Enhancement LaB_6's emission properties after the oxygen ion bombardment

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Abstract: The main component of electric propulsions is the hollow cathode with thermionic emitter. At present single crystals of lanthanum hexaboride LaB_6 are generally used as the emitter materials. If the emitter is characterized by lower electron work function it is possible to reduce the operating emitter temperature. The latter leads to the power inputs reduce on discharge maintenance in hollow cathode, to abrupt decrease evaporation rate, to absence of the structural members overheating, and as it follows, to the resource increase and propulsion efficiency growth in toto. For these goals achievement it is proposed to use enhanced LaB_6 single crystal emitters. The enhancement consists in oxygen ion bombardment.

Nomenclature

a	lattice constant, nm
D	O_2^+ ion fluence, cm^{-2}
d	depth of the oxygen-enhanced emitting surface, μm
E	O_2^+ ion energy, keV
G	evaporation rate, μm/h
I	poisoned emission current
I_0	unpoisoned emission current
j	emission current density, A/cm^2
n	concentration, m^{-3}
P	O_2 partial pressure, Pa
R	universal gas constant
T	temperature, K
t	sample heating time, h

I. Introduction

Lanthanum hexaboride is widely applied as highly effective cathode material due to essentially low electron work function. The resistance to poisoning by residual oxygen-containing gases (air for example) or by the inflow gas is one of the most important features of the cathode materials, including LaB_6.

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The majority of the studies, dedicated to LaB_6 poisoning (both polycrystalline and single-crystal) indicates the decrease of emission current with the introduction of air or oxygen.[1–3] It was shown earlier,[4] that chemical reaction between LaB_6 and oxygen

$$2\,LaB_6 + \frac{21}{2}\,O_2 = La_2O_3 + 6\,B_2O_3 \tag{1}$$

is the cause of the emission reduction. According to them,[4] the poisoning by the oxygen-containing gases at the temperature $T = 1673$ K starts from the pressure $P \geq (0.01 - 1)$ Pa.

However, the experimental data published by Gallagher[5] attest to the fact, that critical poisoning pressure of LaB_6 cathode by oxygen at the temperature $T = 1573$ K is $7 \cdot 10^{-5}$ Pa, approximately 10^{-3} Pa at $T = 1713$ K and $4 \cdot 10^{-2}$ Pa at $T = 1873$ K. The emission current decreased to $0.2 - 0.4$ of its initial value with further increase of oxygen pressure under corresponding temperature conditions.

The adsorption of O_2 on different faces of LaB_6 single-crystal also causes the decrease of the emission current.[6] Moreover, the reduction of the electron work function by 0.9 eV was discovered[7] during the study of the adsorption O_2 on $LaB_6(100)$ surface.

The decrease of the work function by 0.4 eV for $LaB_6(111)$ surface was also observed[8] after the introduction of O_2 during 10 min with pressure $P = 5 \cdot 10^{-4}$ Pa (under $T = 1100 - 1200$ K). This decrease of work function was explained by faceting surface (111) by surfaces (100).

The decrease of emission current to $0.2 - 0.3$ of its initial value in the cathode temperature range from 1573 to 1873 K was observed[9] for $LaB_6(100)$ under O_2 introduction. The critical poisoning pressure was different for each temperature. For example for $T = 1573$ K cathode poisoning starts at $P_{O_2} = 10^{-5}$ Pa, but for $T = 1873$ K poisoning starts at $P_{O_2} = 10^{-4}$ Pa. However, after reaching of the maximum drop, the emission current starts to grow with the increase of the oxygen pressure. For cathode temperature $T = 1573$ K when the O_2 pressure grows from 10^{-4} Pa to $3 \cdot 10^{-4}$ Pa, the current increases from $0.2\,I_0$ to $0.6\,I_0$. If O_2 pressure is higher then $P_{O_2} \approx 5 \cdot 10^{-4}$ Pa under $T = 1673$ K, the emission current grows from $0.2\,I_0$ to I_0, i.e., cathode completely recover from poisoning.

We also observed the growth of emission current with the introduction of atmospheric air for the sintered cathode of $ZrB_2 - LaB_6$ of eutectic composition under $T = 1660$ K.[10] At this temperature and pressure $P = 6 \cdot 10^{-4}$ Pa the cathode remains unpoisoned, moreover, the emission current increase by 5%. Also it was found that for gas pressure $P = 1.3 \cdot 10^{-2}$ Pa the drop in the emission current was only by 24%.

In the present work new type of a stable $LaB_6 - O$ cathode has been developed. The main feature of this material is that oxygen is provided to the cathode surface from emitter bulk. To conduct the emission tests for long time (up to tens of hours and more), a quantity of oxygen in the volume of LaB_6 should be quite high. This is possible with the implantation of the sufficiently large fluences of the accelerated ions of oxygen into lanthanum hexaboride.

II. Experimental Procedure

$LaB_6(100)$ surfaces were bombarded by oxygen ions O_2^+ ions with energies $E = 15$, 25, 30, 35 keV. Irradiation were exposed to the ends of the single crystal cathodes, cut out in the form of rectangular parallelepiped by a cross-section of 2 mm × 2 mm and the length of 8 mm. The O_2^+ ion current density was regulated from 2 to 8 mA/cm^2. The diameter of ion beam was equal to 6 mm. Samples with fluences $D = 3.2 \cdot 10^{16}$; $1.6 \cdot 10^{17}$; $8 \cdot 10^{17}$; $4 \cdot 10^{18}$; $2 \cdot 10^{19}$ and 10^{20} cm^{-2} were obtained for the above-indicated four values of ion energy by the variation the of ion current density and exposition time. It should be noted that after ion bombarding the emitting (irradiated) surfaces had greenish color, which indicate formation on the surface of the diboron trioxide B_2O_3. The temperature of samples increased to $700 - 750$ K during ion bombardment.

Energy range of bombarding ions was chosen in such way that crystal surface remain unviolated. Oxygen ions O_2^+ with the energy $E = 50$ keV or higher cause intensive dispersion of surface and produce craters. Low energy (to 10 keV) ions do not give the possibility to obtain the required depths of the layer saturated by oxygen.

To estimate the the depth of the oxygen-enhanced layer of LaB_6, the cleavage of the crystal was made perpendicular to the bombarded surface. The depth of the oxygen-enhanced emitting surface reaches $d \approx 30$ μm at the fluences of $D = 4 \cdot 10^{18} - 10^{20}$ cm^{-2} with the energy of the bombarding O_2^+ ions of $E = 30 - 35$ keV.

Emission tests were conducted simultaneously for five samples of $LaB_6(100)$ with the fluences from $D = 3.2 \cdot 10^{16}$ to $2 \cdot 10^{19}$ cm^{-2} and original (without ion bombardment) single-crystal of $LaB_6(100)$.

It should be noted that the splitting off of the enhanced layer of LaB_6 occurred for the samples with the fluences $D = 10^{20}$ cm^{-2}. This is a result of the extremely high brittleness of the crystal within the layer with thickness of $0.5 - 0.7$ mm.

To stabilize emission, samples were activated under temperature of $T = 1700$ K for 12 h.

III. Results and Discussions

In order to reproduce results on poisoning of $LaB_6(100)$ obtained elsewhere[9] we carried out the experiments. The influence of the of air pressure on the emission properties in the wide temperature range were investigated. The curves of poisoning of $LaB_6(100)$ are shown in Fig. 1.

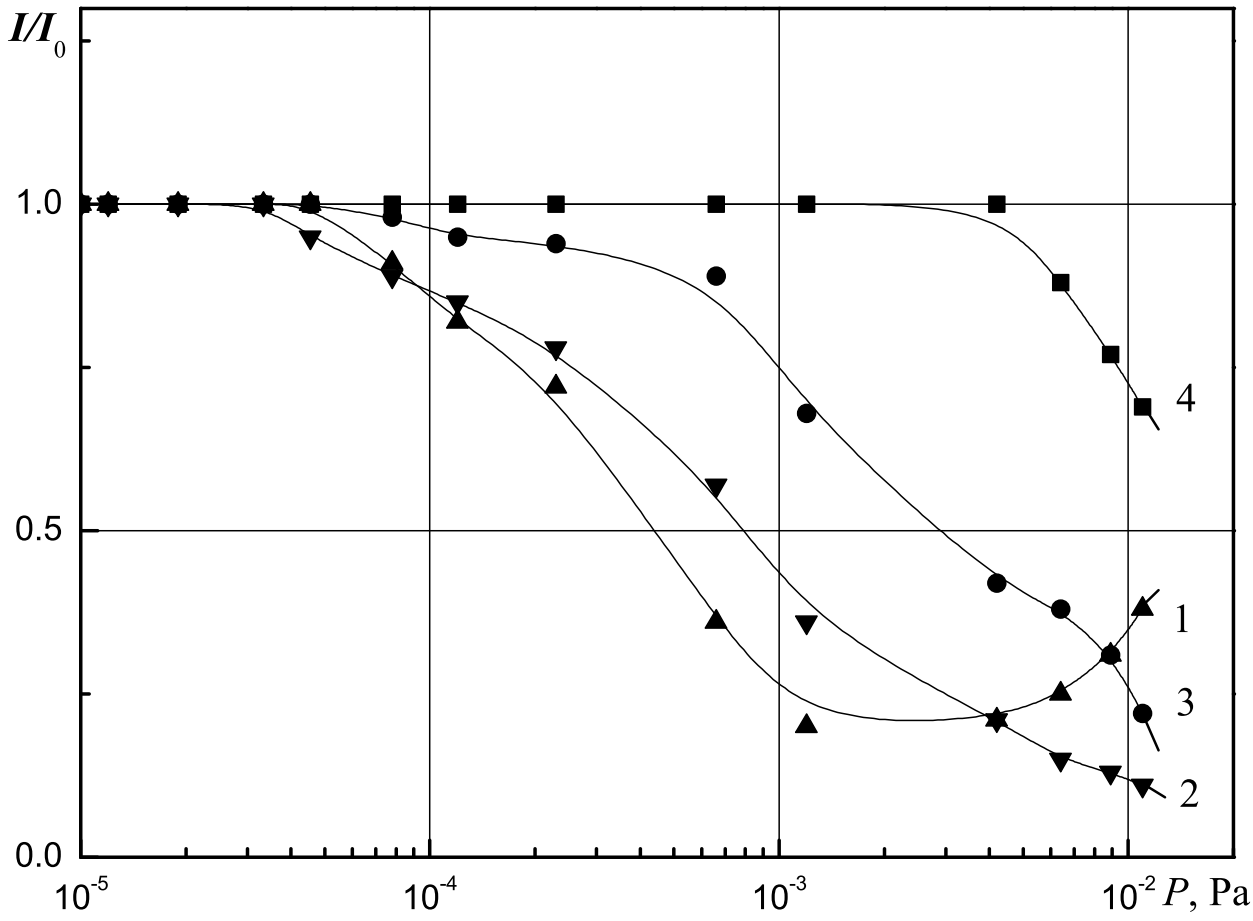

Figure 1. Relative decrease of $LaB_6(100)$ emission current after oxygen leaking at different temperatures T, K: $1 - 1573$; $2 - 1680$; $3 - 1776$; $4 - 1862$.

These experiments proved, that the emission properties of $LaB_6(100)$ do recover after poisoning at $T = 1573$ K (see Fig. 1, curve 1) with the growth of pressure from $1.3 \cdot 10^{-3}$ Pa to $1.3 \cdot 10^{-2}$ Pa (current increases 2.1 times: from $0.19\, I_0$ to $0.39\, I_0$).

If temperature $T = 1573$ K and the gas pressure $P = 1.3 \cdot 10^{-2}$ Pa were maintained constant, then the emission current $I = 0.39\, I_0$ remains stable during entire observation time (up to 30 min). However, an increase of the temperature or the decrease of the pressure leads to the decrease of the thermo-emission current.

Emission tests indicates that the highest electron emission takes place for the fluence $D = 2 \cdot 10^{19}$ cm^{-2} and for all energies of the implanted ions. The emission current density values for all samples processed by O_2^+ ions with energy of $E = 30$ keV and at different temperatures and fluences are represented in Table 1.

The emission data for pure LaB_6 sample is also shown in Table 1.

Table 1. Emission current density of LaB_6 (100) after oxygen ion bombardment

	Temperature T, K				
Fluence D, cm^{-2}	1480	1540	1600	1700	1800
$3.2 \cdot 10^{16}$	0.16	0.43	1.00	4.68	13.7
$1.6 \cdot 10^{17}$	0.16	0.44	1.07	4.70	13.8
$8.0 \cdot 10^{17}$	0.17	0.54	1.43	5.01	16.4
$4.0 \cdot 10^{18}$	0.18	0.63	1.54	6.15	16.8
$2.0 \cdot 10^{19}$	0.33	0.73	1.92	24.1	65.8
0	0.19	0.47	1.24	4.37	8.80

The temperature dependences of emission current densities $j = f(T)$ for the samples of $LaB_6(100)$ enhanced by O_2^+ ion bombardment with energies $E = 15$, 25, 30, 35 keV and the fluence $D = 2 \cdot 10^{19}$ cm^{-2}, are given in Fig. 2. The emission current for original LaB_6 single crystal, that was not enhanced by oxygen (reference sample) also shown in Fig. 2.

All samples processed by O_2^+ ion bombardment with fluence $D = 2 \cdot 10^{19}$ cm^{-2} demonstrate the higher emission ability than it was observed for a pure LaB_6 control sample. Maximum current density occurs for sample enhanced by O_2^+ ion bombardment with ion energy $E = 25$ keV at the temperature up to $T = 1660$ K. However, at higher temperatures (from $T = 1670$ to 1800 K) maximum increase of emission ability was observed for sample processed by positive oxygen molecular ions with energy $E = 30$ keV. Highest registered emission current density $j \approx 66$ A/cm^2 (for sample with $D = 2 \cdot 10^{19}$ cm^{-2} and $E = 30$ keV) remained constant during heating time $t = 120$ h with the cathode temperature $T = 1800$ K.

Thus, the method of the modification (production) of thermionic cathode from lanthanum hexaboride has been developed. It includes interaction of LaB_6 with oxygen by the ion bombardment of the crystal surface. The energy of O_2^+ ions is equal to 25 $-$ 30 keV, and the fluences of cathode $D = 10^{19} - 10^{20}$ cm^{-2}. In this case the emission ability of lanthanum hexaboride substantially rises: the emission current grows almost in 7.5 times at $T = 1800$ K (reduction in the work function by 0.3 eV).

Let us estimate the lifetime of the service of this modified cathode from single-crystal hexaboride of lanthanum.

According to the data[9] evaporation rate of a single crystal of LaB_6 in the temperature range from $T = 1800$ K to 2200 K are described by the equation

$$G = 4 \cdot 10^{14} \exp[-(570 \cdot 10^3)/RT)] \ \mu\text{m/h}. \quad (2)$$

Calculations give the values $G = 1.13 \cdot 10^{-2}$ μm/h with $T = 1800$ K and $G = 5.10 \cdot 10^{-1}$ μm/h with $T = 2000$ K. Then the layer of LaB_6 with implanted oxygen with a thickness of 30 μm has to evaporate during the time $t_{evap.} \approx 2650$ h with $T = 1800$ K cathode temperature and for $t_{evap.} \approx 60$ h with $T = 2000$ K. These estimations show that the operation of this cathode modified by oxygen ion bombardment is possible without emission reduction at least, during $t = 2000$ h at the current density $j = 60$ A/cm^2.

The lattice constant of LaB_6 on La (simple cubic lattice) equals $a = 0.41563$ nm (from 2), which corresponds to the concentration the lanthanum atoms $n_{La} = 1.4 \cdot 10^{28}$ m^{-3} ($1.4 \cdot 10^{22}$ cm^{-3}).

If we consider that all ions of oxygen, implanted with $D = 2 \cdot 10^{19}$ cm^{-2} into the layer with a thickness of 30 μm, are uniformly distributed in this layer, then the O_2^+ ion concentration in this layer will be equal $n_{O_2^+} = 0.67 \cdot 10^{22}$ cm^{-3}. Earlier[11] it was shown that with the entry of molecular oxygen O_2 to the LaB_6 surface, it dissociates into separate atoms (ions). Then the concentration of the atoms (ions) of oxygen is equal to $n_O \approx 1.34 \cdot 10^{22}$ cm^{-2}, which practically coincides with lanthanum concentration in the LaB_6 single crystal. Consequently, a maximum increase in the emission current occurs when the concentration of the atoms (ions) of oxygen in the volume it approaches atom concentration of lanthanum into LaB_6. Obviously with the fluence $D = 10^{20}$ cm^{-2}, when concentration of oxygen in the volume exceeds lanthanum concentration, an essential embrittlement of LaB_6 can occur. The last is connected with the formation of the pores, filled with oxygen.

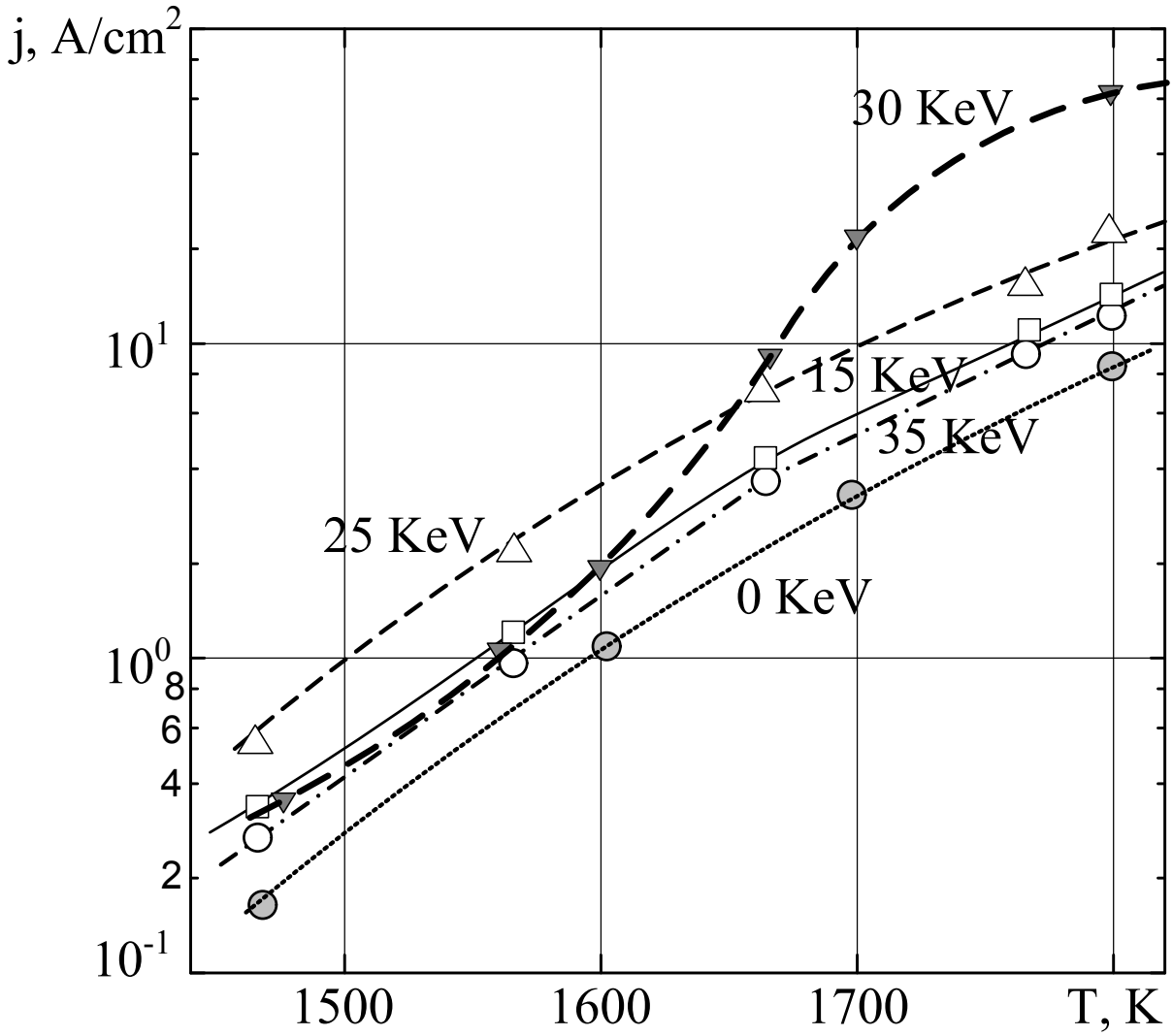

Figure 2. Temperature dependences of thermionic current density for irradiated by oxygen ions LaB_6. $D = 2 \cdot 10^{19}$ cm^{-2}.

The scanning electron microscope (SEM) analysis of the oxygen enhanced LaB_6 samples shows that on the emitting surface after emission tests the randomly distributed micropores appear. Such micropores were not observed on the surface directly after of ion implantation (prior to the tests). Number of these micropores is maximal for the samples with the maximum fluence (see Fig. 3). Apart from the appearance of tracks of the surface erosion the inclusions of different shape (including of spherical) were also observed. See Fig. 4 for details. It should be noted that after the conducting of emission tests the samples acquired their usual for lanthanum hexaboride violet-purple color.

From the energy spectrum of X-radiation from the inclusion of the spherical form one can make a conclusion that this inclusion is the lanthanum oxide La_2O_3. (The melting point of La_2O_3 is 2588 K[12]). Our results are in agreement with data of Kawanowa et al.[11] They claimed that atomic oxygen is adsorbed only on lanthanum atoms. However, directly after the ion bombardment the inclusions of La_2O_3 on the enhanced surface of LaB_6 were not observed.

IV. Conclusion

The oxygen-enhanced layer of thickness about $d = 30$ μm is formed on LaB_6 single-crystal emitting surface under O_2^+ ion bombardment due to the thermo- and radiation-stimulated diffusion. The concentration

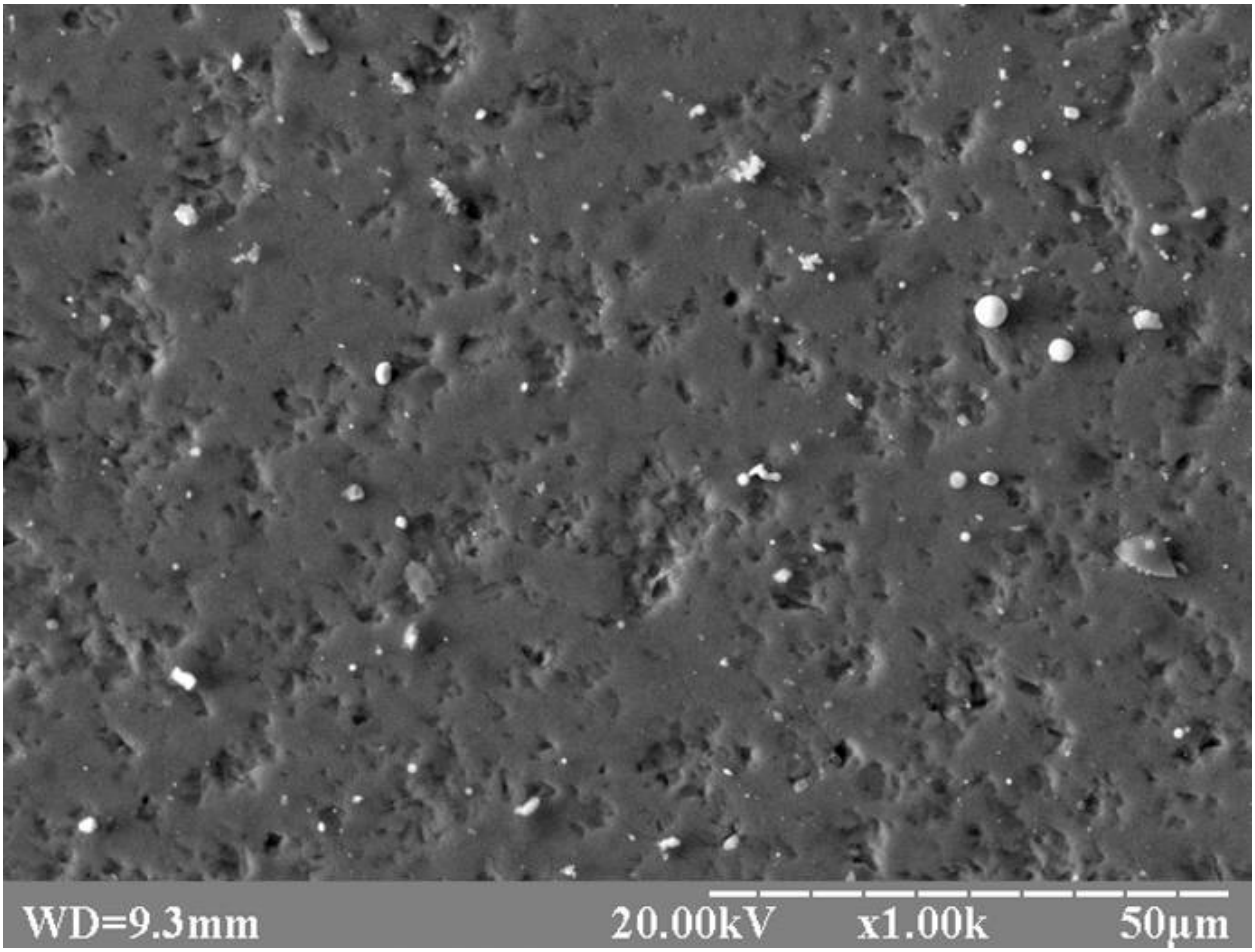

Figure 3. SEM images of a cathode surface after emission testing. $E = 30$ **KeV,** $D = 2 \cdot 10^{19}$ **cm**$^{-2}$**,** $T = 1800$ **K,** $t = 120$ **h.**

of oxygen atoms in the layer is comparable with concentration of lanthanum atoms in LaB_6. The diffusion of oxygen to the surface occurs simultaneously with the evaporation of LaB_6 with implanted oxygen during heating of enhanced lanthanum hexaboride crystal. Oxygen that is diffused from the bulk is adsorbed on surface (100) of LaB_6, creating the steady adsorptive structure of $La - O$. Oxygen atoms of this system are characterized by "dangling" chemical bonds and reduce the electron work function of the cathode material (the width electrical double layer is decreased).

Thus, the steady increase of the emission capability of LaB_6 after bombarding the $LaB_6(100)$ surface by O_2^+ ions with the energies from $E = 15$ to 35 keV and the fluence of $D = 2 \cdot 10^{19}$ cm^{-2} occurs. In the temperature range to $T = 1600$ K a maximum increase of the thermo-emission current was observed for the LaB_6 samples that were exposed to O_2^+ ions with energy of $E = 25$ keV. However, for cathode heated to the temperature $T \geq 1670$ K, the most efficient emission observed for samples processed by oxygen molecular ions with $E = 30$ keV.

The enhancement of LaB_6 single-crystal by O_2^+ ion bombardment results in the lowering electron work function. Use of such cathodes in the ion-plasma jet engines will make it possible to substantially decrease power consumption for heating of emitter in the cathode-heating unit due to reduction in the cathode operating temperature. In this case the evaporation rate of LaB_6 will extremely decrease. As a result the life time of electric propulsion plasma jet engines as a whole will increase.

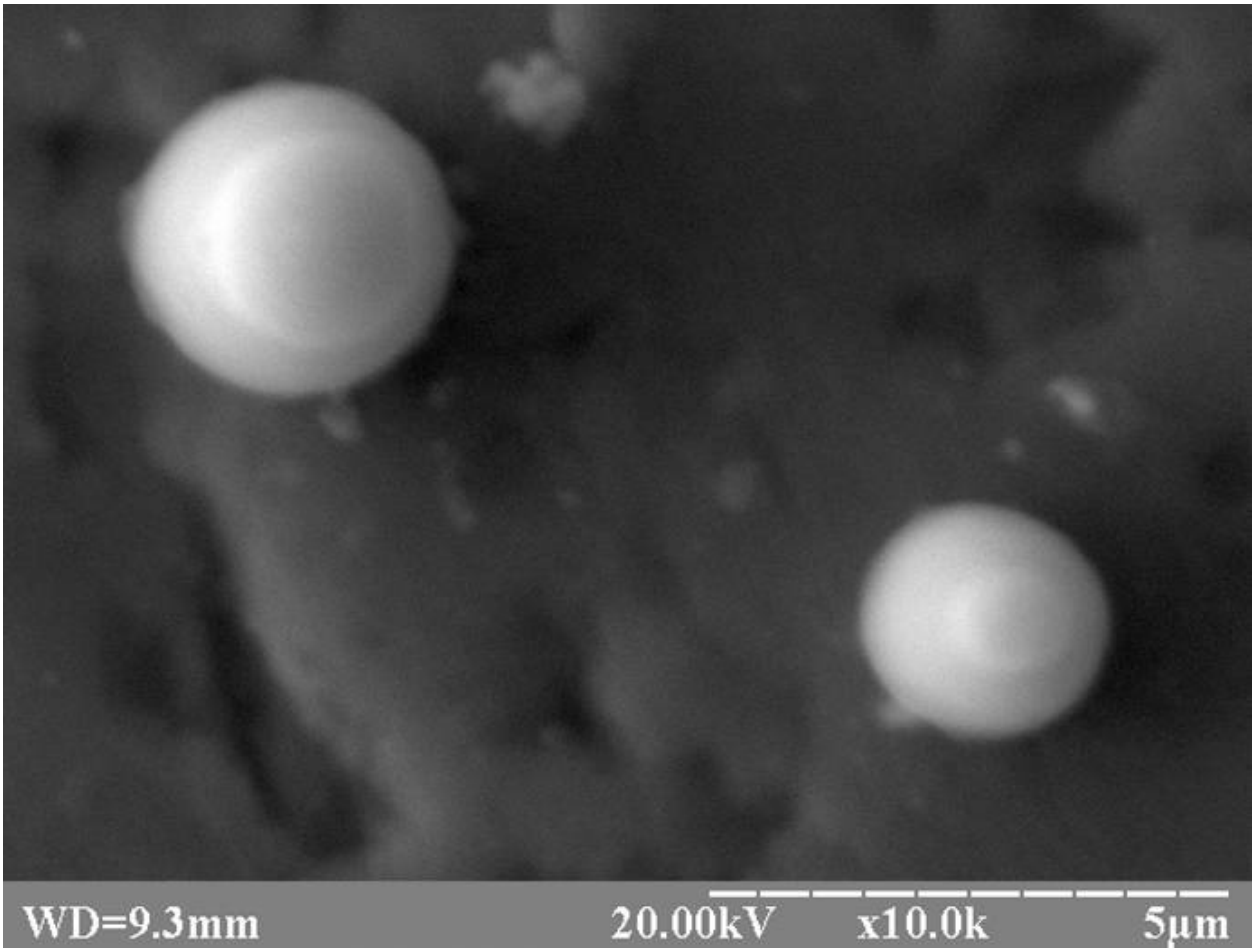

Figure 4. SEM images of La_2O_3 inclusions on LaB_6(100) surface after emission testing. $E = 30$ **KeV,** $D = 2 \cdot 10^{19}$ **cm**$^{-2}$**,** $T = 1800$ **K,** $t = 120$ **h.**

References

[1]Kudintceva, G. A., Melnikov, A. I., MOrozov, A. V., and Nikonov, B. P., *Thermionic Cathodes*, Energiya, Moscow-Leningrad, 1966.

[2]Serebryakova, T. I., Neronov, V. A., and Peshev, P. D., *High-temperature borides*, Cambridge International Science, Cambridge, 2003.

[3]Kresanov, V. S., Malakhov, N. P., Morozov, V. V., Semashko, N. N., and Shliuko, V. I., *Efficient electron emitter based on lanthanum hexaboride*, Energoatomizdat, Moscow, 1987, in Russian.

[4]Avdienko, A. A. and Malev, M. D., "Poisoning of LaB_6 cathodes," *Technical Physics (Zhurnal Tekhnicheskoi Fiziki)*, Vol. 27, No. 10,11, 1977, pp. 599–604.

[5]Gallagher, H. F., "Poisoning of LaB_6 Cathodes," *Journal of Applied Physics*, Vol. 40, No. 1, 1969, pp. 44–50.

[6]Nishitani, R., Oshima, C., Aono, M., Tanaka, T., Kawai, S., Iwasaki, H., and Nakamura, S., "Oxygen adsorption on LaB_6(100), (110) and (111) surfaces," *Surface Science*, Vol. 115, No. 1, 1982, pp. 46–80.

[7]Yamamoto, N., Rokuta, E., Hasegawa, Y., Nagao, T., Trenary, M., Oshima, C., and Otani, S., "Oxygen adsorption sites on the PrB_6(100) and LaB_6(100) surfaces," *Surface Science*, Vol. 348, No. 1-2, 1996, pp. 133–142.

[8]Gorodetskii, L. A., Kosheluk, A. S., Melnik, Y. P., Tskhakaja, V. K., Shudlo, Y. G., and Yasko, A. A., "Interaction of LaB_6(111) surface with oxygen," *Surface. Physics, Chemistry, Mechanics*, , No. 8, 1987, pp. 27–32, in Russian.

[9]Futamoto, M., Nakazawa, M., Usami, K., Hosoki, S., and Kawabe, U., "Thermionic emission properties of a single-crystal LaB_6 cathode," *Journal of Applied Physics*, Vol. 51, No. 7, 1980, pp. 3869–3876.

[10]Taran, A. A., Ostrovskii, E. K., Paderno, V. N., and Filipov, V. B., "Influence of residual gases on emission properties of composition materials $LaB_6 - Me^{IV}B_2$," *Borides: collection of scientific reports*, No. 16, Kiev, 1990, pp. 7–10, in Russian.

[11]Kawanowa, H., Souda, R., Otani, S., Ikeuchi, T., Gotoh, Y., Stracke, P., Krischok, S., and Kempter, V., "Interaction of O_2 with LaB_6(001) surfaces as studied with MIES and UPS," *Surface Science*, Vol. 482-485 Part 1, 2001, pp. 250–253.

[12]"Lanthanum(III) oxide," URL: http://en.wikipedia.org/wiki/Lanthanum%28III%29%5Foxide, [cited August 19, 2011], [Wikipedia, the free encyclopedia].