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An interpretation involving atoms and charge exchange collisions

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Time-dependence of ion charge state distributions of vacuum arcs: An interpretation involving atoms and charge exchange collisions

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Abstract

Experimentally observed charge state distributions are known to be higher at the beginning of each arc discharge. Up to know, this has been attributed to cathode surface effects in terms of changes of temperature, chemical composition and spot mode. Here it is shown that the initial decay of charge states of cathodic arc plasmas may at least in part due to charge exchange collisions of ions with neutrals that gradually fill the discharge volume. Sources of neutrals may include evaporated atoms from macroparticles and still-hot craters of previously active arc spots. More importantly, atoms are also produced by energetic condensation of the cathodic arc plasma. Self-sputtering is significant when ions impact with near-normal angle of incidence, and ions have low sticking probability when impacting at oblique angle of incidence. Estimates show that the characteristic time for filling the near-cathode discharge volume agrees well with the charge state decay time, and the likelihood of charge exchange is reasonably large to be taken into account.

I. INTRODUCTION

Over the last decade, much progress has been made in characterizing cathodic vacuum arc plasmas. For example, detailed, material-dependent information is now available on ion velocity and charge state distributions (CSDs) [1-3].

It is understood that plasma is primarily formed in microscopic explosive events at the cathode surface [4]. Non-stationary cathode spots are centers of plasma production. The power density fluctuates and can reach peak values up to 10^{13} W/m^2. Higher currents (e.g. > 100 A) imply the existence of several, simultaneously active spots. Cathode spots are dissipative structures showing self-organization and fractal properties such as self-similarity (to be further discussed in a separate publication). Plasma parameters are generally obtained by averaging over many individual measurements. While momentary values and distributions show large and fast fluctuations, tendencies and rules can be found for *averaged* values. The evolution of velocities and CSDs are considered in the sense of being averaged over many repeated measurements.

Ion charge states are enhanced at the beginning of each arc discharge [5-7]. The charge state distribution for a given cathode material settles to an approximate steady-state distribution within 100-300 μs after arc initiation (again: a steady-state of *averaged* values is considered, as mentioned above). Up to now, the effect of initial enhancement was attributed to a number of possible reasons, including change of the surface state of the cathode due to erosion by the cathode spot, heating of the cathode surface, plasma-cathode interaction, and initially greater specific energy input in the plasma. Although there is still an ongoing debate about relevant characteristic times of cathode processes, there is no doubt that the observed characteristic times for reaching steady-state of averaged charge state distributions (100-300 μs) exceed characteristic cathode spot times by at least two orders of magnitude. Therefore, individual spot processes cannot be responsible for the much slower changes.

In this contribution, effects are considered that could shift charge state distributions via charge exchange collisions with neutral atoms. These effects may contribute to, or even dominate, the observed shifting of CSDs.

II. TYPICAL MEASUREMENTS OF ION CHARGE STATE DISTRIBUTIONS

In all experimental setups used for the determination of ion charge state distributions, the plasma expanded on its way from the cathode spot region to the location of the detector. In some experiments, the detector was a quadrupol mass spectrometer, and in most other experiments a vacuum arc ion source in combination with a time-of-flight charge-to-mass spectrometer was used. The extraction grid represents the detector location in the above sense. The typical size of the cathode-detector distance was of order $s \approx 0.1\,\mathrm{m}$ (Fig.1).

The expanding plasma has a typical velocity of 10^4 m/s (a compilation of material-dependent, average ion velocity values can be found in Ref. [3], for example). The plasma will arrive at the grid and other surfaces at the time $t_0 \approx s / v_{pl} \sim 10^{-5}\,\mathrm{s}$ after arc initiation. This is the time when charge state measurements begin.

The initial charge state distributions are produced at and near the cathode spot. To stress it gain: the actual source distributions are rapidly fluctuating, and the evolution of an averaged distribution is considered. Because the plasma is expanding and streaming from the spot, the ion charge states are transported with increasingly less change to the detector. Considering a volume element of drifting and expanding plasma, moving with a frame of reference attached to the mass center of the volume element, one may define the local characteristic expansion frequency as

$$f_{\exp}\left(r\right)=\left|\frac{\partial n\left(r\right)}{\partial t}\right|\Big/ n\left(r\right), \tag{1}$$

where both the density gradient $\left|\partial n/\partial t\right|$ and the density n are local variables. The charge state distribution is said to be "frozen" when inelastic (ionizing and recombining) collisions become much less frequent than the characteristic expansion frequency. In the absence of an external magnetic field or background gas, "freezing" occurs very close to the spot, at distances of order 100 μm [8]. Note that the "freezing" criterion refers to a ratio of characteristic times or frequencies and not, as sometimes simplified and misinterpreted, to the complete absence of inelastic collisions. That is, some changes in the distribution will occur while the plasma is expanding but the actual local distribution will increasingly differ from the equilibrium (Saha) distribution that corresponds to the local electron density and temperature. In a simplified freezing model, though, one may assume that the ratios of charge states do not significantly change as the plasma expands, and under this condition one may use measured charge state ratios to determine plasma parameters in the freezing zone [9].

It should be stressed that the freezing model is powerful but has its limits, as all models do. Freezing does not exactly simultaneously occur for all charge states but highly charged ions tend to be earlier detached from equilibrium. This concept led to the refined model of Local Partial Saha Equilibrium [10]. Freezing models cannot be applied when background gases are introduced, or an external magnetic field is present, or the discharge is of very high current (> 1 kA) such that expansion is hindered by the magnetic self-field. Charge state measurements are useful for applications in all cases but should not be used for spot parameter determination unless the assumption of freezing can be justified.

III. NEUTRALS IN CATHODIC VACUUM ARC PLASMA

The amount of neutrals directly produced in explosive plasma formation was calculated to be negligibly small [9]. This result is associated with the argument that the observed charge state distributions peak in most cases at +2 or even greater charge state. However, there are four possible sources of neutrals in a cathodic arc system: (i) evaporating macroparticles [11], (ii) vapor from cooling, yet still-hot craters of previously active cathode spots [12], (iii) neutrals formed by recombining ions, and finally (iv) the contribution of self-sputtering [13] and, in case of oblique angle condensation, low sticking of condensing ions. Because the contribution of atoms evaporated from craters and macroparticles is unknown but estimated small, and volume recombination is insignificant, the discussion in this contribution focuses on neutrals produced as a by-product of energetic condensation via self-sputtering (near-normal incidence) and limited sticking (oblique angle condensation).

The sticking probability is defined as the probability that the incident ion remains bound to the solid, and the sputter yield is defined as the number of surface atoms ejected per incident ion. One speaks of self-sputtering when impacting ion and removed atom are of the same kind, for example, when a copper ion sputters a copper atom from the surface. The sticking probability at normal incidence is close to unity because ions of cathodic vacuum plasmas have sufficient kinetic energy to displace near-surface atoms and come to rest in the sub-surface region. Summarizing the results of molecular dynamics simulation for self-sputtering and sticking probability in the relevant energy range [14-17], one may consider the generic energy and angle dependences shown in Figures 2(a) and (b).

The expanding plasma will condense on walls and the extraction grid facing the plasma flow. For the purpose of further discussion, one may distinguish three plasma condensation zones: (A) the anode, (B) the walls of the chamber, and (C) the extraction grid or a similar detector surface (Fig.1). For simplicity we initially focus on zone (C) because the plasma impacts the surface of zone (C) with near-normal angle, and therefore the assumptions can be made that sticking is close to unity while self-sputtering may be significant (Fig. 2), which is supported by recent experiments [13].

IV. A CONSEQUENCE OF THE PRESENCE OF NEUTRAL ATOMS: CHARGE EXCHANGE COLLISIONS

The flux of neutrals will gradually fill the space between grid and arc cathode. The velocity of sputtered atoms is much slower than the velocity of ions coming from the cathode. The characteristic time will be

$$t_{a1} \approx s/v_a \tag{2}$$

assuming that sputtered neutrals move essentially without collisions, i.e. when their mean free path is large compared to the characteristic length, *s*. In the opposite case, neutrals suffer collisions, and diffusion will be the dominant transport mechanism, having the characteristic time

$$t_{a2} \approx s^2 / D_a \,, \tag{3}$$

where D_a is the diffusion coefficient. In evaluating (3), interaction of neutrals with each other and with ions needs to be considered. Because (2) describes a faster effect, we will focus on it.

The interaction of neutral atoms with ions of the plasma stream is dominated by charge exchange collisions. Charge exchange can generally be written as:

$$Me^{n+} + Me \Rightarrow Me^{(n-1)+} + Me^{+}, \;\; n = 1,2,3,\ldots \tag{4}$$

where Me^{n+} stands for the n-fold charged metal ion. We see that charge exchange reactions will lead to ionization of evaporated and self-sputtered atoms and to a reduction of highly charged ions. Therefore, even as total charge is conserved in individual collisions of type (4), the average charge state number is not conserved because previously neutral particles will now be included in the averaging. Neutral particles are conventionally not included in the averaging procedure mainly for practicality reasons, i.e., because the concentration of neutrals is not known. For example, time-of-flight measurements use electric signals and therefore detect ions but not neutrals.

V. AN ESTIMATE OF FILLING AND CHARGE STATE EQUILIBRIUM TIMES

Evaporated atoms from macroparticles and still-hot cathode craters are much slower than sputtered atoms; their kinetic energy corresponds to the temperature of the evaporating surface. The filling of the discharge volume with evaporated atoms is therefore much slower than the filling with self-sputter atoms. As the vacuum arc plasma condenses, self-sputtering will occur and the volume between surface "C" and cathode will gradually be filled with self-sputtered atoms. The fastest filling process is given by the time (2), and we will focus on this fastest of neutrals-based effects.

From many works in sputtering it is known that the energy of sputtered atoms is about 1/100 of the average ion energy. Since the velocity-energy relationship is $v : \sqrt{E_{kin}}$, the velocity of self-sputtered atoms is about 1/10 of the ion velocity, corresponding to ion and atom velocities of typically 10^4 m/s and 10^3 m/s, respectively. With an expansion length ~ 0.1 m in most previous experiments, the characteristic time t_{a1} is of order 100 μs, which is at the low end, yet in the right order of magnitude of observed times for establishing a steady-state (averaged) ion charge state distribution. Most experimental characteristic times for establishing steady-state charge state distribution functions are somewhat longer, which is consistent with the consideration of the fastest processes leading to filling of the discharge volume with atoms.

VI. ESTIMATE OF THE MEAN FREE PATH

After the time constant has been determined to be in the right order of magnitude, the relevance of ion-atom interaction must also be discussed, revealing the likelihood that an ion of the plasma flow interacts with a neutral atom before it arrives at the detector or chamber wall. The mean free path,

$$\lambda_{Qa} = \left(n_a \sigma_{Qa}\right)^{-1}, \qquad (5)$$

is determined be the density of targets (i.e. atoms) and the ion-atom collision cross section. The latter is dominated by charge exchange collisions, as mentioned above. The cross sections for charge exchange reactions (4) depend on the internal energy defect, ΔE, which is the difference in potential energies (ionization, excitation energy) between pre-collision and after-collision particles. If the energy defect is negative, $\Delta E < 0$, the cross section is negligibly small. Charge exchange with n = 1 has zero energy defect and its cross section is very large. This reaction, generally known as resonant charge exchange, creates fast neutrals and slow singly charged ions, though the number of singly charged ions is not changed. Because the energy defect is zero, resonant charge exchange is an elastic collision by definition; all other charge exchange reactions are inelastic. For higher charged ions, n > 1, the energy defect is positive because the colliding partners are of the same kind and the ionization energy generally increases with charge state.

For positive energy defect, the cross section depends only slightly on the ion charge state and relative velocity of colliding particles (essentially, that is the ion velocity in the laboratory frame), see, for example [18]. According to data from Smirnov [19], the cross section is $(1-4)\times 10^{-18}$ m^{-2} for a wide range of materials and relevant energies.

The density of self-sputtered atoms will depend on the kind of metal and on the impact energy. Recent experiments for Zr and Au cathodic arc plasma indicated a self-sputter yield of about $\gamma \approx 0.05$ in the absence of bias [13]. The flux of self-sputtered atoms from the surface is

$$n_a v_a = \gamma n_i v_i \,. \tag{6}$$

The density of arc plasma ions can be estimated by Jüttner's formula [20]

$$n_i \approx C \frac{I_{arc}}{s^2} \tag{7}$$

where C is a constant (for copper and similar materials, $C \approx 10^{13}$ A^{-1}m^{-1}), and I_{arc} is the arc current, which was typically 100-300 A in many experiments. The ratio of the characteristic length of the discharge volume and mean free path can be regarded as the collisionality or the non-normalized collision probability:

$$P = s/\lambda_{Qa} \, . \tag{8}$$

Using Eqs.(5)-(8) one arrives at

$$P = \sigma_{Qa} C I_{arc} \gamma \frac{v_i}{s \, v_a} \, , \tag{9}$$

giving numerically about $P \approx (1-10)\%$. This means that a great majority of ions will arrive at the detector or wall without charge exchange collisions, however, a noticeable fraction will undergo collisions caused by the neutrals originating from self-sputtering on the surface of zone (C).

The greatest effect should be expected for the most highly charged ions because the collision will de-populate the highest charge stage present in the plasma while singly charged ions and ions of the next lower charge state are created. The estimate has a large uncertainty because the parameters entering (9) can vary from experiment to experiment.

VII. DISCUSSION AND CONCLUSION

Reactions (4) require the presence of neutral atoms. Initially, there are only very few neutrals in the discharge volume, and therefore one may suspect and argue that the charge state distribution measured at the beginning of an arc discharge represents the "true" distribution as emitted by the explosive spot processes, while any distribution measured at later times is "skewed" to lower charges states by the increasing presence of atoms causing charge-exchange collisions. After some time, when the concentration of neutrals has reached its steady-state value, the detector will see lower, "skewed" distributions. This thought is the core of the here-presented alternative interpretation of time-dependence of averaged ion charge state distributions.

By discussing only the contribution of zone (C) to the generation of neutrals, the magnitude of the effect is underestimated. Zones (A) and (B) will contribute in a similar manner, though more difficult to deal with due a rather complicated geometry and variation of impact angles. Roughly, one may estimate that energetic condensation on the anode and the chamber wall contribute with at least similar magnitude, which is due to low sticking probability at ion impact angles off the surface normal. The collision probability (8) is hence increased beyond the previously estimated $P \approx (1-10)\%$.

The estimates of characteristic times and mean free path have shown that the experimentally observed decay of the average charge state of cathodic arc plasma may at least in part due to charge exchange reactions of ions with neutrals that gradually fill the discharge volume. As sources of neutrals one can identify evaporated atoms from macroparticles and still-hot craters of previously active arc spots, as well as non-sticking ions (turned into neutrals upon impact on the surface) and self-sputtered atoms produced in energetic condensation of cathodic arc plasma. More detailed experiments and simulation are needed to confirm the relevance of charge exchange collisions.

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Figure Captions

Fig. 1 Schematic of a typical setup for ion charge state measurements using the time-of-flight method. A cathode spot on the cathode surface is the source of streaming plasma. Part of the plasma propagates beyond the anode and is used for analysis. For the sake of discussion, the surface areas of plasma condensation can be split into three regions: the anode region "A," the walls of the plasma expansion chamber "B," and the plasma-facing detector or extractor grid "C."

Fig.2 Generic dependence of self-sputter yield (a) and sticking probability (b) in energetic condensation as a function of angle of incidence with respect to the surface normal. The values are examples for Ni calculated by molecular dynamics simulation [17]; other simulations give approximately the same shape and similar numerical values.

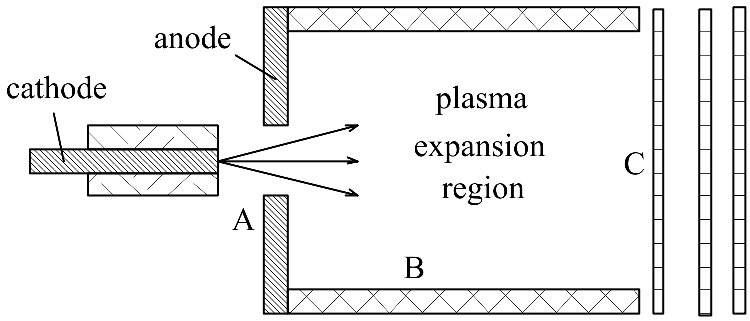


Fig. 1

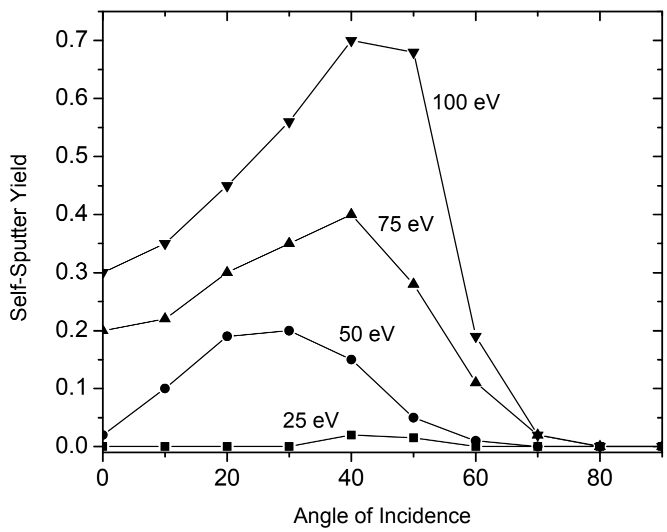
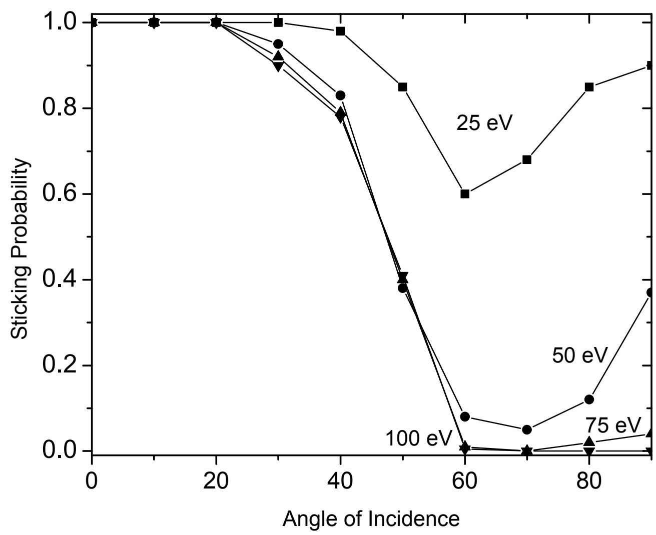

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Self-Sputter Yield
100 eV
75 eV
50 eV
25 eV
0
20
40
60
80
Angle of Incidence

FIG. 2 (a)



1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Sticking Probability
Angle of Incidence
25 eV
50 eV
75 eV
100 eV

Fig. 2(b)