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Thermionic emission of LaB_6–ZrB_2 quasi-binary eutectic alloy with different ZrB_2 fibers orientation

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Comparative thermionic properties investigations of the quasi-binary eutectic alloy LaB_6–ZrB_2 having both zirconium diboride fibers orientations (perpendicular and parallel) relative to the emitting surface were conducted for the first time. Thermionic current density time dependences for cross and longitudinal sections suggest that the eutectic composite material LaB_6–ZrB_2 can be used as an effective thermionic emitter also with the fibers orientation parallel to the emitting surface.

Впервые проведены сравнительные исследования термоэмиссионных свойств квазибинарного эвтектического сплава LaB_6–ZrB_2 с двумя ориентациями волокон диборида циркония: перпендикулярно и параллельно эмитирующей поверхности. Временные зависимости плотности термоэмиссионного тока для поперечного и продольного сечений свидетельствуют о том, что эвтектический композиционный материал LaB_6–ZrB_2 можно использовать как эффективный термоэмиттер и в случае ориентации волокон параллельно эмитирующей поверхности.

Термоелектронна емісія квазібінарного евтектичного сплаву LaB_6–ZrB_2 з різною орієнтацією волокон ZrB_2. *А.Таран, Д.Воронович, Д.Оранська, В.Філіпов, О.Подшивалова.*

Вперше проведено порівняльні дослідження термоемісійних властивостей квазібінарного евтектичного сплаву LaB_6–ZrB_2 з двома орієнтаціями волокон диборіду цирконію: перпендикулярно та паралельно емітуючій поверхні. Залежності густини термоемісійного струму від часу нагріву для поперечного і повздовжнього перерезів свідчать про те, що евтектичний композиційний матеріал LaB_6–ZrB_2 може використовуватися як ефективний термоемітер і в випадку орієнтації волокон паралельно емітуючій поверхні.

1. Introduction

Thermionic properties and structure of directionally crystallized eutectic alloys based on lanthanum hexaboride LaB_6–$Me^{IV}B_2$, where Me^{IV} = Ti, Zr, Hf, have already been studied [1, 2]. It has been established that these composites are characterized by lower work function, higher thermionic current density, enhanced thermal-shock resistance, and increased resistance to oxygen-containing gases poisoning compared with individual lanthanum hexaboride.

Under the directional crystallization of LaB_6 and $Me^{IV}B_2$ alloys of eutectic composition, formation of LaB_6 single-crystal matrix phase takes place. In this phase *d*-transition metal diboride is evenly distributed in

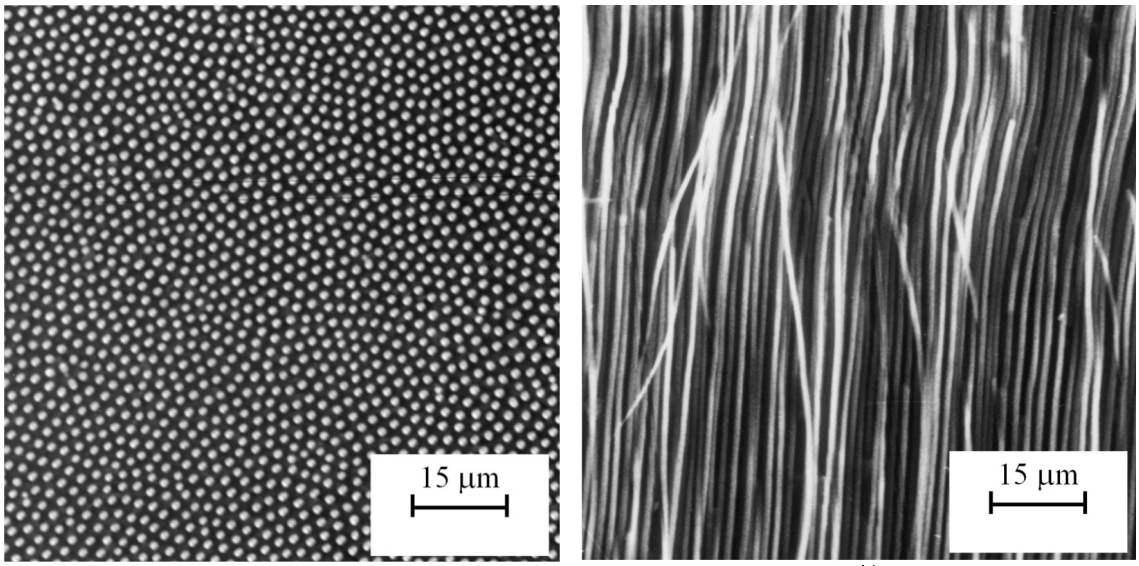

Fig. 1. Initial structure of the directionally crystallized LaB_6–ZrB_2 composite: a) cross section, b) longitudinal section.

the form of single-crystal fibers (whiskers) with almost equal thickness less than 1 μm in diameter.

Earlier the thermionic properties of directionally crystallized eutectic alloys based on lanthanum hexaboride have been investigated only for the cathodes with *d*-transition metal diboride fibers oriented perpendicular to the emitting surface.

The purpose of this work was to investigate the thermionic properties (activation processes, thermionic current density time dependence) of the composite cathode material LaB_6–ZrB_2 having both fibers orientations (perpendicular and parallel) relative to the emitting surface.

2. Experimental

Quasi-binary eutectic alloys were obtained in the IPMS NASU under directional crystallization of LaB_6–ZrB_2 alloys in the setup "Crystal-111" using vertical crucibleless zone melting with high-frequency heating. As initial materials, LaB_6 and ZrB_2 powders were mixed in the proportions corresponding to the eutectic composition. Content of zirconium diboride was 21.0 wt. % (32.5 mol. % or 17.1 vol. %) [3]. In grown single crystals the LaB_6 matrix phase orientation was along [100] direction and the fibers orientation was along [0001] one.

Then samples in the shape of a $6\times2\times2$ mm^3 parallelepiped were cut out from the grown single crystals by using electroerosion method. Some of the samples were cut out along the fibers of ZrB_2 others were cut out perpendicular to them. Smaller faces of the samples were treated by diamond pastes. One of the smaller faces of each sample acted as an emitting surface. In the other smaller face a cylindrical hole was made by electroerosion method. The hole acted as a blackbody for determination of a real (thermodynamic) temperature of the sample by optical pyrometer LOP-72 using a red light filter ($\lambda = 0.65$ μm). The hole depth-diameter ratio was not less than seven in order to consider the hole as a blackbody. Initial structure of the cathode emitting surface is shown in Fig. 1. Diameter of the ZrB_2 fibers is about 0.6 μm.

Emission current was measured under the pulse current take-off (signal frequency of 1 Hz, pulse duration of 5 μs). The maximum thermionic current density j was measured at the electric field of $2.5\cdot10^6$ V/m in the region between the cathode and anode.

3. Results and discussion

Earlier [1] it has been shown that the emitter heating (activation) at $T = 1673$ K during 10–11 h was sufficient for stable emission of cathodes based on the eutectic alloy LaB_6–ZrB_2. It is also known that under heating in vacuum (pressure of 10^{-5} Pa) the emitter's surface state changes due to LaB_6 selective evaporation. In order to examine the surface state influence on the cathode thermionic properties at different fibers orientations relative to the emitting sur-

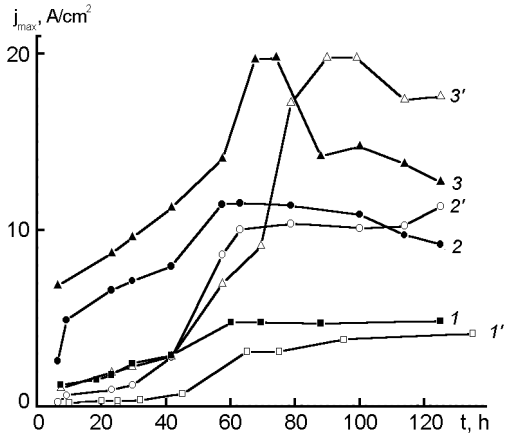

Fig. 2. Time dependences of thermionic current density at T, K: *1*, *1′* — 1623; *2*, *2′* — 1703; *3*, *3′* — 1803. *1*, *2*, *3* — cross section; *1′*, *2′*, *3′* — longitudinal section.

face, we have chosen prolonged heating conditions consisting of three stages: the first — 5 h at $T = 1400$ K, the second — 57 h at $T = 1500$ K, and the third — 73 h at $T = 1873$ K. The total heating time was 135 h.

During prolonged heating the emission current was measured at three temperatures of the cathodes ($T = 1623$, 1703, and 1803 K) every 3–10 h (Fig. 2).

Fig. 2 shows that after 62 h of heating the values of thermionic current density $j_\perp$ for cross section are greater than the values of $j_\parallel$ for longitudinal section at all measured temperatures. The third stage of the prolonged heating results in stabilization of $j_\perp$ which exceeds the value of $j_\parallel$ at that. For example, at the temperature $T = 1873$ K after 73 h heating $j_\perp$ is 2.2 times greater than $j_\parallel$ (curves *3* and *3′*, Fig. 1). The values of $j_\parallel$ have stabilized after a longer time of heating: during $t = 97$ h at $T = 1803$ K, $t = 95$ h at the temperatures 1623 and 1703 K. However, during the further heating at $T = 1803$ K cathodes emission activity is decreasing. And after 135 h heating the values of $j_\parallel$ have already exceeded the values of $j_\perp$ by a factor of 1.4. Exceeding of $j_\parallel$ over $j_\perp$ is also observed at $T = 1703$ K at the end of the testing (curves *2* and *2′*). For $T = 1623$ K permanent exceeding of $j_{\parallel\ \text{over}}\ j_\perp$ is typical.

The increase of emission activity of the eutectic alloy LaB_6–ZrB_2 in comparison with emission activity of a single crystal lanthanum hexaboride is caused by eutectic interaction between LaB_6 and ZrB_2 components. These components have a noticeable difference in their electron structures and, under the rise of temperature, mutual excitation of atoms in the LaB_6 and ZrB_2 contact zone is intensifying. As a result, lanthanum atoms leave their stable positions and their diffusion mobility increases. In such heterophase cathode material, a great number of interphase boundaries causes more accelerated flow of lanthanum atoms (ions) to the surfaces of ZrB_2 fibers and LaB_6 matrix [4], resulting in the work function reduction (adsorption systems of La–LaB_6 and La–ZrB_2 have appeared).

It has also been shown in [4] that such growth of lanthanum diffusion over the developed network of interphase boundaries has started at the temperature of $T = 1275$ K, resulting in maximum ZrB_2 covering by lanthanum at $T = 1700$–1750 K. At further heating, lanthanum desorption from either the matrix LaB_6 or the metal diboride increases.

The obtained behavior distinctions of the samples with different fibers orientations relative to the emitting surface are caused by competition of lanthanum diffusion and desorption processes, as well as direct evaporation of the LaB_6 matrix. At the finishing of the prolonged second stage of heating of the cathode having fibers perpendicular to the emitting surface ($t = 62...75$ h), the diboride phase effective area (to which lanthanum atoms have already diffused) exceeds the effective area for the case when fibers are parallel to the emitting surface. Exactly that is the cause of greater thermionic current density ($j_\perp > j_\parallel$).

Fig. 3 shows the emitting surface structures of the cathodes after 135 h testing.

Indeed, in the initial samples having fibers perpendicular to the emitting surface the diboride phase area is 17.1 % of the total emitting surface area. In the initial samples having fibers parallel to the emitting surface, for the case of ideal fibers orientation, the diboride phase area should be 44 %. However, in a real case of longitudinal slicing of the sample, practically the whole area of the emitting surface is covered with diboride zirconium fibers (Fig. 1b). In our experiments the emitting surfaces were situated in a vertical plane parallel to the anode. As the LaB_6 evaporation rate is greater than the ZrB_2 one, uncovering ("stripping") of ZrB_2 whiskers occurs under the prolonged heating. For the samples having fibers arallel to the emitting surface, there takes place a total whiskers uncovering (Fig. 3b) with their subsequent fall on the bottom of the working chamber. And diboride phase covered 44 % of the total cathode area at that. This, in turn, results

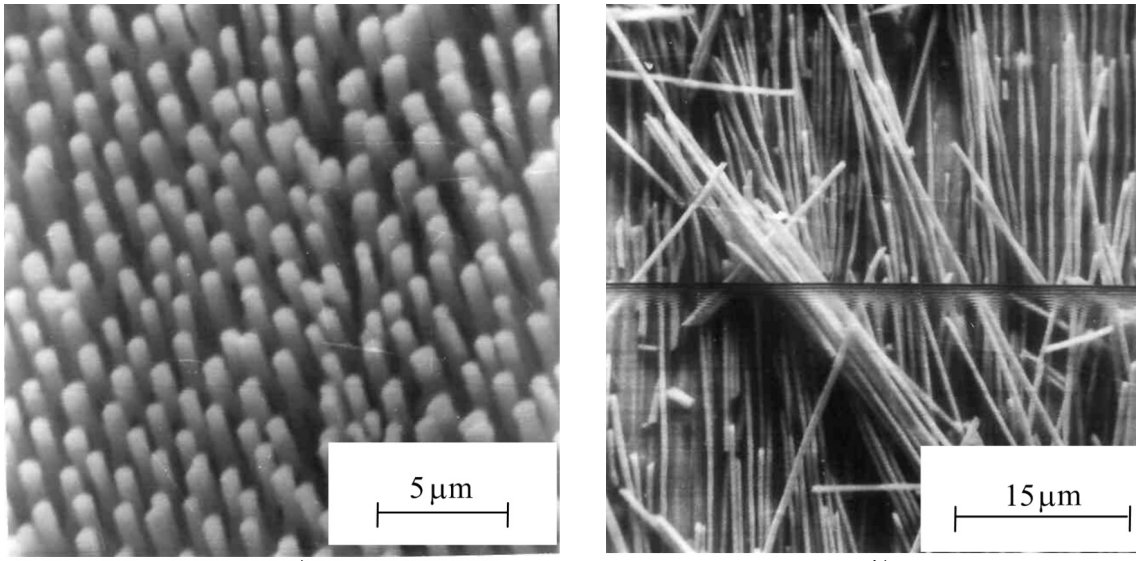

Fig. 3. Structure of the directionally crystallized LaB_6–ZrB_2 composite after the emission tests. a) cross section, b) longitudinal section.

in stabilization of $j_{\parallel}$. In the case of fibers orientation perpendicular to the emitting surface, at further heating ($t > 100$ h) uncovering of ZrB_2 fibers occurs (Fig. 3a) and that causes increase of lanthanum diffusion ways and decrease of $j_{\perp}$ for $T = 1803$ K and $T = 1703$ K. In the case of fibers orientation parallel to the emitting surface, at long-time heating and $T = 1803$ K the value of $j_{\parallel}$ also decreases due to the raised lanthanum desorption from the ZrB_2 fibers surfaces.

Summarizing the conducted experiments, we note that for LaB_6 single crystal (100) thermionic current density is equal to 12.7 A/cm^2 at 1900 K [1]. There is the same value of $j = 12.7$ A/cm^2 for the fibers orientation perpendicular to the emitting surface at smaller temperature $T = 1803$ K and $j = 17.6$ A/cm^2 for the fibers orientation parallel to the emitting surface at the same temperature.

4. Conclusions

The analysis of the thermionic current density time dependences of the quasi-binary eutectic alloy of LaB_6 with fibers orientations parallel and perpendicular to the emitting surface shows that the dependences of $j_{\perp}(t)$ and $j(t)$ are caused by the competition of lanthanum diffusion and desorption processes from the surface of LaB_6 and ZrB_2 as well as by structure features of the cathodes surfaces after long term heating.

It is shown that the eutectic composite material LaB_6–ZrB_2, having fibers orientation parallel to the emitting surface, can be used as an effective thermionic emitter as well.

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