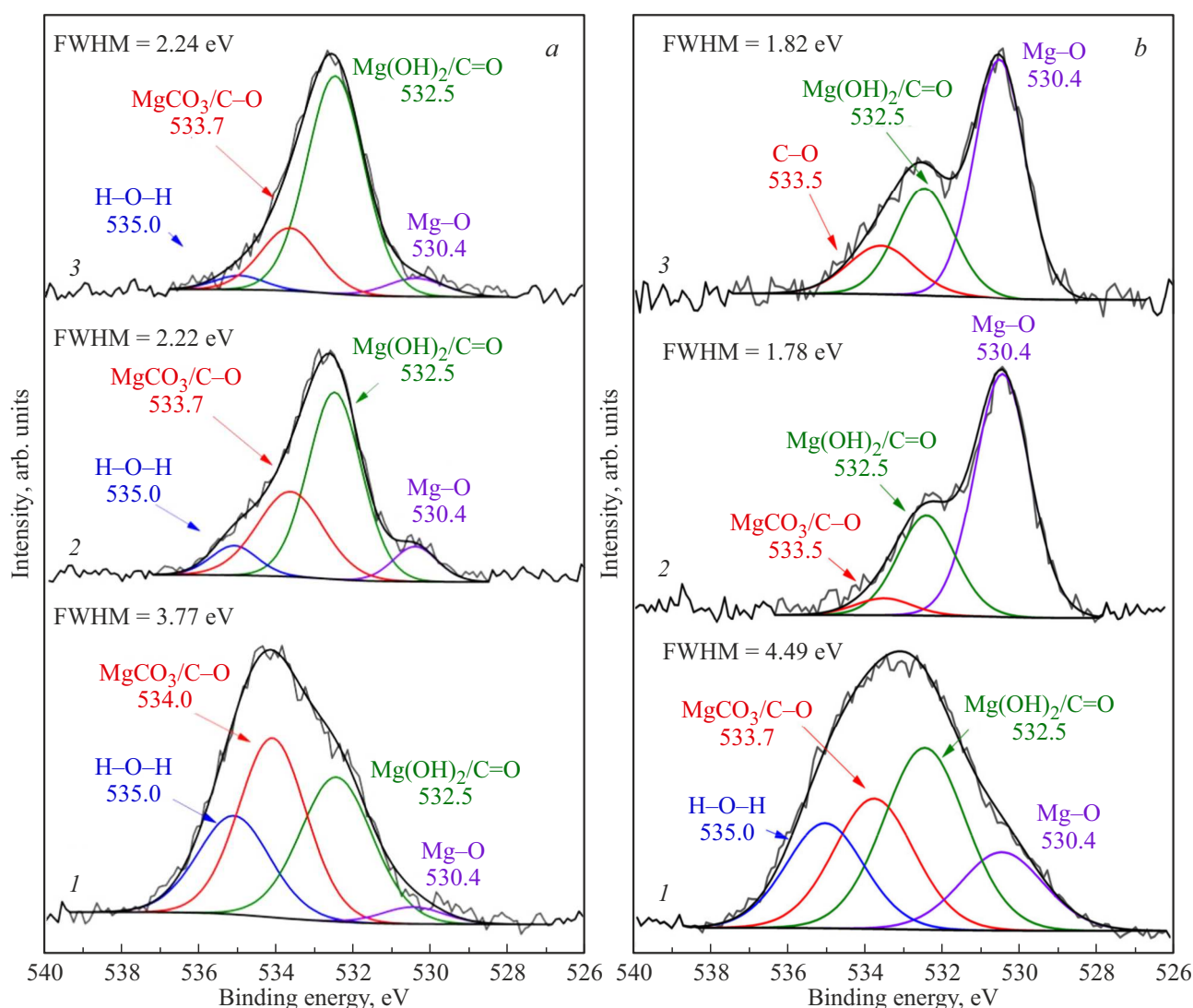
Figure 3. XPS spectra of O1s of the initial (a) and etched (b) surfaces of Mg: 1 — unirradiated; 2 — 1 pulse; 3 — 3 pulses.

The shape of the Mg KLL Auger transition line for irradiated samples before ion etching also differs markedly from the case of the spectrum of an unirradiated sample (Figure 2, a). An intense maximum is observed at the binding energy of 301.1 eV, indicating the presence of magnesium in the metallic state [10]. The main maximum of the Auger transition is shifted to low binding energies (308.3 eV), which indicates a less oxidized state of magnesium in the irradiated samples. It can be noted that the lower intensity of peaks at 301.1 eV and 308.3 eV is associated with a higher carbon content on the surface of this sample.

The main maximum of Mg KLL in the spectra of irradiated samples after ion etching (Figure 2, b, curves 2 and 3) is located at $\sim$ 306.3 eV. A higher intensity of the „metallic" maximum at 301.1 eV is observed, and this trend is much more noticeable with an increase of the number of pulses to 3. This indicates a higher content of metallic magnesium in the near-surface area of the irradiated sam-

ples, which indicates a decrease of atmospheric corrosion for the irradiated samples. The line C1s, in the spectra of irradiated samples, after ion etching (Figure 2, b, curves 2 and 3) contains 2 intensive components corresponding to the carbon states in C$-$C/C$-$H (285.1 eV), as well as C$-$O bonds (286.6 eV). The shift of the latter component relative to the spectra of the unetched samples ($-$0.3 eV) is probably attributable to the different chemical environment. The component associated with C=O-groups has a minimal intensity (especially in the spectrum of a sample irradiated by 3 pulses). The components corresponding to the carbon states in O=C$-$O-groups, as well as carbonate, bicarbonate, and magnesium are not present. The relative intensity of the carbon line is slightly higher in the spectrum of a sample irradiated by 3 pulses, than in the spectrum of a sample irradiated by a single pulse, which is consistent with the results of quantitative analysis (see Table 1 and 2). It is also worth noting that the relative intensity of the component corresponding to „free" carbon (C$-$C/C$-$H) is significantly

higher in the spectrum of a sample irradiated by 3 pulses (Figure 2, *b*, curve *3*) compared to the intensity of the carbon in C−O.

The component corresponding to oxygen in the magnesium oxide has the highest intensity in the spectra O1*s* of samples after etching (Figure 3, *b*, curves *2* and *3*). There is also a component with a binding energy of 532.5 eV, which in this case mainly corresponds to magnesium hydroxide, since there are practically no C=O groups according to the results of the analysis of the carbon line. The 535.5 eV binding energy component in the spectra of the irradiated samples is completely associated with C−O groups, since the results of the analysis of the spectra C1*s* showed the complete absence of magnesium carbonate on the surface of the irradiated samples after ion etching.

4. Conclusion

As a result of the study of the elemental and chemical composition of the surface layers of magnesium after various modes of irradiation with a high power ion beam (2015) and after long-term storage in the surrounding atmosphere (2023), it was found that an increase of the relief (roughness) of the surface, characteristic of repeated irradiation, slightly affects its atmospheric corrosion. The initial (unirradiated) magnesium contains mainly magnesium carbonates and bicarbonates, while the irradiated magnesium contains oxides and hydroxides. Moreover, the concentration of the latter is lower in case of irradiation by 3 pulses. An increased carbon content in the magnesium surface layer after irradiation was also found, which is apparently associated with the introduction of carbon ions under the impact of a high power ion beam. It is assumed that the increased carbon content, as well as the formation of Mg−O−C bonds in the surface layer of magnesium significantly slows down atmospheric corrosion of magnesium during prolonged storage in the surrounding atmosphere.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov