

INFLUENCE OF MATRIX MATERIAL ON THE MECHANISM OF EMISSION FROM Sc–Ba IMPREGNATED THERMIONIC EMITTERS

I.I. BEKH, O.I. GETMAN¹, V.V. IL'CHENKO,
A.E. LUSHKIN, V.V. PANICHKINA¹, S.P. RAKITIN²

Taras Shevchenko Kyiv National University, Faculty of Physics
(64, Volodymyrska Str., Kyiv 01033, Ukraine; e-mail: sun@univ.kiev.ua),

¹I.M. Frantsevych Institute for Materials Science Problems, Nat. Acad. of Sci. of Ukraine
(3, Krzhyzhanovskiy Str., Kyiv 03680, Ukraine),

²Government enterprise "Orion Research Institute"
(8a, E. Pottier Str., Kyiv 03057, Ukraine)

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A comprehensive analysis of the influence of rhenium and scandium oxide on the mechanism of emission from impregnated tungsten thermionic emitters has been carried out. The emission abilities of scandium-barium, rhenium-tungsten, and purely tungsten emitters and their dependences on the electric field strength are demonstrated to be independent of the cathode matrix material but related to the presence of scandium oxide in their emission-active substance. However, the processes of emitting surface formation turned out substantially different for emitters with different matrix materials. In the case of tungsten matrix, scandium oxide gives rise to an increase of the number of crystallites and a variation of their shape on the emitting surface of the emitter, which creates favorable conditions for thermo-field emission. If a rhenium-tungsten matrix is applied, the presence of scandium oxide not only increases the dimensions of crystallites of active substance, but stimulates the composition variations in the emitting layer of the emitter, which is also accompanied by the thermo-field effect.

1. Introduction

Nowadays, dispenser emitters (DEs) are one of the most powerful thermionic emitters that are widely used in various types of electrovacuum devices, especially those operating in the microwave range. Scandium oxide additives make the emitters of such a type more efficient. For instance, according to the literature data [1], the best scandate emitters provide the density of emission current of 460 A/cm² at the temperature $T = 1030$ °C. However, DEs—in particular, scandate ones—demonstrate a number of shortcomings, among which a non-uniformity of the emission distribution over the emitter surface and an anomalous dependence of the current emission density on the electric field strength should be pointed out. These shortcomings do not allow DEs to be widely applied in various branches of instrument engineering, despite that a good many works

were devoted to the study of these problems during last years [2–9].

The DE matrix substance affects its physical, chemical, and emission properties. In practice, tungsten matrices are used most often for conventional emitters. However, in special cases, a substance that contains 80% of rhenium and 20% of tungsten is used [10, 11]. But the overwhelming majority of published papers were devoted to studying the properties of DEs with a tungsten matrix.

At the same time, the influence of the matrix substance on the interrelation between the chemical structure of emitting surface and the operational characteristics of conventional and scandate emitters has not been studied at length.

This work aims at a comprehensive research of the influence of rhenium and scandium oxide on the emission mechanism in impregnated tungsten thermionic emitters.

2. Experimental Research Techniques and Experimental Specimens

Experimental researches were carried out in a working chamber of an ultra-high-vacuum installation with oilless evacuation. The pressure of residual gases was monitored with the help of a Bayard–Alpert ionization manometric converter, and it did not exceed 5×10^{-9} mmHg.

To analyze the composition of emitter surfaces under investigation, the working chamber was equipped with a cylindrical mirror Auger analyzer with a 09 IOS-3 gage post.

Emission properties of emitters were measured in a single-pulse operation mode, in a plane diode system

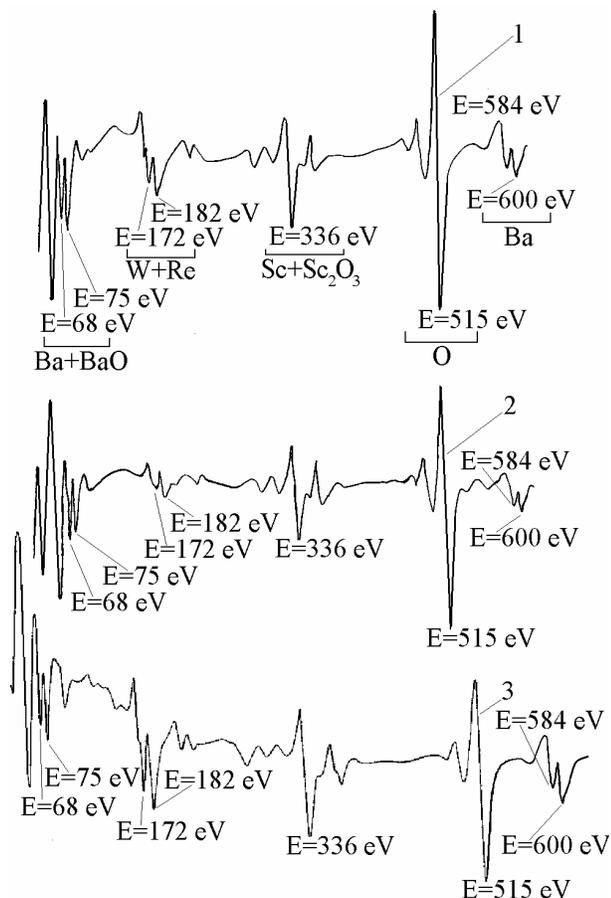


Fig. 1. Auger spectra that characterize the surface composition of DEs with various matrix materials at the temperature $T = 1400$ K: (1) Auger spectrum of the surface of a Re–W matrix DE at the beginning of activation, (2) Auger spectrum of the surface of a Re–W matrix DE at the end of activation, (3) Auger spectrum of the surface of a highly active W matrix DE

located immediately in the ultra-high-vacuum chamber. The duration of a anode pressure pulse was $7 \mu\text{s}$, and the pulse amplitude was varied within the interval from 0 to 5 kV. A $20 \times 20\text{-mm}^2$ molybdenum wafer which could be degasified by electronic bombardment served as an anode. The emitter–anode distance was rigorously monitored to be of 1 mm.

As was indicated above, the metal porous matrix fabricated of refractory metal powders is a very important part of DEs. However, the emission-active substance (EAS), which is used to impregnate the ready porous structure, is not less important. Provided identical chemical compositions of EASs, the emission properties of DEs can be substantially different depending on the EAS phase content [12]. Taking

all that into account, the emitters to study were fabricated following a special technology developed at the Orion government enterprise. A metallic porous matrix of emitters was composed of rhenium (80%) and tungsten (20%), or the matrix was purely tungsten. The chemical compositions of EASs for the impregnation of Re–W emitters were $2.6\text{BaO} \cdot 1.9\text{CaO} \cdot 0.5\text{Sc}_2\text{O}_3 \cdot 0.5\text{Al}_2\text{O}_3$ and $2.6\text{BaO} \cdot 1.9\text{CaO} \cdot 1.0\text{Al}_2\text{O}_3$, whereas those for the impregnation of W emitters were $2.4\text{BaO} \cdot 0.6\text{CaO} \times 0.1\text{Sc}_2\text{O}_3 \cdot 0.9\text{Al}_2\text{O}_3$ and $2.4\text{BaO} \cdot 0.6\text{CaO} \cdot 1.0\text{Al}_2\text{O}_3$.

3. Experimental Results and Their Discussion

Experimental researches of scandate rhenium-tungsten DEs showed that the composition of their surfaces before thermal vacuum treatment in the Auger spectrometer chamber practically did not differ from that for scandate DEs with a tungsten matrix. The Auger spectra revealed pronounced Auger lines of barium and its oxide, calcium oxide, scandium, and oxygen. In addition, the emitter surfaces were polluted: the Auger lines of chlorine, potassium, and carbon were observed.

Auger electron spectrometry researches demonstrated that the growth of the annealing temperature was accompanied by a concentration reduction of potassium and chlorine on the emitter surfaces. At the annealing temperature $T = 1300$ K, the Auger lines of carbon disappeared. However, the increase of the emission current from 1.7 to 6.5A/cm^2 was already observed at the temperature $T = 1200$ K, when the emitter surface got free from volatile barium compounds, in particular, $\text{Ba}(\text{OH})_2$. The emitters attained a high activity ($j \approx 70 \text{A/cm}^2$) only at the end of annealing procedure at the temperature $T = 1400$ K. The maximal activity was observed only in several hours, if the emitters were exploited at the same temperature.

In Fig. 1, the Auger spectra recorded at the temperature $T = 1400$ K are depicted. They characterize the emitter surface composition for various substances the emitter matrices consist of. The following features attract our attention. First, when the emitters with the Re–W matrix attain a high activity, the ratio between the amplitudes of barium Auger line (at $E = 75$ eV) and that of its oxide (at $E = 68$ eV) amounts to 0.65. Provided similar conditions, this ratio is known to be appreciably more than unity for DEs without scandium oxide [13]. Hence, we may suppose that the oxidation degree of barium in scandate emitters is higher. Second, the analysis of the results obtained testifies that the coverage degree of a matrix material by the emission-active substance is higher for emitters with the Re–W

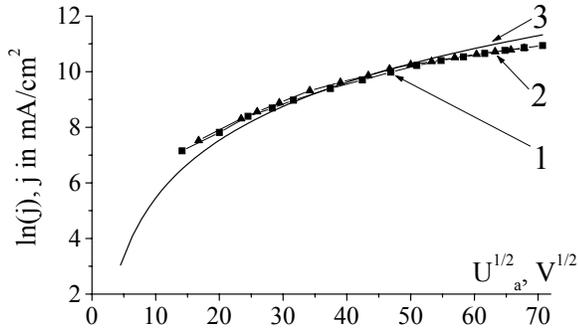


Fig. 2. CVCs of active DEs of various types measured at the temperature $T = 1300$ K: (1) Sc-Ba DE with the W matrix, (2) Sc-Ba DE with the Re-W matrix, (3) theoretical Child-Langmuir dependence

matrix. In the Auger spectra, the lines that are characteristic of the matrix material (at $E = 160$ and 180 eV) are smeared and hardly noticeable (Fig. 1, curve 2). It is in contrast to the DE with the W matrix (Fig. 1, curve 3), where the Auger lines, characteristic of matrix material are pronounced, and their amplitudes are comparable with those of other surface components. It is evident that the overwhelming part of the rhenium-tungsten emitter surface is covered with an activator layer, the thickness of which has an order of the escape depth of Auger electrons from the matrix bulk, and it is this layer that provides the high emissive ability of such emitters. At the same time, in the case of emitters with the tungsten matrix, their high emittance is associated with the presence of micro-sized three-dimensional formations—activator crystallites—on their surface [7].

In Fig. 2, the current-voltage characteristics (CVCs) of DEs with different matrix materials are exhibited; they were obtained at the beginning of emitter exploitation and at the temperature $T = 1300$ K. At the start of exploitation, the emittances of scandate DEs with tungsten and rhenium-tungsten matrices are identical (curves 1 and 2 in Fig. 2 practically coincide). Therefore, we may suppose that the emissive abilities of both rhenium-tungsten and tungsten scandate DEs, as well as their dependences on the electric field strength, are practically independent of the matrix substance, being related to the presence of scandium oxide in the emission-active substance.

As was shown in works [7,9], a peculiarity is observed in the CVCs for dispenser emitters with the tungsten matrix, especially for scandate ones, at fields when the anode current is restricted by a spatial charge (it is the range of anode voltages up to 1000 V); namely, the CVC

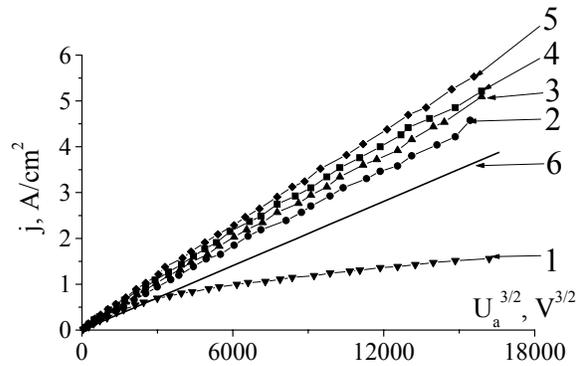


Fig. 3. CVCs of an active Sc-Ba DE with the Re-W matrix at temperatures $T = 1100$ (1), 1200 (2), 1300 (3), 1400 (4), and 1525 K (5). Curve 6 is the Child-Langmuir dependence

behavior does not obey the Child-Langmuir law (the three-halves power law). In this case, experimental values of the anode current density exceed – in case of DEs with a scandium oxide additive, considerably exceed – the magnitudes obtained from the three-halves power law.

A similar picture is observed for scandate emitters with the rhenium-tungsten matrix (see the corresponding dependences in Fig. 3). Such a behavior of the CVC for a scandate DE with the Re-W matrix is another evidence in favor of a conclusion about the crucial role of the scandium oxide additive in the formation of high DE emittance.

This conclusion is also proved by the results of researches of rhenium-tungsten DEs without scandium oxide additive. In the whole range of operating temperatures, the CVCs satisfy the Child-Langmuir law in the field range where the anode current is restricted by a spatial charge (the range of anode voltage up to 1000 V). However, it is not true for non-scandate emitters with the tungsten matrix. In Fig. 4, the characteristics of highly active non-scandate emitters with different matrix materials, which were measured at the temperature $T = 1300$ K, are depicted.

By comparing the characteristics given in Fig. 4, we are allowed to draw conclusion that, under identical conditions, emitters with the rhenium-tungsten matrix demonstrate a much higher emissive ability in comparison with those with the tungsten matrix. In particular, the emission current density at zero field is more than twice lower (1.8 A/cm² against 8.1 A/cm²). The explanation of this fact is as follows. It is worth noting that a high emittance of emitters with the tungsten matrix is associated with three-dimensional

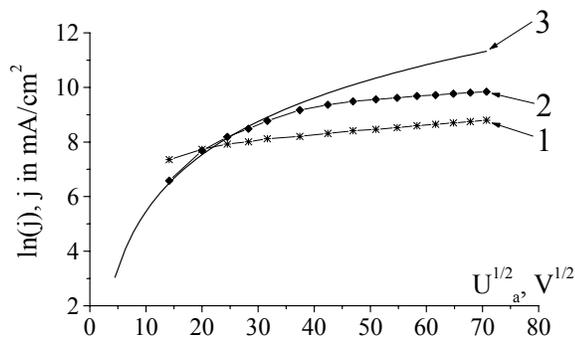


Fig. 4. CVCs of highly active non-scandate DEs measured at $T = 1300$ K: (1) DE with the W matrix, (2) DE with the Re-W matrix, (3) the Child-Langmuir dependence

islands of emission-active substances, which, according to literature data [14], occupy only 2-3% of working surface. At the same time, the results reported in this work testify that the main contribution to the emissive ability of rhenium-tungsten emitters is given by the surface sections covered with the emission-active substance layer, the thickness of which has an order of the escape depth of Auger electrons from the matrix material. It is evident that the higher emittance of emitters with the rhenium-tungsten matrix stems from a larger integral area occupied by emission-active substance.

Hence, the substance the emitter matrix consists of actually plays an essential role in the determination of its physico-chemical and emission properties, if no scandium oxide is introduced into DEs. A scandium oxide additive to the active substance of DEs with the rhenium-tungsten matrix substantially increases their emissive ability, as it was in the case of DEs with the tungsten matrix. The corresponding CVCs of emitters with different matrix materials measured under identical conditions practically do not differ by the current density magnitude (see the dependences in Fig. 2).

The analysis of the results of our experimental researches demonstrated that, if a scandate rhenium-tungsten emitter is degased at the temperature $T = 1400$ K, the subsequent high-temperature activating annealing at the temperature $T = 1525$ K for 1 h induces only surface composition variations. For instance, a triad of Auger lines in the energy range $E = 160 - 180$ eV becomes more pronounced, and their amplitudes grow in comparison with line amplitudes of other components present at the emitter working surface. Moreover, the ratio between the Auger line amplitudes of barium and its oxide approaches unity, i.e. the amount of free barium

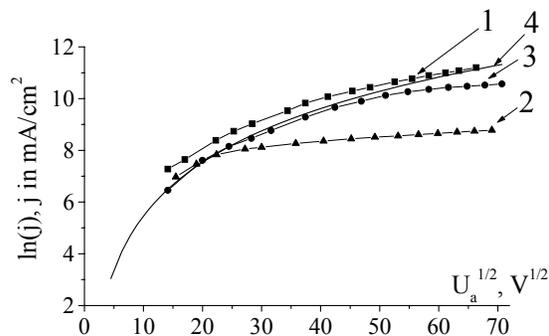


Fig. 5. CVCs of a scandate rhenium-tungsten DE measured at the temperature $T = 1400$ K: (1) before durability test, (2) after durability test, (3) CVC of a non-scandate rhenium-tungsten DE, (4) the Child-Langmuir dependence

on the surface grows as well. These facts seem to have pointed at the emitter activity growth, as it occurs in the case of ordinary DEs (without the scandium additive) [12]. However, these data characterize, in effect, an emitter with a lower activity: the emission current density is reduced by 20% (from 47.5 to 38.5 A/cm²) at an anode voltage of 3000 V. The further annealing of the emitter at the temperature $T = 1400$ K for 15 h practically did not affected its emittance. The corresponding surface composition did not change as well.

The reason for such a reduction of the emittance of the scandate rhenium-tungsten emitter after the high-temperature annealing could be the noncongruent evaporation of components from the thick layer of the active substance on its surface. Such an evaporation gives rise to the violation of the optimum composition of emission-active substances that was obtained in the course of the previous thermal vacuum treatment.

To confirm or refute this assumption, we carried out a rapid high-temperature durability test of a scandate rhenium-tungsten dispenser emitter with the same composition: after the functioning for 200 h at the temperature $T = 1525$ K, the emitter lost its activity. Curve 1 in Fig. 5 characterizes the emittance of this emitter at the beginning of the durability test, curve 2 after the test termination, and curve 4 corresponds to the theoretical Child-Langmuir dependence. The CVC presented by curve 3 characterizes the emittance of a non-scandate emitter with the rhenium-tungsten matrix. The figure demonstrates that the behaviors of curves 2 and 3 are identical in the anode voltage range to 1000 V, i.e. the three-halves law is not violated. This means that the scandate DE with the rhenium-tungsten matrix lost its properties characteristic of DEs with the

scandium additive in the course of the rapid durability test.

The Auger spectrometry data convincingly testify to the validity of such a statement. This can be seen from Fig. 6, where a detailed Auger spectrum of the emitter surface after the rapid durability test is depicted.

A comparison of this spectrum with those given in Fig. 1 demonstrates that the surface composition of the scandate DE with the rhenium-tungsten matrix is substantially different at the end of the exploitation term. First, the degree of barium oxidation appreciably diminished, and the oxygen concentration also decreased very considerably. Second, the amount of the emission-active substance on matrix grains decreased appreciably, which is evidenced by the fact that the amplitudes of the Auger line triad in the interval $E = 160 - 180$ eV became comparable with those of Auger lines characterizing the barium component, as well as that the Auger lines of scandium component substantially decreased.

Hence, having analyzed the results of Auger spectroscopy researches of non-scandate emitters with various matrix materials, we may assert that the latter play an exclusive role in the formation of final CVCs in the range of anode voltages lower than 1000 V. In the case of an emitter with the rhenium-tungsten matrix, its working surface is covered by a layer of emission-active substances. The corresponding mechanism of emission from DEs practically does not differ from that for an ordinary oxide emitter. In the case of emitters with the tungsten matrix, as was shown in work [12] earlier, crystallites of an active substance are formed on the emitter working surface. Therefore, such emitters operate in a regime, in which the spatial charge near their surface practically does not confine the anode current. This occurs due to a different mechanism of electric field influence on emission from DEs with the tungsten matrix. In particular, a combination of thermionic and field emissions rather than a simple thermal electron emission is realized [7, 9].

In addition, the results of experimental researches convincingly testify that the scandium oxide additive in the active substance of DEs with the rhenium-tungsten matrix substantially enhances their emissive ability, as it takes place in the case of DEs with the tungsten matrix, and the emitter CVCs measured under identical conditions practically do not differ by the current density. However, in contrast to the tungsten matrix emitters, for which three-dimensional formations – activator crystallites – on their surface are responsible for their high emittance, the main contribution to a high emission activity of DEs with the scandate rhenium-

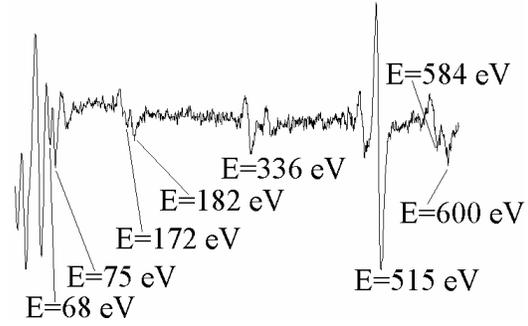


Fig. 6. Auger spectrum of a scandate rhenium-tungsten DE which characterizes the composition of its surface after the rapid durability test

tungsten matrix is made by a layer of emission-active substance, the thickness of which is of the order of the Auger electron escape depth in the matrix material.

Concerning the role of the scandium component in the formation of features in CVCs for rhenium-tungsten matrix emitters, it obviously consists in the creation of a complicated chemical compound on the basis of alkaline-earth metal oxides and scandium oxide on their working surface. A new substance promotes the field to penetrate considerably deeper into the emitting layer. As a result, thermal field emission also takes place. The fact that the CVCs of scandate Re–W matrix emitters do not differ from the CVCs of non-scandate ones after rapid durability tests (the emitter annealing at the temperature $T = 1525$ K for 200 h) testifies in favor of this assumption (see the dependences in Fig. 5). Moreover, the data of Auger spectrometry demonstrate that the amount of the scandium component substantially decreased on the emitter working surface after the test, which is illustrated by the Auger spectrum exhibited in Fig. 6.

4. Conclusions

The emissive abilities of scandium-barium, rhenium-tungsten, and purely tungsten DEs and their dependences on the electric field strength are practically independent of the emitter matrix material, being related to the presence of scandium oxide in their emission-active substance. However, the processes of formation of emitter working surfaces with different matrix materials are essentially different. For instance, the main contribution to the high emission activity of scandate rhenium-tungsten matrix DEs is made by a layer of emission-active substance, the thickness of

which is of the order of the escape depth of Auger electrons from the matrix material. On the contrary, the emitters with purely tungsten matrix contain three-dimensional formations, crystallites of the active substance components which are responsible for a high emittance, on their surfaces.

If a tungsten substrate (matrix) is used, the influence of scandium oxide consists in an increase of the number of crystallites and a variation of their shape on the DE emitting surface, which gives rise to the emergence of conditions favorable for thermo-field emission. If a rhenium-tungsten matrix is used, the presence of scandium oxide stimulates both the growth of the active substance crystallite dimensions and the composition change in the DE emitting layer, which is also accompanied by the same thermo-field emission effect.

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ВПЛИВ МАТЕРІАЛУ МАТРИЦІ НА МЕХАНІЗМ ЕМІСІЇ ІМПРЕГНОВАНИХ СКАНДІЙ-БАРІЄВИХ ТЕРМОЕМІТЕРІВ

I.I. Бех, О.І. Гетьман, В.В. Ільченко, О.Є. Лушкін, В.В. Панічкіна, С.П. Ракітін

Р е з ю м е

Проведено комплексне дослідження впливу ренію та окису скандію на механізм емісії імпрегнованих вольфрамових термоемітерів. Показано, що емісійна здатність скандій-барієвих, реній-вольфрамових та вольфрамових емітерів та її залежність від напруженості електричного поля не визначається матеріалом матриці, а пов'язана з наявністю в їхній емісійно-активній речовині окису скандію. Проте процеси формування емітуючої поверхні емітерів з різним матеріалом матриці істотно різні. Під час використання вольфрамової матриці вплив окису скандію полягає в збільшенні кількості та зміні форми кристалітів на емітуючій поверхні емітера, що приводить до формування умов термо-автоелектронної емісії. Під час використання реній-вольфрамової матриці наявність окису скандію поряд зі збільшенням розмірів кристалітів активної речовини приводить до змін складу емітуючого шару емітера, що супроводжується тим же термо-автоелектронним ефектом.