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Thermionic properties of LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ material

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The thermionic emission peculiarities of fiber reinforced boride composite ceramic material LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ produced by directional crystallization of eutectic alloy have been studied. Activation modes, electron work function temperature dependence, poisoning under air leaking have been determined. The obtained data are compared with emission characteristics of (100) LaB_6 single crystal and quasi-binary eutectic materials LaB_6–TiB_2 and LaB_6–ZrB_2.

Исследованы особенности термоэлектронной эмиссии волокнового боридного композиционного керамического материала LaB_6–$(Ti_{0,6}Zr_{0,4})B_2$, полученного методом направленной кристаллизации эвтектических сплавов. Определены режимы активирования, температурная зависимость работы выхода, отравляемость при напуске воздуха. Полученные данные сопоставлены с эмиссионными характеристиками монокристалла (100) LaB_6 и квазибинарных эвтектических материалов LaB_6–TiB_2 и LaB_6–ZrB_2.

The emission properties of a novel class of composite ceramic materials being the directionally crystallized eutectic alloys based on lanthanum hexaboride LaB_6–$Me^{IV}B_2$ where Me^{IV} = Ti, Zr, Hf have been studied before [1]. Those composite materials have been established to show improved thermionic properties, poisoning resistance and thermal shock strength in comparison with the individual lanthanum hexaboride. The structure of such composite materials is the single crystal matrix phase LaB_6 with *d*-transition metal diborides single crystal fibers (whiskers) having essentially equal thickness homogeneously distributed in LaB_6. The fibers are 0.4–0.6 μm in diameter, and the length to diameter ratio is at least about 500 to 1000 [1]. Using the directional crystallization method, multicomponent eutectic alloys of lanthanum hexaboride with transition metal diborides have been obtained, too. Their reinforcing fibers are the mutual solid solutions of metal diborides $Me^{IV}B_2$: $(Ti,Zr)B_2$, $(Ti,Hf)B_2$, $(Zr,Hf)B_2$, and $(Ti,Zr,Hf)B_2$. Those composites are characterized by the same regular fiber structure, as the quasi-binary alloys LaB_6–$Me^{IV}B_2$ [2]. The structure peculiarities have been studied systematically for composite materials based on lanthanum hexaboride and obtained by directional crystallization where the diboride phase is formed by solid solutions of titanium and zirconium diborides LaB_6–$(Ti_xZr_{1-x})B_2$ in different ratios. Such composite materials were found to have fibrous structure with the regularity degree depending on volume ratio of diboride phases [3]. It has been shown that the zirconium diboride addition to titanium diboride favors considerably the formation of di-

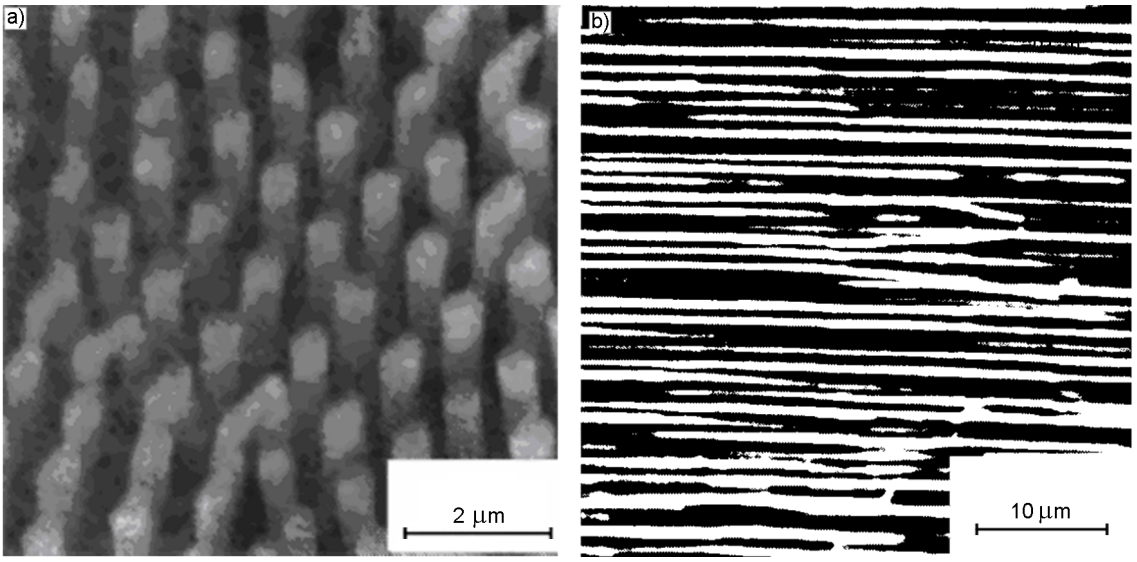

Fig. 1. Initial structure of LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ composition: a, transversal section; b, longitudinal section.

boride phase solid solution fibers. The structure perfection degree and thus the mechanical properties in this case are not so sensitive to small composition changes as in the case of individual diborides. This is related to the broadened existence areas of eutectics in multicomponent systems [4].

Taking into consideration improved (in comparison with the individual lanthanum hexaboride) thermoemission properties of the directionally crystallized eutectic quasibinary alloys LaB_6–$Me^{IV}B_2$, it is of a great interest to study the same properties for materials where the reinforcing diboride phase is the solid solution of transition metal diborides. The purpose of this work is to study some thermoemission properties (activation conditions, temperature dependence of electron work function, poisoning resistance in oxygen-containing environments) of a novel composite cathode material LaB_6–$(Ti_xZr_{1-x})B_2$, and also to compare the obtained data and the emission characteristics of a (100) LaB_6 single crystal and quasi-binary eutectic alloys LaB_6–TiB_2 and LaB_6–ZrB_2.

The directional crystallization of multicomponent boride alloys LaB_6–$(Ti_xZr_{1-x})B_2$ was carried out by vertical induction floating zone melting using a "Crystal-111" setup [5]. As initial materials, LaB_6, TiB_2 and ZrB_2 powders mixed in appropriate proportions were used. Eutectic composition was determined basing on the microstructure features of obtained materials because it was shown before [3] that the perfect regular structure in such alloys is formed when their composition coincides with the eutectic. The LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ alloy has been chosen for emission investigations. The diboride content in this alloy is 16.7 vol % (18.0 wt. % or 34.0 mol. %). Just for that composition with ratio Ti/Zr ~ 3/2, the most regular eutectic structure (Fig. 1) was formed in the composite with fibers of substantially equal thickness (0.7–0.8 μm diameter). When mutual solid solutions of Ti and Zr diborides are used as the reinforcing phase, the thickness is somewhat larger as compared to the composite materials containing individual borides (0.4–0.6 μm) and obtained in the same conditions.

The samples for the emission properties study were shaped as 6 mm long rods of 2×2 mm^2 cross-section. The matrix phase LaB_6 was oriented along the sample [100] axis and the whiskers along [0001]. The emission current and temperature were measured at the sample butts which after cutting were treated by standard diamond pastes and finally electrolytically polished (1 N nitric acid) followed by washing. The true cathode temperature was measured by pyrometry of the hole in one of the sample butts. The hole depth to diameter ratio was at least 7 (absolutely black body model). The emission was measured under the pulse current take-off: pulse duration of 5 μs, signal frequency 1 Hz. The electron work function was calculated using the total current method at an accuracy of 0.04 eV. The maximum thermoemission current density j_s was measured at electric field intensity between the cathode and the anode $2.5\cdot10^6$ V/m. The extent of cathode poison-

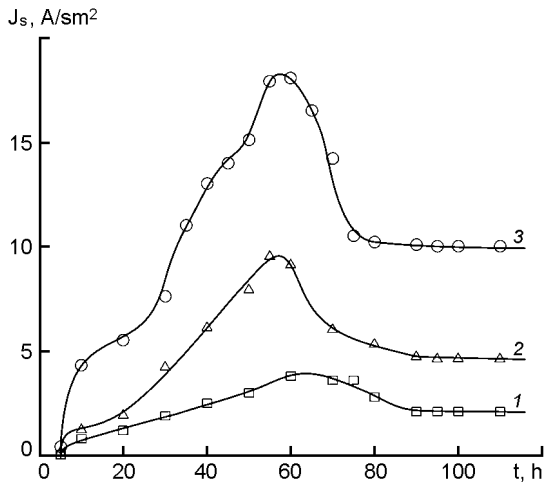

Fig. 2. Activation curves of LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ composition: *1* — T = 1700 K; *2* — T = 1800 K; *3* — T = 1900 K.

ing by residual gases (at the air leaking and under operating magnetodischarging pump) was evaluated using the relation I/I_0, where I is the emission current under air leaking and I_0, that in the highest possible vacuum. Each experimental value I/I_0 was obtained after 10–20 min exposure till the emission current stabilization.

At the first stage of this work, the cathode activation process was studied in working chamber at the residual gas pressure of 10^{-5} Pa during first 5 h at 1700 K and then at 1800 K during the rest of the time. The electron emission was measured in the course of activation each 5 to 10 h (Fig. 2). The activation time t_a was determined by obtaining j_s values stable in time. For LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ composition, it is 85 to 90 h which substantially exceeds the activation time of quasibinary eutectic alloys LaB_6–TiB_2 and LaB_6–ZrB_2 (t_a = 10–11 h at T = 1700 K). Fig. 3 shows the temperature dependences of electron work function φ calculated for the time moments of maximum LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ cathode emission (after t_a = 57 to 60 h) and when electron emission reaches its stable values (t≥90 h). At the same Fig. 3, the φ(T) dependences for LaB_6 single crystal and LaB_6–ZrB_2 and LaB_6–TiB_2 eutectic alloys are presented.

At t_a = 57–60 h, the LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ cathode has higher emissivity than LaB_6. Nevertheless, at T = 1800 K and T = 1900 K, it is characterized by lower φ values as compared to LaB_6–TiB_2 and LaB_6–ZrB_2 eutectics. By 90 h of work at T = 1800 K, the multicomponent cathode loses its emissivity con-

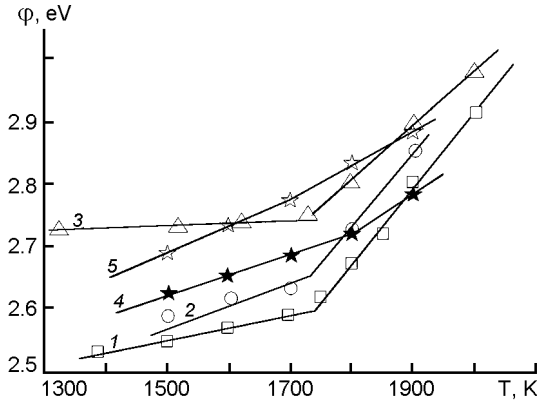

Fig. 3. Temperature dependences of electron work function: *1* — LaB_6–ZrB_2; *2* — LaB_6–TiB_2; *3* — LaB_6; *4* — LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ (t_a = 55 h); *5* — LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ (t≥90 h).

siderably (the drop of current by a factor of 1.7 to 2.1 takes place). In the temperature range from 1600 up to 1870 K, the emission current values become even lower than for LaB_6 (100). Such a long-term activation of cathodes with a dropping emission current after reaching maximum, considerably higher φ values as compared to LaB_6–TiB_2, LaB_6–ZrB_2 and even with LaB_6, can be due to both peculiarities of matrix/diboride fiber phase interface and to essential structural rearrangements of emitting surface.

It has been shown [6] that semi-coherent boundaries between phases are formed at directional crystallization in a system LaB_6–ZrB_2. The mismatch of phase crystalline lattices at room temperature for planes (110) LaB_6 and $(1\bar{1}0)$ ZrB_2 does not exceed 7 % (in cross-section). At the same time, using of solid solution of diboride instead of individual zirconium diboride, must provide (at certain Ti/Zr ratio) the matching of translational periods for above-mentioned planes that will result in formation of more perfect phase interface and hence to more perfect fiber. However, the lanthanum diffusion rate from bulk material to its emitting surface along such interface will be rather hindered as compared to the case of individual diboride. The latter fact must decrease the material emissivity to a certain extent.

The electron-microscopic research of cathode structure after 100–120 h work shows the "brush" of naked diboride fibers at its surface. The naked fibers are of about 20 μm height (Fig. 4). Before, for cathodes of eutectic composition made of LaB_6–ZrB_2 and LaB_6–ZrB_2 quasi-binary alloys, the height of naked fibers ("brush") was about

4–5 μm after 300 h operation time at 1800 K. It follows from the results that evaporation rate of LaB_6 matrix increases in the presence of reinforcing fibers consisting from solid solution of diboride phases, which, in turn, results in decreasing diffusion delivery of lanthanum to the fiber surface.

Obviously the larger is the area of fiber side surface, the greater is the diffusion flow of lanthanum to the emitting surface. As the solid solution of diboride is used as the reinforcing phase, the radius of reinforcing fibers increases up to 0.7–0.8 μm, which is 1.25 times larger than for fibers formed using individual diborides. As a result, the volume proportion of diboride phase being the same, the side surface area of diboride phase will decrease by the same factor and, hence, decrease of cathode emissivity.

The study results of cathode poisoning degree under air leaking up to pressure $1.3 \cdot 10^{-2}$ Pa are presented in the Table. For previously studied cathodes based on lanthanum hexaboride, a characteristic feature is the decrease of thermoemission current (increasing cathode poisoning) with increasing air pressure in working chamber and decreasing poisoning at temperature rise practically at any studied pressure. However, for LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ multicomponent cathode, there are several differences. At the pressure of $1.3 \cdot 10^{-2}$ Pa, the temperature elevation from 1800 up to 1900 K results in a greater current drop. It is to note that at $1.3 \cdot 10^{-2}$ Pa and temperatures 1700 and 1800 K, the cathode of composite material LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ is characterized by

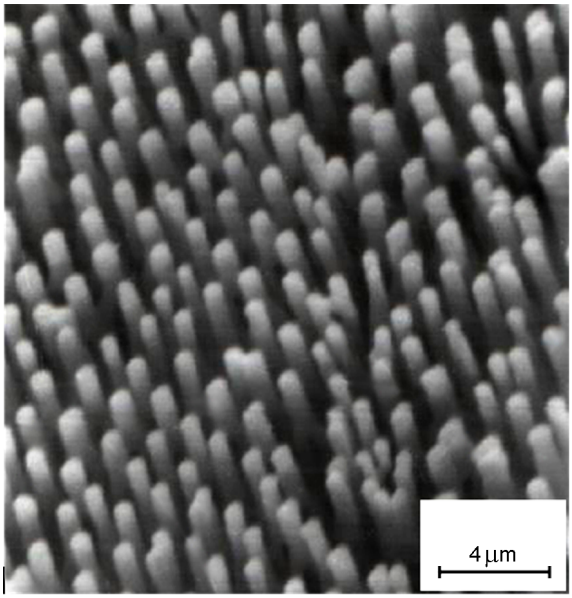

Fig. 4. Structure of LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ composition after the experiments (transversal section).

minimum poisoning in comparison with other cathodes presented in the Table. At $T = 1900$ K and the same pressure, the single crystal lanthanum hexaboride is most resistant to poisoning. In this work, an attempt was made to study the poisoning character of multicomponent cathode at even greater air leaking. As the research results show, at $T = 1700$ K and $p = 6.7 \cdot 10^{-2}$ Pa, the drop of emission current up to $0.43 I_0$ precedeed its increase up to $0.74 I_0$ at $p = 0.12$ Pa took place. Such an increase was not observed at $T = 1800$ K ($I/I_0 = 0.09$) and $T = 1900$ K ($I/I_0 = 0.04$), when pressure reached 0.12 Pa.

Table. Relative changes I/I_0 of cathode thermionic current at air leaking

Cathode material	Temperature T, K	Pressure p, Pa						
		$1.3 \cdot 10^{-5}$	$6.7 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$6.7 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$6.7 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$
LaB_6 (100)	1700	1	0.91	0.86	0.55	0.35	0.16	0.11
	1800	1	0.96	0.95	0.79	0.66	0.38	0.22
	1900	1	1	1	1	1	0.90	0.70
LaB_6–TiB_2	1700	1	0.94	0.92	0.73	0.69	0.37	0.35
	1800	1	1	1	1	0.86	0.44	0.30
	1900	1	1	1	1	1	0.85	0.48
LaB_6–ZrB_2	1700	1	0.94	0.85	0.68	0.69	0.83	0.47
	1800	1	0.97	0.97	0.96	0.84	0.19	0.17
	1900	1	1	1	1	1	0.51	0.11
LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$	1700	1	1	1	1	0.71	–	0.50
	1800	1	1	1	–	0.65	–	0.57
	1900	1	1	1	–	0.84	–	0.46

At higher gas loading on cathode and in case of need of cathode working with $j \approx 1.5$–1.6 A/cm^2 take-off, the composite cathode LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ can be used, as it shows higher resistance to poisoning.

Thus, we have studied the thermoemission properties of directionally crystallized eutectic multicomponent composed material LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$, where the reinforcing fibers (whiskers) consist of mutual solid solution of lanthanum and zirconium diborides. It is shown that establishment of stable emissivity needs a longer time as compared to directionally crystallized quasi-binary eutectics LaB_6–TiB_2 and LaB_6–ZrB_2. The emission activity of cathode formed on the base of system containing solid solution of Ti and Zr diborides is lower than activity of cathodes made from directionally crystallized LaB_6–TiB_2 and LaB_6–ZrB_2 composites, and exceeds that of LaB_6 (100) only in narrow range of temperatures. It is to note especially that the cathode from multicomponent LaB_6–$(Ti_{0.6}Zr_{0.4})B_2$ alloy in the temperature range of 1700 to 1800 K is characterized by lower degree of poisoning in comparison with emitters made from LaB_6 (100) single crystal and composite quasi-binary alloys LaB_6–TiB_2 and LaB_6–ZrB_2.

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Термоемісійні властивості матеріалу LaB_6–$(Ti_{0,6}Zr_{0,4})B_2$

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Вивчено особливості термоелектронної емісії волоконного боридного композиційного керамічного матеріалу LaB_6–$(Ti_{0,6}Zr_{0,4})B_2$, одержаного методом спрямованої кристалізації евтектичних сплавів. Представлено режими активування, температурну залежність роботи виходу електрона, отруювання при напуску повітря. Проведено порівняльний аналіз одержаних даних з емісійними характеристиками монокристала (100) LaB_6 та квазібінарних евтектичних матеріалів LaB_6–TiB_2 і LaB_6–ZrB_2.