Operational testing of self-heated cathode made from compacted TiN powder

N V Gavrilov, A S Kamenetskikh, D S Koleukh, S N Paranin, V S Pasmurov, A V Spirin

Institute of Electrophysics, 106 Amundsen str., Yekaterinburg, 620016, Russia

E-mail: alx@iep.uran.ru

Abstract. The results of tests of a self-heated hollow cathode made by magnet-pulse pressing of the mixture of TiN (90 %) and Ti (10 %) powders with further high-temperature annealing and fusing during operation of the compact as a cathode in high-current (10 - 45 A) discharge are presented. It was found that the rate of the cathode mass loss during operation in Ar/N₂ mixture made 2.3*10⁻⁷ g/C. The possibility of the cathode use for oxygen-argon plasma generation at separated gas feeding (argon – through cathode cavity, and O₂ – to anode area of discharge) was shown. Testing of massive tubular cathodes with the increased thickness of the wall (up to 2.5 mm) and large inner diameter (up to 12 mm) possessing an enhanced resource (300 - 500 h) was carried out.

1. Introduction

High-current (10 - 100 A) discharge with a self-heated hollow cathode (SHHC) is used in physical and chemical vapor deposition for ion sputtering, activation of plasma-chemical processes in a working chamber and for ion assistance [1]. SHHC are most often made of high-melting metals and lanthanum hexaboride. The lifetime of such cathodes is restricted by the intensive erosion of the high-temperature active zone (this area is usually ten times smaller than area of the cathode). The active zone is shifted in the direction of the outlet aperture of the hollow cathode with the growth of the discharge current, and its area is reduced. The rate of cathode erosion increases as a result. The erosion rate of niobium cathode makes ~ 3·10⁻⁷ g/C under discharge currents near 10 A, which restricts the lifetime of a tubular cathode Ø 8 mm with the wall 1 mm thick to 250 h [2]. Lifetime of a self-heated cathode can be enhanced by increasing its diameter and wall thickness. However the high cost of cathode materials traditionally used for SHHC (tantalum, niobium) makes hollow cathodes noncompetitive in comparison with rod thermo-emission cathodes even at attaining acceptable lifetime. The authors’ work experience with SHHC of titanium nitride (TiN) showed high effectiveness and the stability of emission of such cathodes in nitrogen-argon mixtures and comparable with metallic cathodes rate of erosion ~ 1·10⁻⁷ g/C [3, 4]. However, the method of TiN cathodes preparation by high-temperature nitriding of titanium tube does not permit to significantly increase the cathode wall thickness because of the reduction of the nitriding rate. In the present work, the method of production of tubular cathodes with a wall 2.5 mm thick and inner diameter up to 12 mm by magnet-pulse pressing of TiN powder with further annealing in nitrogen flow and agglomeration in high-current discharge plasma is described. Phase composition of compacts in the initial state and after 70 h tests as SHHC was studied. The results of tests of such a cathode at discharge currents up to 45 A in DC mode and up to 100 A in AC mode are shown.
2. Experimental Technique

2.1. Preparation of hollow cathode from titanium nitride

Cathodes were made in the form of tubes of two type-sizes, one having external diameter 11.1 mm and thickness 2.4 mm, and the other – 16.9 mm and 2.6 mm, correspondingly. The mixture of powders, containing TiN (Technical Conditions 6-09-112-75, produced by JSC «Vecton») with grain no more than 100 μm, 10 wt.% of Ti with grain no more than 50 μm (State Standard 17746-79) and 2 wt.% of polyvinylbutyral (PVB), was used as precursor. Polymer and metallic components were introduced as binding and plastifying agents. The mixture was prepared in a form of suspension on the base of isopropanol by mixing of components in a low-speed device of «drunken barrel» type with steel balls. Dried obtained agglomerate was milled in a ball grinder by steel balls and then sifted. Only the fraction smaller than 40 μm was used. Optic microphotograph of composite powder particles are shown in figure 1. They have an irregular form of splints with clear edges not changing under the treatment of powder in blender and ball grinder.

![Composite powder particles](image)

**Figure 1.** The composite powder particles.

Tubular blanks from composite powder were formed by a magnet-pulse pressing method [5]. A steel spiral inductor with a working channel Ø 22.5 mm was connected to a pulse current generator on the base of capacitive energy accumulator PCG-135 (425 μF, 25 kV). Press-stem with a layer of composite powder placed between external copper casing and coaxially located form-generating rod of tempered steel was installed into the inductor channel. The press-stem was encapsulated and pumped till residual pressure reached ~ 5 Pa, which level was maintained during all the process of pressing. Powder was pressed due to the compression of the copper casing under the action of pulse magnetic field of inductor. Magnetic field with an amplitude up to 25 T provided pressure up to 0.25 GPa on the conductor. After pressing tubular compacts were extracted from press-stem and annealed in a vacuum furnace in nitrogen flow during 1 h at pressure 2.7 Pa and temperature 600 °C for thermolysis of PVB and removal of its products from the compact.

2.2. Methods of tests of a self-heated hollow cathode

The tests of TiN compacts as SHHC were accomplished in a facility shown in figure 2. Tubular compact I with inner, external diameters and height: 6, 11 и 70 mm, correspondingly, was placed inside of water-cooled case 2, thermally isolated from other elements of the system and used as a hollow cathode. A hollow anode 3 Ø of 80 mm and 100 mm height was installed opposite the outlet aperture of hollow cathode I. A mesh with 1.2 x 1.2 mm cells was placed at the flat end of the hollow anode. The gas mixture with the ratio of Ar/N₂ flows rate 28/5 (sccm) was leaked through the cathode cavity. Ar (30 sccm) was fed through the cathode cavity and O₂ (7 до 30 sccm) directly into vacuum chamber 4 in tests with Ar/O₂ working gas. Gas mixture pressure in the vacuum chamber made 0.2-0.5 Pa. The glow discharge with current up to 4 A and voltage ~ 500 V was ignited to provide hollow cathode heating to temperatures at which
thermionic emission becomes the main mechanism of the discharge maintenance. The discharge voltage reduced to values less than 100 V in this regime. The value of the discharge current was set in 5 – 45 A range. SHHC was tested in AC discharge which provided pulse heating of the near surface layer of the cathode (several tens of μm thick) by 10-10²°C and the increase in the discharge current by several hundreds of A [4].

The duration of cyclic tests of SHHC was from 0.5 to 6.0 h. Mass changes for the compacts were measured after every cycle by means of analytic scales VL-210 (Gosmeter) with 0.0001 g discretion.

Phase composition of SHHC material was studied by means of XRD using diffractometer XPert PRO (PANalitical) in copper radiation with beta-filter on diffracted beam. X-ray patterns were exposed to total-profile analysis using XPert High Score Plus software. The coherent-scattering region (CSR) was determined by Scherer’s method based on reflexes in narrow angles of dispersion (form factor 0.9).

Compacts density and porosity were measured by the attested method of hydrostatic weighing. The density was determined based on the results of weighing a sample fragment in air and in water. Compacts were covered with a thin waterproof layer of nitrocellulose for weighing in water. A fractional error of density measurement did not exceed 1 %. Open porosity was determined by water-consuming. Compacts were saturated by water in a vacuum chamber with water feeding and boiling. A fractional error of open porosity measurement did not exceed 4 %.

The structure of compacts in the initial state and after the tests was studied by means of optic microscope Olympus BX51TRF-5 with maximum magnification 100. Fragments of compacts were grinded in the plane of the cross section of the tube by means of grinding-polishing mill Phoenix Beta 1c (Buehler, Germany) using diamond suspension with dispersion not more than 1 μm in the finish phase.

3. Results and discussion

The appearance of compacts before tests and after operation in discharge during 70 h is shown in figure 3. Density and porosity of initial compacts made 3.56 g/cm³ и 29.6 %, correspondingly. During test procedure, the outer diameter of the cathode was reduced to 9.1 mm in the medial part, corresponding to the active zone, to 10.1 mm on the upper flat-end and to 10.9 mm on the lower flat-end (initial values being: 11.1, 10.1, 11.2 mm, correspondingly). The compact density grew up to 3.93 g/cm³, and porosity was reduced to 25.8 % after the tests.
The dependence of SHHC mass on the electric charge of DC discharge in Ar/N₂ mixture is presented in figure 4. At the initial period (shown by dashed line at the figure 4) when the charge is less ~ 3.6·10⁵ C, the cathode mass increased due to the conversion Ti → TiN. The process of nitrogen diffusion through the nitride layer is described by relation: \((\Delta m/S)^2 = Kl\), where \(\Delta m\) is the mass of consumed nitrogen, \(S\) is the area of diffusion, \(l\) is the period of nitrogen consuming [6]. The constant \(K\) of nitrogen consuming rate by titanium, as estimated by test results, made 1.8·10⁻⁸ g²/cm²·s, that is several times less than cited values [7]; that can be connected with the restricted access of nitrogen to the compact bulk.

The increase in weight corresponds to total transition of 10 % Ti addition into TiN of stoichiometric composition, which is confirmed by the results of XRD. XRD patterns of the compact after vacuum annealing at 600 °C and of the sample after cyclic tests as SHHC for 70 h are shown in figure 5. The position and intensity of peaks of TiN phase with FCC lattice and of \(\alpha\)-Ti correspond to a standard sample [8, 9]. The portion of TiN and Ti phases makes 92.4 and 7.6 wt. %, and the average size of the CSR – 85 and 25 nm, correspondingly. Peaks of \(\alpha\)-Ti phase are absent on the XRD pattern of SHHC sample passed cyclic tests. Crystallites of TiN have lattice constant 0.424 nm that corresponds to defect-free samples synthesized in equilibrium conditions [8]. The average size of crystallites grew up to 115 nm due to sample exposure at high temperatures.

SHHC operation after conversion of Ti into TiN is accompanied by mass reduction (see figure 4) caused by the erosion of the cathode inner surface in the gas discharge. The rate of erosion made 2.3·10⁻⁷ g/C independently of the discharge current. The measured value is comparable with the magnitude of the erosion rate of SHHC produced by the method of nitriding of Ti tube in a discharge [3]. At comparable values of erosion rate, the cathode made from TiN powder possesses higher lifetime owing to increasing the wall thickness from 1 to 2.5 mm. The SHHC from TiN compact, unlike the Ti cathode, does not require long-continued training in N₂ flow which provides the formation of heat-resistant TiN across the overall thickness of the cathode wall.

The calculated time of increasing the erosion depth to 1 mm makes ~500 h under discharge current 10 A for SHHC with inner diameter 6 mm. Estimation was done under the hypothesis that cathode erosion takes place within the limits of 3.5 cm² active zone. The cathode lifetime could be significantly enhanced in the case of the increase in the cathode diameter or acceptable erosion depth. It must be noted that the erosion rate of hollow cathodes made of pure high-melting materials, i.e. tantalum [10] in Ar atmosphere is close to that obtained in this work (~ 10⁻⁷ g/C).

The cross-section of samples are shown in figure 6. A dense layer of material near 0.1 mm thick had been formed in the active zone from the inner side of the tube surface while samples were tested as SHHC. Closed pores with linear sizes from units till tens of \(\mu\)m are present in SHHC bulk. The porous structure with crystallites of unequal size is observed in an untreated compact sample. Thus, during cathode operation at characteristic temperatures of 2000 - 2200 °C agglomeration of powder
compact takes place, which allows to make massive cathodes of TiN with enhanced wall thickness and increased lifetime.

**Figure 4.** The dependence of SHHC mass on electric charge of DC discharge in Ar/N\textsubscript{2} (1, dashed segment of 2) and Ar/O\textsubscript{2} (2) mixture.

**Figure 5.** XRD patterns of compact after vacuum annealing at 600 °C (1) and of sample after cyclic tests as SHHC for 70 h (2).

**Figure 6.** The cross-section of the sample tested as SHHC (a) and untreated sample (b).

The SHHC from compacted TiN powder was tested in an electron source generating the assisting plasma in a magnetron sputtering system for reactive deposition of oxide coatings. SHHC operates steadily under partial O\textsubscript{2} pressure in a working chamber up to 0.5 Pa. The duration of working cycles made 2 - 6 h. It is known that the lifetime of metallic thermo-emiss cathodes is significantly reduced at O\textsubscript{2} partial pressure more than 10\textsuperscript{-5} Pa. [11]. Poisoning of cathodes based on metal borides (i.e., LaB\textsubscript{6}) in the presence of both O\textsubscript{2} or N\textsubscript{2} leads to multiply reduction of the cathode emission current [12]. The result of tests of SHHC from compacted TiN powder during operation in Ar/O\textsubscript{2} atmosphere is presented in figure 4. It was determined that the erosion rate of SHHC grew by 1.6, as compared with the regime of work in Ar/N\textsubscript{2} mixture, and reached 3.6·10\textsuperscript{-7} g/C. It was shown in the work [13] that intensive oxidation of TiN begins at temperatures more than 700 - 800 °C. The compounds of Ti and O\textsubscript{2} transform into a liquid phase when temperature exceeds 1900 °C (the characteristic of the working range of tested SHHC) [14]. Obviously, the erosion rate of SHHC of TiN increased during the operation in Ar/O\textsubscript{2} gas mixture because of the formation and sublimation of
titanium oxides. However, the rate of this process in experimental conditions is relatively low. SHHC had operated for 70 h in Ar/O₂ atmosphere (carried charge 4*10^6 C) and further tests of the cathode were held in Ar/N₂ mixture. In figure 4 the segment of dependency 2 marked with dashed line corresponds to the additional stage of tests. As can be seen the rate of cathode erosion was reduced to values close to value for SHHC that operated in Ar/N₂ mixture only. Thus, the tested SHHC is able to restore its resource characteristics after a long-term work in Ar/O₂ atmosphere that points at the absence of total poisoning of the cathode bulk.

In figure 7 the current-voltage characteristic of the discharge with SHHC operating in Ar/N₂ mixture is shown. Transition into the regime of thermo-electronic emission accompanied with the reduction of the discharge voltage to 100 V takes place after cathode heating in glow discharge plasma (4 A, 500 V).

Discharge voltage monotonously decreased to ~25 V as discharge current grew up to 45 A. The oscillograms of current and voltage of discharge in high-current pulsed mode are shown in figure 8. The discharge is stable in a wide range of frequency (1-1000 Hz) and pulse duration (10-1000 μs) if the surface temperature of the cathode during a pause does not fall below minimum level providing initial current of thermo-electronic emission when voltage pulses are applied across the discharge gap. The value of initial current depends on conditions of discharge transition into low-voltage burning regime supported by thermo-electronic emission of the cathode. The initial current made ~ 4 A in experiments and minimum necessary temperature of cathode surface was ~ 1700 °C. The pulse current of the discharge reaches 100 A and the discharge voltage makes 240 V at frequency 200 Hz and pulse duration 200 μs.

Figure 7. The current-voltage characteristic of discharge with SHHC operating in Ar/N₂ mixture.

Figure 8. Oscillograms of current (I) and voltage (U) of discharge with SHHC made from TiN.
Frequency: a, b – 200 Hz; c – 1 kHz. Pulse duration: a, c – 200 μs; b – 1 ms. Scale division of I: a - 50 A/div; b, c – 10 A/div; and of U - 100 V/div.
4. Conclusion

Testing of SHHC made of titanium nitride by the method of magnet-pulse pressing of powder material in the form of tubes with walls 2.5 mm thick, inner diameter 6 and 12 mm was accomplished. The work of tubular compacts as a SHHC provides their agglomeration across all the wall thickness that allows forming of mechanically strong massive cathodes of TiN with the enhanced wall thickness and increased operational resource.

Cathodes show stable work in a DC mode under the following conditions: discharge currents ~ several tens of A, discharge voltage less than 100 V and in pulse mode in a wide range of frequencies (10-1000 Hz) and pulse duration (10-1000 μs) at average current ~ 4 A, current amplitude up to 200 A and discharge voltage up to 300 V. It was shown that SHHC of titanium nitride is suitable for stable operation in Ar flow at high (up to 0.5 Pa) partial O₂ pressure in the anode area of discharge. The rate of cathode erosion makes 2.3·10⁻⁷ and 3.7·10⁻⁷ g/C at plasma generation in Ar/N₂ and Ar/O₂ gas mixtures, correspondingly, which provides the lifetime not less than 500 and 300 h (supposed that erosion depth does not exceed 1 mm) under discharge current 10 A.

References

[1] Muhl S., Pérez A. 2015 Thin Solid Films 579 174
[2] Gavrilov N V, Men’shakov A I 2011 Instruments and Experimental Techniques 54(5) 732
[3] Gavrilov N V, Men’shakov A 2012 Technical Physics Letters 38(11) 1031
[4] Gavrilov N V, Men’shakov A 2016 Technical Physics 61(5) 669
[5] Lee J G et al. 2015 Metallurgical and Materials Transactions A 46A 3139
[6] Gulbransen E.A., Andrew K.F. 1949 Trans. Am. Inst. Min. (Metal) Eng. 185 741
[7] Samsonov G V et al. 1972 Metodi polucheniya, svoistva i primenenie nitridov. (Kiev: Izdatel’ svo IPM AN USSR, ONTI) (in russian)
[8] Wong-Ng W et al. 1987 (NBS, Gaithersburg, MD, USA., ICDD Grant-in-Aid) CAS Number: 12033-66-8
[9] Sailer R, McCarthy G 1993 (North Dakota State University, Fargo, North Dakota, USA., ICDD Grant-in-Aid) CAS Number: 7440-32-6
[10] Grishin S D et al. 1977 TVT 15(4) 906 (in russian)
[11] Kresanov V S at al. 1987 Visokoefectivniy emitter electronov na osnove gesaborida lantana (Moscow, Energoatomizdat) (in russian)
[12] Gallacher H.E. 1969 J. Appl. Phys. 40 44
[13] Samsonov G V 1969 Nitridi (Kiev, Naukova dumka) (in russian)
[14] Hazin L G 1970 Dvuokis’ titana (Leningrad, Himiya) (in russian)

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