A study of zirconium plasma flow generated by a vacuum arc evaporator

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Abstract. In the industry of hard coatings, the vacuum arc evaporator is one of the commonly used devices due to its high productivity, reliability and ability to operate in a non-gaseous medium. Apart from this, the imposition of an external magnetic field allows to control the localization of the arc spots both on the simple and sectioned (i.e. made from different materials) cathode surfaces. Another important feature of the vacuum arc evaporators is their capability to generate multi-charged ions. Applying a high voltage negative bias to the substrate, there can be formed the coatings with high adhesion due to the implantation effect. This paper presents some results of the study of the plasma flows generated by an industrial vacuum arc evaporator with a sectioned disk cathode composed of a zirconium in its central part with a titanium ring surrounding it. The mode of evaporator functioning is such that the arc spot motion gets limited by the zirconium disk, which results in producing the zirconium plasma flow. The quantitative characteristics and the energy distribution function of ions have been measured by a multigrid probe with a retarding potential. It has been proved that the multiply charged ions make up a significant part of the flow. The relations between the detected ion components are found as 87.4% Zr⁺, 10.6% Zr²⁺, 1.5% Zr³⁺ and 0.3% Zr⁴⁺. The presence of multi-charged ions is also confirmed by optical spectrometry measurements.

1. Introduction

In a cold-cathode vacuum arc evaporator, the discharge arises in cathode spots that spontaneously move along the cathode surface. The spot current density runs into a very high value of 10¹² A/m² at an average discharge current in the range of 50 A to 500 A and a relatively low discharge voltage of 16 V to 40 V [1,2]. It is important to note that the growth of the discharge current leads to an increase in the number of cathode spots, without affecting the processes occurring in each individual spot [3,4]. The power released in the spot of more than 10¹² W/m² is enough to start the evaporation process in an explosive mode which produces a sufficient amount of cathode material vapor to burn the arc discharge in the self-sustained regime. The explosive production of a vapor plasma flow in a high ionization state provides very high film growth rates on the substrate. The presence of the ion component in the flow makes it possible to control the structure formation of the growing film by applying a controlled negative potential to the substrate [5,6]. In addition, on the stage of the initial film formation the ions are implanted into the substrate, providing a high adhesion of the growing film [7,8]. In the latter case, multiply charged ions are of the greatest interest, since their mean projective range is enough to create an interface zone of hundreds of atomic layers [9].

Such materials as titanium, aluminum, zirconium, hafnium, chromium are the basis for modern industrial coatings due to the attractive properties of their nitride compounds which can be obtained in
the process of evaporation in the nitrogen atmosphere [4]. The application of the evaporators of this type in the regime of impulse reactive gas supplying and with sectioned cathodes allows creating unique multi-component and multilayer coatings [10-12]. The ion composition of vapor flows generated by cathode spots on the surface of a zirconium cathode is of primary interest of the present article.

2. Experimental set
The work was carried out on the “MÓdificador de Superficies METálicas (MOSMET)” reactor [13] at the residual pressure better than 1 mPa provided by a turbomolecular pump. An arc evaporator with a sectioned cathode of a diameter of 198 mm whose central disc of a diameter of 80 mm is made from zirconium. The evaporator placed on the upper flange of the vacuum chamber is equipped with a magnetic system which permits to locate the motion of the cathode spots within the central disc of the cathode (see Figure 1(a)).

![Figure 1](image1.jpg)

Figure 1. Scheme of the experiment: (a) placing the ion probe in a vacuum chamber; (b) sketch of the probe with a collimator.

The voltage-amperage dependence of the vacuum arc discharge is presented in Figure 2. The parameters of the cathode plasma flow generated at the operating current of 167.0±3.4 A and the voltage of 20.3±1.2 V were examined. It should be noted that the instantaneous values of current and voltage, measured with a response time better than 0.5 µs, are characterized by a large scattering with the growing peak current tendency when the peak voltage applied to the discharge is increased. Apparently, this can be associated with the peculiarity of the functioning of the power supply. The entire field deviations are presented for the studied operating conditions in the same Figure 2 through grey dots.

![Figure 2](image2.jpg)

Figure 2. Voltage-amperage dependence of a vacuum arc discharge at the operating conditions of 20.3 V at 167 A. The grey dots present the field of deviation.
At these operating conditions, the arc evaporator provides a high film growth rate. The distribution of the cathode material flow on the substrate disc surface at different distances from the cathode is presented in Figure 3(a). The film thickness measurements were fulfilled by determining the thickness of the thin film that is fabricated by the “step” method: a part of the substrate was masked, and the film heights between the film and the substrate surface after each deposition session were measured by using an interference microscope. The results are shown in Figure 3(b).

The energy spectrum of the ion flow is measured by using a three-grid electrostatic probe [14] which is placed at the distance of 20 cm from the cathode (Figure 1(a)). The ion retarding potential is applied to the disk collector whose current is recorded. The repelling grid which is mounted in front of the collector must be maintained under a negative potential of $-50$ V to withdraw the electrons from the flow that evidences a high-level electron temperature of 15 eV to 20 eV in the plasma flow. The probe body and input grid are at the potential of the grounded anode.

![Figure 3. Spatial distribution of the flow of cathode material in the volume of vacuum camera: (a) thin film growing rate; (b) interferogram of thin film coating with a step provoked by mask.](image)

The analyzing saw-like potential on the collector is synchronized with the ion current entering the collector in order to determine the energetic composition of the incoming flow. For this purpose, the scheme with a high-speed comparator of 10 ns response time is used. The scheme turns on the increasing potential of the controlled duration and amplitude when the predetermined value of the incoming ion current is exceeded.

The solid angle of entrance which determines the flow portion incident onto the collector is defined by the probe geometry and the outer collimator sizes, its scheme being presented in Figure 1(b). In our case, the probe–collimator system provides the ion flow reach from a cathode surface zone with a diameter not larger than 20 mm. This geometry makes it possible to select a zone on the sectioned titanium–zirconium cathode for the ion energy spectral analysis. Obviously, the ion flow enters the probe only when the arc spot passes through the selected zone. The ion current “burst” of 2 ms to 4 ms long is observed under a close to zero collector’s potential, as shown at Figure 4(a). Figure 4(b) and Figure 4(c) give the structural scheme for pulse measurements of the ion energy and a typical ion current vs. an analyzing potential signal.

An analyzing collector voltage of about 1.5 ms duration is used to measure the retarding characteristics. To obtain more accurate ion energy spectrum data, the probe total ion current is kept unchanged during the measurement process. It is complicated to meet this requirement in the case of the vacuum arc flow because it is not easy to predict the rise or drop of the burst current. To make an energetic analysis of the ion flow possible, the retarding potential curves are selected as follows: the
amplitudes of the input ion current before and after the analyzing potential application are made to be approximately equal. The energetic analysis of the ion flow is fulfilled in accordance with the standard technique through the program module ProbeDAM [14].

![Diagram](a) (b) (c)

**Figure 4.** Ion probe measurement scheme and signals: (a) ion current signal on a collector shunt at a zero analyzing potential; (b) the structural scheme for pulse measurements; (c) typical retarding signal at a saw-like analyzing potential.

The charge composition of the ionized flow is also found with the help of the optical diagnostics. To keep a record of the optical spectrum, an Ocean Optics HR4000 spectrophotometer with a fiber-optics enclosed in a protecting copper tube is used. The tube-fiber system is directed towards the cathode that permits to recollect optical information from a circle area with a diameter of 10 mm. The spectrophotometer is operated in the 100 ms accumulation regime which guarantees an acquisition of signals from numerous cathode spots.

### 3. Results

The energetic ion spectra measured by the probe differ rather widely from “burst” to “burst”, as illustrated in Figure 5. But all these measurements share the fact that the main fraction of ions has the energy which corresponds to the cathode voltage that is maintained during the “burst”. Each curve represents the ion distribution for the fluxes arriving at the probe collector within each “burst” at an analyzing potential duration of 1.5 ms.

![Graph](Graph)

**Figure 5.** Normalized ion energy distribution for four different “bursts”.

The scatter in the main peak ion energies position is like a cathode voltage dispersion of 18 V to 26 V. This dependence stresses the fact that the leading role in the ion acceleration belongs to the cathode drop and not to the explosion emission processes in the spots. The principal ion fraction is formed close to the cathode surface and is accelerated when passing the entire cathode drop zone. In addition, all spectra are characterized by the presence of the energetic peaks that are observed in both the “low energy” (the left-hand) and “high energy” (the right-hand) regions determined with the reference to the main peak position. In the low-energy region, an ion fraction of (12 eV to 16 eV) energy can be
distinguished, meanwhile the “threshold fraction” with energies close to the ionization potential (6.84 eV for zirconium) is not always well manifested.

The high-energy peaks are characterized by the multiple-fold (from 2 to 4) energies of the principal ion fraction that can be associated uniquely with the multiple ionization of ions. These ions come into being in the vicinity of the cathode surface and are accelerated in the cathode drop zone. An ion fraction of about 30 eV is clearly observed but its origin remains unclear. One can assume that they are two-fold ionized ions of the “low-energy” fraction (12 eV to 16 eV) but its amplitude is frequently of the same order or even higher than that of the low-energy fraction that takes place in very high dense plasmas. On the other hand, the bursts with the powerful low-energy fraction do not have ions of energy of 40 eV in their compositions as presented in Figure 5.

The average retarding curve (Figure 6(a)) is based on the analysis of 150 ion current “bursts” by ProbeDAM software. The average energy distribution function (Figure 6(b)) shows that the principal ion fraction is characterized by the energy close to the average cathode voltage of 20.3 V and the multiple-fold peaks correspond to the accelerated fractions of double-, triple- and four times ionized zirconium atoms. The part of curve up to 90 eV which is associated with the multicharged ions is under study.

To estimate the relation between concentrations of different charge ions, the experimental energy distribution function is fitted by the amplitude version of Gaussian peak function. The distribution function is well approximated by four Gaussian peaks. The main peak corresponds to the single charged ions of energy of 21.3 eV that is close to the discharge voltage and cathode drop. The maximum value of the second peak of 44.3 eV is two-fold of the first peak. This fact can be accounted for by the above-mentioned peculiarity of the power supply operation. The deviation of the third of 64 eV and forth of 80 eV peaks from the multiplicity values of 21.3 eV can be attributed to a high statistical error while recording the weak signals. It is important to stress that the peak width is diminished from 9.4 eV for the single charged ions to 3.5 eV for four times-charged ions, thus indicating that the multicharged ions are generated in a thin layer in the vicinity of the cathode surface.

![Energy distribution of Zr plasma flow](image)

**Figure 6.** Energy distribution of Zr plasma flow: (a) average retarding curve treated by ProbeDAM software; (b) normalized ion energy distribution and distributions fitted by four peaks Gaussian function ($E_n$ - the mean energy value, $A_n$ - normalized area under fitting curve, $W_n$ – standard deviation).

The areas under the normalized Gaussian peaks, shown in Figure 6(b), corresponding to the ion quantity. For the first peak, the discrepancy with a real distribution at the energies smaller than 10 eV is corrected. Thus, the zirconium plasma flow of the cathode arc is comprised of 87.4% Zr$, 10.6%$ Zr$^2$, 1.5% Zr$^3$ and 0.3% Zr$^4$. 

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Multi-charged zirconium ions have enough high-intensity spectral lines that can easily be identified in the spectrum [15]. The obtained spectrum is presented in Figure 7 where the multicharged ion lines are clearly shown.

4. Conclusion
It is demonstrated that the arc discharge generates not only dense plasmas but also multi-charged ions with an amount of more than 10%. An energy analysis revealed that the composition of the plasma flows coming from each cathode spot can be very different from the average, both in the direction of the presence of a larger fraction of high-energy ions and in the complete absence of ions with energy above the cathode voltage.

The presence of a noticeable fraction (more than 0.3%) of four-charged ions is reliably detected by both the retard potential probe method and optical measurements.

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