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Puzzling differences in bismuth and lead plasmas: evidence for the significant role of neutrals in cathodic vacuum arcs

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Abstract

Time-dependent ion charge state measurements for Pb and Bi cathodic arc plasmas revealed unexpected differences: the mean Bi ion charge state dropped much stronger and with a longer time constant. It is shown that the differences in thermal conductivity and vapor pressure led to much higher neutral density for Bi, which in turn can cause charge exchange collisions. The results have implications beyond Pb and Bi plasmas: most importantly, they imply that the "true" ion charge states, as emitted from the cathode spots, are higher than what is generally measured and published.

Cathodic vacuum arc plasmas are generally considered to be fully ionized, with the mean ion charge state numbers exceeding unity for almost all cathode materials.[1-4] For example, the mean ion charge state numbers for Pb and Bi are 1.64 and 1.17, respectively, measured about 200 µs after arc initiation for 100 A arc current.[5] Saha charge state calculations and consideration of the transition to non-equilibrium showed that the arc spot plasma contains only very small amounts of neutrals for practically all cathode materials.[6] However, it also known that neutrals may be produced from sources other than cathode spots. Among the possible sources of neutrals are (i) evaporating macroparticles, (ii) evaporation from the hot surface of cathode craters produced by previously active cathode spots, (iii) singly charged ions recombining with an electron, and (iv) the condensing arc plasma itself, because non-sticking and self-sputtering produce neutrals that "bounce back" into the plasma volume. In a recent contribution[7] it was suggested that the characteristic time of filling the plasma volume with neutrals could explain the characteristic time of reducing the observed ion charge states after arc initiation. It was stressed that the source (iv) should be applicable to all arc plasmas. However, little direct evidence for the existence of neutrals and the evolution of its density was provided. The ion-to-neutral ratio is notoriously difficult to measure because equipment such as time-of-flight or quadrupole spectrometers are based on detectors for charged ions, not neutrals. One could use an ionizing stage for neutrals such as a radio-frequency section of a plasma analyzer, however, its ionization efficiency is much less than unity and depends on the atomic species.

In this contribution, we report about the initially puzzling observation that lead and bismuth arc plasmas behave quite differently although most physical and chemical parameters are very similar. We will show here that Bi plasma is likely to contain much

higher concentration of neutrals than Pb plasma, in strong support of the understanding that the ion charge state distribution, as emitted from an active cathode spot, is significantly higher than observed some time after arc ignition.

The experiments were performed at the upgraded vacuum arc ion source "Mevva V"[3] which operates with arc pulses of 250 μs duration (full-width-at half-maximum of the rectangular-like shape), now up to 10 pulses per second, and with a typical arc current of 300 A. The cathode was a ¼ inch (6.25 mm) diameter rod of 30 mm length inserted in an alumina ceramic such that the cathode spots can only exist on the rod's circular front face. An annular anode of inner diameter ½ inch (12.5 mm) is positioned about 1 cm from the cathode. The plasma expands through the anode opening into vacuum for about 10 cm until it reaches a multi-aperture, three-grid extractor of the acceleration-deceleration type.[8] The ion extractor is part of the time-of-flight (TOF) mass/charge spectrometer.[9] The suppressor voltage (center grid) was -2 kV, the extractor voltage was 40 kV, the TOF gate pulse about 200 ns, and the distance between TOF gate and magnetically suppressed Faraday cup was 1.03 m. The whole system was cryogenically pumped to a base pressure of less than 10^{-4} Pa. No gas was added during arc operation.

By controlling the delay of the TOF gate pulse with respect to the arc pulse initiation, the evolution of the charge state distribution can be mapped. The arc is generally "noisy," i.e., each arc plasma parameter fluctuates, which is due to the explosive[10] and fractal[11] character of cathode spots. All data were recorded by a digital storage oscilloscope (Tektronix TDS744); and the reported data are averaged over 32 individual measurements.

The result of charge state measurements for Pb and Bi are shown in Fig. 1. A number of different elements have been investigated[12] but here we report specifically about the

puzzling data for lead and bismuth because they will most strikingly illustrate the role of neutrals in cathodic arc plasma. As we can see, no steady-state of the ion charge state distribution is obtained by the end of the arc pulse, rather, the higher charge states drop rapidly while the charge state 1 is increasing. The mean ion charge states drop throughout the pulse without reaching their final values. The decay of the mean charge states, $\overline{Q}(t)$, can be well fitted with a first-order exponential function of the form

$$\overline{Q}(t) = C\exp(-t/\tau) + \overline{Q}_{ss} \tag{1}$$

where C is a factor that describes the relevance of the decay, τ is the characteristic decay time, and $\overline{Q}_{ss}$ is the steady-state average charge state number. The very different fit parameters for Pb and Bi are given in Table I. Note that the extrapolated early mean ion charge states, $\overline{Q}(t \rightarrow 0)$, are 2.22 and 2.56 for Pb and Bi, respectively, which are much higher than the generally reported $\overline{Q}$ values.

It was proposed[7] that the long characteristic times (long compared to spot processes) for the establishment of steady state are due to the evolution of the neutral atom density and the effect of the neutrals on ions via charge exchange collisions

$$M^{Q+} + M \rightarrow M^{(Q-1)+} + M^{+}, \tag{2}$$

where M^{Q+} stands for a Q-fold ionized metal ion. If that was true, the Bi arc must have a much higher neutral density than Pb because the experimentally observed drop of the mean charge state of Bi is much more pronounced than that of Pb. This hypothesis initially appeared puzzling because most of the physical properties of Pb and Bi are very similar (Table II).

In the work[7] emphasis was put on the universal neutral source (iv), i.e., the fact that not all ions stick to the surface upon arrival, and that significant self-sputtering should be expected in the energetic condensation process. Monte Carlo simulation[13] using the binary collision approximation with the universal ZBL potential showed that a significant amount of neutrals can be produced, however, this source cannot explain the differences seen in Fig. 1, quite contrary, Pb produced slightly *more* neutrals this way. Therefore, the other sources of neutrals deserve closer examination.

The most striking difference between Pb and Bi is the much lower electrical and thermal conductivity of Bi, which is due to the electronic structure and different crystalline phases: Pb is cubic phase centered whereas bismuth is rhombohedral. The consequences are clear: (a) the higher electrical resistance of Bi for the same arc current will lead to stronger ohmic heating of the Bi cathode bulk, and (b) the lower thermal conductivity of the Bi cathode will lead to reduced heat removal from the Bi cathode surface of the energy dissipated by the arc spot action.

Taking the cylindrical geometry of the cathode rod, the given electrical resistivity, and an arc current of 300 A we can readily determine that the ohmic heating in the cathode is about 115 W for Bi and only 19 W for Pb, hence, the electrical conductivity effect is negligible for both Bi and Pb.

To estimate the effect of heat conductivity and surface heating by the plasma on evaporation, we may consider the simplified heat conduction equation to determine an approximate surface temperature[14]

$$T_S(t) \approx T_S(t=0) + \frac{2P_S}{\sqrt{K\rho c_p \pi}}\sqrt{t} \ , \tag{3}$$

where P_S is the surface power density, K is the thermal conductivity, ρ is the density, and c_p is the specific heat (assumed to be a constant pressure). For the surface power density we can estimate that about 1/3 of the dissipated power is brought to the cathode,[15] heating an area A, and hence

$$P_S \approx \frac{1}{3} \frac{V_{arc} I_{arc}}{A} \qquad (4)$$

where $I_{arc} = 300\ \text{A}$, and the other parameters are given in Table II, including V_{arc}, the arc burning voltage.[16] If we consider the entire cathode surface, $A = \pi r_c^2$ with $r_c = 3.12\ \text{mm}$, we obtain a surface temperature that is substantially greater for Bi (Fig. 2). Plugging the temperature in a fourth-order polynomial fit for the logarithm of the temperature-dependent equilibrium vapor pressure,[17] $p^*(T)$, we obtain much higher values of p^* for Bi than Pb (Fig. 2). The equilibrium vapor pressure determines the flux of evaporated atoms according to the Hertz-Knudsen equation

$$\Gamma_a = \frac{1}{A} \frac{dN_a}{dt} = \alpha \left(2\pi m_a kT\right)^{-1/2} \left(p^* - p_a\right) \qquad (5)$$

where p_a is the hydrostatic gas pressure acting on the evaporant in the condensed phase, k is the Boltzmann constant, m_a is the mass of the atom, and α is the vapor accommodation coefficient (which could be set to unity for estimates).

The point of the above estimate, however, can only be to show that one should expect much higher production of Bi neutrals than Pb neutrals. The choice of the entire cathode area does not reflect the physical processes that actually occur at cathode spots. When choosing a much smaller area for the power dissipation in Eq.(4), e.g. an area corresponding

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to the typical crater size, the surface temperature exceeds the boiling temperature in nanoseconds, which is indicative of the nonstationary spot processes.

To model vapor production from crater-sized areas, much more sophisticated considerations are needed that take into account the local time-dependent energy balance, including evaporation and radiation cooling, and the thermophysical properties of solid and liquid phases. This has been done by Prock for cater formation[18] and crater cooling.[19] Considering Cu and W cathodes, he showed that the crater cooling time is typically ten times greater than the crater formation time. This supports the interpretation that the plasma produced at cathode spots can be fully ionized while neutrals are produced by several still-cooling craters of previously active emission sites. The concentration of neutrals in the discharge volume can therefore be much higher than one would expect from Saha calculations based on ion measurements,[6] especially for materials of high vapor pressure.

The presence of metal vapor leads to charge exchange collisions, Eq.(2). Even as charge is conserved, the mean ion charge state is reduced because previously neutral atoms are now included in the determination of the mean ion charge state, $\overline{Q} = \sum Q n_Q / \sum n_Q$. The flux of ions of charge state Q emitted from active cathode spots, Γ_Q, will be reduced by[20]

$$d\Gamma_Q = -\sigma_{Qa} \Gamma_Q n_a dz \tag{6}$$

where z is the coordinate normal to the cathode surface, σ_{Qa} is the cross section for charge exchange collisions, which is large,[21] typically $(1-4) \times 10^{-18} \, \text{m}^{-2}$, and n_a is the density of the vapor atoms. Far from the crater-size vapor source, $z \gg r_0$, where r_0 is the characteristic radius of the evaporating area, the density falls according to

$$n_a(z) = n_a(0)(r_0/z)^2. \tag{7}$$

The initial density $n_a(0)$ can be estimated from the ideal gas equation $p_a = n_a kT$ and Eq.(5). The expansion of the neutrals according to Eq.(7) requires that the pressure at the vapor source is very high in order to obtain reasonable neutral densities at macroscopic distances from the evaporation centers. The local pressure at the evaporation sources points may in fact exceed atmospheric pressure.

The evaluation of (6) is difficult for several reason: first, one needs to have information on the evaporating area (e.g. number and size of cooling, yet-evaporating craters, cooling rates, etc., and second, the atom density is not constant but dependent on the distance.

Therefore, at this point, we can only summarize the following findings: (a) for a given heating power, the surface temperature depends strongly on the heated area (i.e. power density) and thermal conductivity; (b) the flux of neutral vapor from cooling craters can be very large, especially for high vapor pressure materials, leading to a significant density of neutrals in the plasma; (c) for the same power density, a much higher vapor flux is produced for Bi compared to Pb; (d) neutral vapor causes charge exchange reactions which lead to a reduction of higher charge states and thereby a reduction of the mean ion charge state; (e) the charge state values reported in the literature are generally smaller than the charge states produced at cathode spots.

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Table I. Fit parameters for the experimentally found decay of the average ion charge states, *cf*. Eq.(1).

	Pb	**Bi**
Q_{ss}	1.906 ± 0.003	0.893 ± 0.004
C	0.315 ± 0.011	1.672 ± 0.025
τ (µs)	62.6 ± 3.5	117.3 ± 8.5

Table II. Physical properties[16,17,22] of lead and bismuth.

	Pb	Bi
Atomic number	82	83
Atomic mass (a.m.u.)	207.2	208.98
Density (kg/m^3)	1134	978
Melting point (K)	600.6	544.7
Surface binding energy (eV/atom)	2.03	2.17
Heat capacity (J kg^{-1} K^{-1})	128.6	122.1
First ionization energy (eV)	7.417	7.286
Second ionization energy (eV)	15.03	16.7
Third ionization energy (eV)	31.94	25.56
Electrical resistivity, (nΩ m) @ 20°C	208	1029
Thermal conductivity, (W m^{-1} K^{-1})	35.3	7.97
Arc burning voltage (V) @ 300 A	15.5	15.6

Figure Captions

FIG. 1 Evolution of the ion charge state distribution of cathodic vacuum arcs for (a) lead plasma, (b) bismuth plasma. Arc current 300 A, ion extraction about 10 cm from the cathode, 7 pulses per second.

FIG. 2 Evolution of surface temperature and equilibrium vapor pressure assuming a power density of 10^8 W/m^2, which corresponds to the assumption of distributing the heating power evenly over the cathode rod surface.
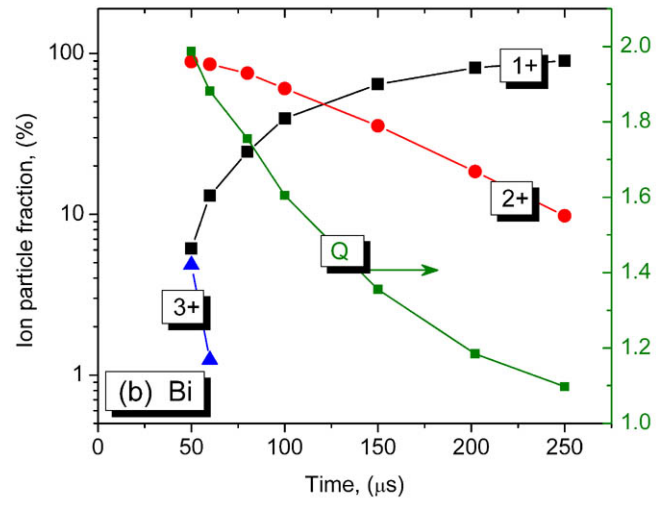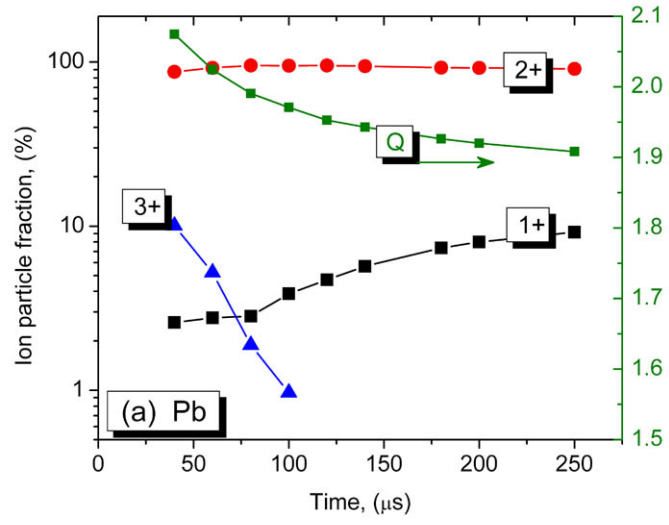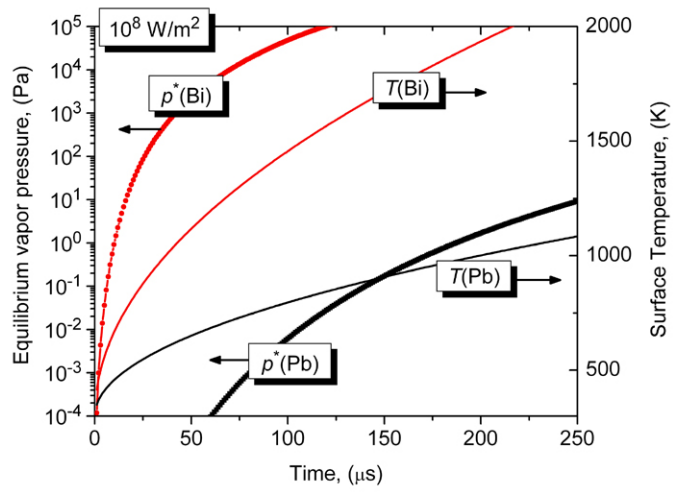
Fig. 1

Fig. 2