Generation of gas-metal plasma of arc low-pressure discharges and investigation of the deposition mode of wear-resistant nitride coatings

O V Krysina, V V Shugurov, N A Prokopenko and S S Kovalsky
Institute of High Current Electronics SB RAS, 2/3 Akademichesky Ave., Tomsk, 634055, Russia

E-Mail: krysina_82@mail.ru

Abstract. The modes of gas-metal plasma generation are investigated at independent and combined operation of plasma generators of the different construction. The dependences of an ion current on a collector on the current of the arc discharge of plasma sources, on the pressure and on the composition of working gas in the wide ranges of parameters are obtained. The distributions of metal and nitride coatings growth rate along vacuum chamber radius at the use of the system of magnetic plasma flow separation from droplet fraction are revealed. The service properties of the plasma sources of different type are defined. The parameter ranges for the optimum modes of ZrN and ZrNbN coating deposition by vacuum arc plasma-assistance method are revealed. The parameters of gas-metal plasma at simultaneous functioning the different type plasma sources are measured.

1. Introduction
Vacuum arc deposition of coatings is a promising method of obtaining relatively thin (tens of nanometers – tens of micrometers) wear-resistant coatings. This method is characterized by high productivity, a wide range of operating parameters and environmental safety [1, 2]. The main problem of significantly increasing the mechanical, tribological and operational properties of the surface of materials and products, as well as increasing their service life, consists of the several scientific problems. They are (1) the generation of gas-metal plasma of arc low-pressure discharges at the combination of several plasma flows of different type, the research of its parameters and composition, the control of its parameters; (2) the development of a method for vacuum arc plasma-assisted deposition of functional coatings; (3) the study of structural, strength and tribological properties of the synthesized coatings.

One of the perspective types of the coatings for the increase of wear resistance and service life of a working surface of details, the tool and various products is zirconium nitride [3]. The coatings based on that have the increased hardness, high resistance to wear and corrosion [4, 5]. Therefore, the coatings are developed by scientists and take root into the industry as protective coatings [6, 7].

The aims of the present work were (1) the research of the service properties of the different type plasma sources used at ZrN and ZrNbN coatings; (2) the obtainment of the dependences of an ion current on a collector on the arc current of the plasma sources, on the pressure and on the composition of working gas under the wide ranges of parameters; (3) the revelation of the distribution of the metal and nitride coatings growth rate along the chamber radius at the use of filtering system of a plasma.
flow from droplet fraction; (4) the measurement of gas-metal plasma parameters by the probe technique; (5) the definition of the ranges of key parameters for the optimum modes of ZrN and ZrNbN coatings deposition by vacuum arc plasma-assisted method.

2. Material and research techniques

The experiments on the generation of gas-metal plasma for the formation of ZrN and ZrNbN coatings were carried out on the QUINTA automated vacuum ion-plasma installation (figure 1). The detailed description of the principle of its operation, the main devices and the examples of application are noted in the [8] article of this issue and in the [5]. For the generation of gas-metal plasma for the purpose of ZrN coatings formation a PINK-P gas plasma source based on non-self-sustained arc discharge with thermionic and hollow cathodes of an extended design [9]; DI80 standard arc evaporator [10] with magnetic filtration of plasma from droplet fraction in a curvilinear plasma-guide [11] were used. For the generation of gas-metal plasma for the aim of nanocrystalline ZrNbN coatings synthesis a PINK-P gas plasma source; the DI80 arc evaporator with magnetic filtration of plasma; the DI100 upgraded arc evaporator with the improved cooling of a back surface of the cathode [12] were used. The materials of the cathodes were zirconium alloy (E110; Zr–1 weight. Nb %) and niobium alloy (NbSh-00; 99.8 wt. Nb %). The diameter of the zirconium cathode was 80 mm, that of niobium – 100 mm.

Figure 1. The simplified scheme of the QUINTA ion-plasma installation with a diagnostic system: 1 – hollow cathode; 2 – thermionic cathodes; 3 – cylindrical collector; 4 – anode (chamber wall); 5 – the DI100 arc evaporator with the metallic cathode; 6 – Langmuir’s probe; 7 – the case of the magnetic filter, 8 – the DI80 arc evaporator with the metallic cathode.

The vacuum arc method of coating deposition has a disadvantage; these are macroparticles (the droplets of the melted metal with the sizes of ~ 0.1–10 μm) [1] which worsen the uniformity of plasma and synthesized coatings. The gas-metal plasma generated during the combined operation of plasma sources contained only an insignificant share of macroparticles for the following reasons: 1) the system of magnetic filtration allowed to eliminate a flow of zirconium plasma from droplets up to 100 %; 2) molybdenum alloy has high temperature of melting (2468°C) and cooling of the cathode at evaporation was improved due to the increase of the cooled surface square in the DI100 evaporator, therefore the quantity of macroparticles at evaporation of niobium cathode was a low; 3) the use of PINK-P generator allows to decrease of droplet fraction in the coating volume due to reflection of the macroparticles which are negatively charged to floating potential – (6–8 V) in the plasma of the gas
arc discharge \((T_e \approx 5–7 \text{ eV})\), from the specimen which is under negative potential \((U \sim -100 \text{ V})\) \cite{13, 14}.

The argon, nitrogen and their mixture in the different proportions were used as working gas. The pressure of gas mixture was equal to 0.2 Pa.

For the measurement of ion current density during the independent operation of the plasma sources with different construction the cylindrical collector from stainless steel with rather large area was used \((S_c = 130 \text{ cm}^2)\). The collector was located in the center of the working chamber at distance of 300 mm from the output aperture of the plasma sources (figure 1). The ion current on the collector \((I_c)\) was fixed by means of the milliamperemeter. The density of an ion current was calculated by the known formula:

\[
j = I_c/S_c. \tag{1}
\]

The distributions of Zr and ZrN coatings growth rate on the chamber radius without manipulator rotation were founded by the measurement of the thickness of the coatings synthesized in a single cycle of deposition in the different positions of vacuum chamber volume at \(I_{Zr} = 150 \text{ A}\). The distance between the next specimens was 5 cm. The coatings thickness was measured by the standardized Calotest method under the parameters of a spherical cross-section (Calotest CAT-S-0000).

One of the service properties of the arc evaporator is the cathode erosion rate. The evaporation of the cathode material was measured by weighing of the cathode before and after functioning of the arc discharge during the fixed time at the stabilized current. The erosion rate was calculated by the known formula:

\[
g = \Delta m/I_d t, \tag{2}
\]

where \(\Delta m\) – change of the cathode material mass, \(\mu g\); \(I_d\) – arc discharge current, \(A\); \(t\) – arc discharge burning duration, \(s\).

For a research of gas-metal plasma parameters the single cylindrical probe of Langmuir was used. The probe was made from a tungsten wire with a diameter of 0.8 mm and length of 11 mm. Through Wilson's input the probe was installed in the center of the chamber at the distance of 300 mm from an output aperture of DI80 and DI100 arc evaporators and a PINK-P source of gas plasma. The gas-metal plasma was investigated at independent and combined operation of the plasma sources with the different construction.

3. Results and discussion

In the figure 2 the dependences of ion current density on the collector for gas plasma source (PINK-P) and metal plasma sources (DI80 with the zirconium cathode, DI100 with the niobium cathode) in the different gas mixture on the arc current are presented. The dependences for plasma sources of a different design have linear character within an error for the chosen conditions of the experiments. From the figure 2 it is clear that the relation of ion current density of gas and metal components of gas-metal plasma \((j_p/j_d)\) can be changed in the wide range; that can be used for the synthesis of multilayered and gradient coatings based on Zr, Nb and their nitrides by quick-response vacuum arc plasma-assisted method.

However, the parameters of optimum operation of the plasma sources are limited to the range of currents for the stable burning of arc discharges on the cathodes from the chosen materials (Zr, Nb), to the construction features of the plasma sources and to the opportunities of the power supplies. For the DI80 source with Zr cathode this range is equal to \(I_d = 100–150 \text{ A}\); for DI100 with Nb cathode – \(I_d = (80–200) \text{ A}\), for PINK-P – \(I_p = (10–150) \text{ A}\).

From the obtained results of measurements in the stable modes of burning of arc discharge of different type the values of currents when the relation of ion current density of the gas and metal component of gas-metal plasma based on of Zr, Nb, nitrogen and argon are in the ranges \(j_p/j_d = (0–2.0); (0–4.0); (0–1.5)\) were revealed for the operation of DI80 and PINK-P; DI100 and PINK-P; DI80, DI100 and PINK-P in the argon, respectively; \(j_p/j_d = (0–2.3); (0–2.3); (0–1.1)\) in the nitrogen; for the mixture of Ar and N\(_2\) they have intermediate values.
Figure 2. The dependences of ion current density on the collector on arc discharge current for the plasma source with thermionic and hollow cathodes (1), for the DI100 arc evaporator with the niobium cathode (2) and for the DI80 arc evaporator with magnetic filtration of plasma flow with zirconium cathode (3). The parameters: $p_{\text{total}} = 0.2$ Pa; a) Ar; b) Ar/$N_2$, $p_{N_2} = 0.01$ Pa; c) Ar/$N_2$, $p_{N_2} = 0.04$ Pa; d) Ar/$N_2$, $p_{N_2} = 0.1$ Pa e) $N_2$. 
The maximum $j_p/j_d$ value is limited to extreme operation parameters of the plasma sources under the chosen configuration and the operating power supplies. It is established that the maximum values of the growth rate of a metal and nitride coatings (figure 3) are displaced concerning to the center of the chamber, these are located at the distance of 8 cm from it and equal to 9 and 11 $\mu$m h$^{-1}$, respectively. The growth rate decreases symmetrically from the maximum in the measurement error limits at increase of the distance on the radius. At distance of 12 cm from a maximum point the value of growth rate is less in 1.2 and 1.5 times, at distance of 60 cm that is less in 1.6 and 3.7 times, than its maximum value for Zr and ZrN coatings, respectively.

Based on obtained results, all probe researches and also coating synthesis were carried out in the areas where ion current density on a substrate and, respectively, coating growth rate are maximum.

Figure 3. The distribution of Zr and ZrN coatings growth rate on the radius of the vacuum chamber.

During ZrNbN coating deposition at simultaneous evaporation of two cathodes (Zr, Nb) with rotation of the manipulator the synthesized specimens were fixed in the two positions: 1) in the center of the working chamber; 2) in a satellite position, i.e. at distance of 15 cm from the center of the chamber. The average growth rate of ZrNbN coating in the first position was 4.5 $\mu$m h$^{-1}$, in the second position – 5.0 $\mu$m h$^{-1}$ at $I_{Zr} = 150$ A and $I_{Nb} = 100$ A. Also the growth rate of NbN coatings was measured, it was made in the both positions; the growth rate is equal to 1 $\mu$m h$^{-1}$ at $I_{Nb} = 100$ A.

For the cathode from zirconium alloy (Zr–1 wt. %Nb) with a diameter of 80 mm, where the arc burned for 3 and 24 hours at average arc current of $I_{Zr} = 147$ A and pressure of working gas of $p = 0.2$ Pa, the erosion rate was 52.0 and 52.8 $\mu$g C$^{-1}$, respectively. That corresponds to the values from references for the standard evaporator at the diameter cathode of 80 mm [15] within the error limits of measurement. For the cathode from niobium of NbSh-00 alloy (99.8 wt. Nb %) with Ø 100 mm the erosion rate was 30 $\mu$g C$^{-1}$ for 3 and 10 h burning of an arc at discharge current of 100 A. According to literary data [15] the erosion rate for the niobium cathode is 38 $\mu$g C$^{-1}$. Some discrepancies with literary data are connected with the features of the experiments.

The gas-metal plasma generated by combined functioning three plasma sources with different construction in the center of the chamber had following parameters ($I_{Zr} = 125$ A, $I_{ Nb} = 100$ A, $I_p = (30–150)$ A: electrons temperature of $T_e = 1.3–1.6$ eV, plasma potential of $\varphi_{pl} = 4.7–6.5$ V, plasma concentration of $n_e = (7.5–9.0)\times10^{10}$ cm$^{-3}$, floating potential of $\varphi_f = -(4.5–7.0)$ V.
4. Conclusion

It is revealed that it is rational to use the mixture of Ar and N$_2$ as the working gas with a ratio not below than 1:1, with the total pressure in the range of 0.2–0.4 Pa for the formation of the coatings based on Zr, Nb and their nitrides by a vacuum arc method with plasma assistance. Based on the results of measurement of ion current density and coating growth rate the positions of specimen where the growth rate of coatings based on Zr, Nb and their nitrides is maximum are chosen.

The parameters of gas-metal plasma are revealed during the work of the plasma sources of different type, including that at change of arc current of the PINK-P plasma source.

It is shown that simultaneous functioning of self-sustained arc discharges with integrated cold cathodes from zirconium and niobium alloys and the non-self-sustained arc discharge with thermionic and hollow cathodes allows to generate the gas-metal plasma with density of $\sim 10^{11}$ cm$^{-3}$, temperature of electrons $\approx 1.3$–1.6 eV at Ar-N$_2$ mixture pressure of $\sim 0.1$ Pa and at working values of arc current of the DI100 arc evaporator of 100 A and for DI80 – 125 A in vacuum volumes of $\geq 0.1$ m$^3$ for effective synthesis of the coatings based on Zr, Nb and their nitrides by vacuum arc plasma-assisted method.

The increase of arc current of the PINK-P gas plasma in the wide range 30–150 A leads to linear increase of ion current density and plasma concentration. It allows to obtain the conditions in gas-metal plasma when the ratio of ion current density of a gas and metal component of plasma will be equal to $j_p/j_d = 0$–2. That will allow deposit the single-, multilayered and also gradient coatings based on Zr, Nb and their nitrides at constants gas pressure and arc current of the arc evaporators. The arc current of PINK-P gas plasma source will be as the varied parameter.

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