

Numerical Simulation of Impact of the Spark Discharge Parameters and Electrode Material on the Intensity of Spectral Lines in the Emission Spectral Analysis

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Numerical modeling was used to calculate influence of discharge power and material of a sample and electrodes on sensitivity of emission spectral analysis with spark discharge in air using lines of atoms, single- and doubly charged ions. Mathematical model incorporates thermodynamic calculation of plasma composition at LTE conditions, mass transfer of electrode vapor and calculation of temperature considering inelastic collisions of electrons with particles. Calculations show that electron concentration in current channel varies in 4 times only whereas power density and evaporation rate vary over one order of magnitude and temperature varies from 11000 to 19000 K. Line intensity of doubly charged ions have a maximum and decreases in 3-10 times at twofold variation of evaporation rate. That defines narrow range of parameters for maximal sensitivity of analysis that is the case at analysis of carbon using the line CIII 229.687 nm. In general the model provides a means for selection of optimal conditions for sensitivity and reproducibility of analysis. Comparison with experiment show that calculated and measured temperatures and electron concentrations are in a good agreement. The model gives also more deep insight into the interconnection between power density, concentration of vapors and parameters of LIB plasma at LTE stage.

Keywords: emission spectral analysis, spark plasma parameters, numerical simulation, intensity of spectral lines, electrode materials

Spark discharge in air is one of the major sources of emission spectra in analysis of metals, alloys (both cast and produced by powder metallurgy methods) semiconductors and solutions. Erosion rate and material of electrodes and sample as well as discharge power determine temperature and electron concentration that affect processes of ionization and excitation and thus control sensitivity and reproducibility of the analytical method. Even small difference between analyte and standard samples in third components may drastically affect intensity of spectral lines because of shift of temperature and ionization equilibrium. Analysis of pressed and sintered samples is the most common task in the powder metallurgy. The first major problem facing analyst is difference in density of standard samples and analyte that cause difference in erosion rate of the samples. To account for these effects one must have a sophisticated understanding of the complex processes occurring on the surface of the electrodes and in the plasma. Literature has accumulated a large amount of experimental data on the influence of electrode and discharge parameters on results of emission spectral analysis [1–6], and also on physical conditions in a spark discharge [7], but up to now there has been done no detailed work on theory of the processes having regard to their self-consistent nature.

Interconnection between sample vapors, power density and intensity of spectral lines is also of

interest in other analytical plasma applications such as laser induced break-down spectroscopy (LIBS) [8]. This method allows direct analysis of any samples regardless of their physical state, be it solid, liquid or gases. Temperature and electron concentration existing at local thermal equilibrium (LTE) stage in LIB plasma at atmospheric pressure are close to those values on the axis of spark plasma at maximum current pulse [9–11]. Although mechanism of plasma heating is substantially different in these plasmas, processes of dissipation of energy at LTE conditions in dense plasmas exhibit some regular trends so results of calculations may be of interest also in this field of analytical chemistry.

The aim of the present work is to study the main relationships between intensities of spectral lines of atoms and ions (single- and double-charged), parameters and composition of the plasma on the one hand, and power density, erosion rate of electrodes, their composition, on the other hand. Calculations were made for the most common case – analysis of samples with Fe matrices. Detailed description of the model may be found in the previous works [12, 13]. In the present study we only briefly mention the system of equations for convenience of discussions of results.

The model allowed conditions to be made for direct determination of carbon using lines of CIII 229.687 nm (excitation potential, $E_{ex}=18.09$ eV) and AgIII 239.565 nm ($E_{ex}=14.76$ eV) at electrospark

deposition of Ag-coatings [12]. Earlier the model was also applied and experimentally tested at calculations of effect of REE additions in W-Cu composite electrodes on plasma parameters at variation of discharge power and pressure [13].

Theory and experimental setup

In the high-density plasmas the energy exchange rate between particles is high so the relaxation time is smaller than duration of discharge and sufficient enough to establish the local thermodynamic equilibrium (LTE) [14, 15]. Spark plasma may be considered in the first approximation as an object with cylindrical symmetry. After breakdown a highly conductive channel is formed capable of carrying strong current while voltage sharply drops to produce short circuiting. All further calculations and measurements relate to the area close to the discharge axis at the moment of maximum current pulse after establishment of a quasi-stationary stage. This region is especially important because of higher temperature and higher density of electrode vapors that creates better conditions for excitation of spectral lines of ions.

The system of equations includes equations of the flow continuity for each component of electrode material, quasi-neutrality condition, the equation of state, electron energy balance equation, the equations of equilibrium for dissociation and recombination of major plasma components (N_2 , O_2 , NO) and Saha equations for each component of the plasma contributing into electron concentration. To create the closed system of equations the constant ratio of nitrogen to oxygen nuclei concentrations in air has been taken into account.

Saha functions were calculated with allowance made for lowering of ionization potentials by fields of charged particles [16]. Equilibrium constants were calculated with use of polynomial approximation for the Gibbs potentials [17]. Effective ionization potential was used to trace reaction of the plasma on external conditions. Intensity of spectral lines at LTE conditions are given by the Einstein-Boltzmann formula. Experiments were carried out using a spark generators for spectral analysis (IBC-23, IG-3) with such parameters: voltage across the capacitor was 14 kV, capacitor – 0.02 μ F, additional inductance was disabled, analytical gap was 1–1.5 mm, auxiliary gap - 3 mm. Design of the spark generator allows generate pulses independent of electrode material, because energy stored in the capacitor is controlled by the auxiliary gap. Diameter of the current channel was estimated from the size of a crater on the surface of electrode after a single pulse. At the current channel radius within ~25 microns and the current amplitude ~220 A maximal pressure owing to the pinch effect is about 1 MPa. Evaporation rates J of sample components are parameters in the model and have been varied. Their absolute values have been measured previously, and fall in the range from

$2 \cdot 10^{26} \text{ m}^{-2}\text{sec}^{-1}$ for W to approximately $5 \cdot 10^{28} \text{ m}^{-2}\text{sec}^{-1}$ for metals with relatively low energy of evaporation (Ag, Al, Mg). Power density at the electrode surface within current channel is about $5 \cdot 10^{11} \text{ Wm}^{-2}$ and the maximum volume power density is approximately $Pow = 5 \cdot 10^{15} \text{ Wm}^{-3}$. Discharge power can be varied by voltage across the capacitor. Increase in capacitance leads to the increase in proportion of energy and the time constant of the circuit, so the power remains constant.

Power density and frequency of inelastic collisions determine temperature of electrons. It depends on composition and concentrations of all species and these values in their turn at LTE conditions are functions of temperature. Frequency and cross-sections of inelastic collisions depend on energy of inelastic processes and also are functions of temperature. Therefore, equations form a set of coupled equations and the problem was solved in iterative cycles to obtain self-consistent values of particles concentrations and temperature. Iterative loops converge rapidly. Only on the boundary of admissible values of the evaporation rate of the electrode, when the particle concentration approaches the value given by the equation of state, the stability of the cycle is broken.

Results and Discussion

Composition of the plasma for Fe-sample at variations of evaporation rate J is shown in Fig.1.

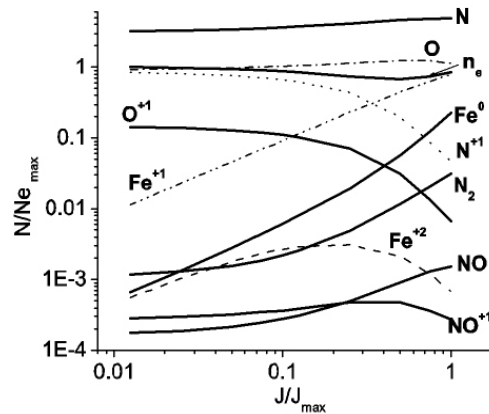


Fig.1. Normalized to the maximal electron number density ($n_{e,max}$) concentrations of particles on the axis of a spark discharge in air at peak current as functions of the evaporation rate of Fe-electrode. $n_{e,max} = 7.9 \cdot 10^{23} \text{ m}^{-3}$; $J_{max} = 8 \cdot 10^{26} \text{ m}^{-2}\text{sec}^{-1}$; pressure $P = 1 \text{ MPa}$; temperature $T_{max} = 15000 \text{ K}$; $Pow \approx 5 \cdot 10^{15} \text{ Wm}^{-3}$.

We consider a range of J from the values do not affecting the plasma parameters to the values at which the electron concentration is determined by the metal vapors. Upper limit is determined by evaporation rate at the boiling point of metal for pressure of about 1 MPa, which is controlled by the pinch effect. At low values of J the electron concentration is determined largely by ionization of nitrogen atoms. Concentration of NO^+ ions being the main contributor to the electron

density in free burning arc is fairly low in spark plasma because of dissociation of NO molecules.

When evaporation rate is growing the quasi-neutrality condition is ensured by equality of electron concentrations and concentration of ions of a metal. Concentration of singly charged ions on the discharge axis is approximately in order of magnitude higher than the concentration of atoms and doubly charged ions. In the presence of lines with high transition probabilities they can provide a more sensitive analysis. Fig.2 shows changes in electron density, temperature and effective ionization potential of the gas mixture under the same conditions.

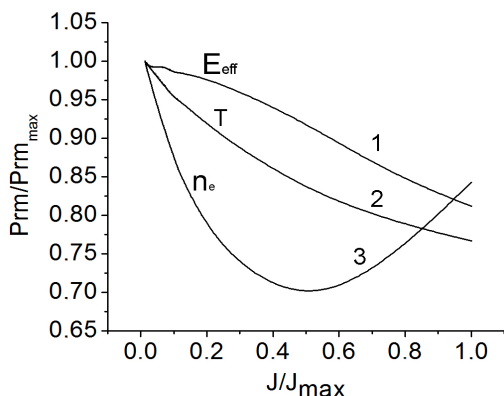


Fig.2. Normalized to the maximum parameters (Prm) of spark plasma as functions of evaporation rate of Fe electrode. 1 – effective ionization potential; 2 – temperature, 3 – electron concentration. $J_{max} = 8 \cdot 10^{26} \text{ m}^{-2}\text{sec}^{-1}$; $Pow \approx 5 \cdot 10^{15} \text{ Wm}^{-3}$, $E_{eff\ max} = 13.8 \text{ eV}$; $T_{max} = 15000 \text{ K}$; $n_{e\ max} = 7.9 \cdot 10^{23} \text{ m}^{-3}$.

In linear scale it is clearly visible that electron concentration is a curve with minimum. At low evaporation rates the decrease of n_e , is quite understandably taking into account decrease in temperature. However, in the area of higher evaporation rates there is an ascending branch of the curve despite monotonic decrease of temperature. This effect is a result of the growth of the concentration of metal atoms and fall in effective ionization potential that compensates effect caused by lowering of temperature. The position of the minimum depends also on the discharge power (Fig.3b).

Consider dependencies of the main plasma parameters – temperature, electron density and the effective ionization potential (E_{eff}) under changes of two parameters – power density and evaporation rate of an iron electrode (Fig.3).

Decrease in evaporation rate and increase in power results in growth of temperature (Fig.3a) as it follows from the equation of electron energy balance. As it may be expected from Saha equations such change of temperature would results in exponential increase of n_e but dependence is more complicate. An increase in power density and temperature will cause effective ionization potential to increase (Fig.3c) that slows down enhancement of n_e . The growth of vapor concentrations of metals and reduction of power led to the fall of E_{eff} from 13.9 to 9.10 eV. This means that plasma became more easily ionized, which significantly slows down the electron density changes despite of decrease in temperature.

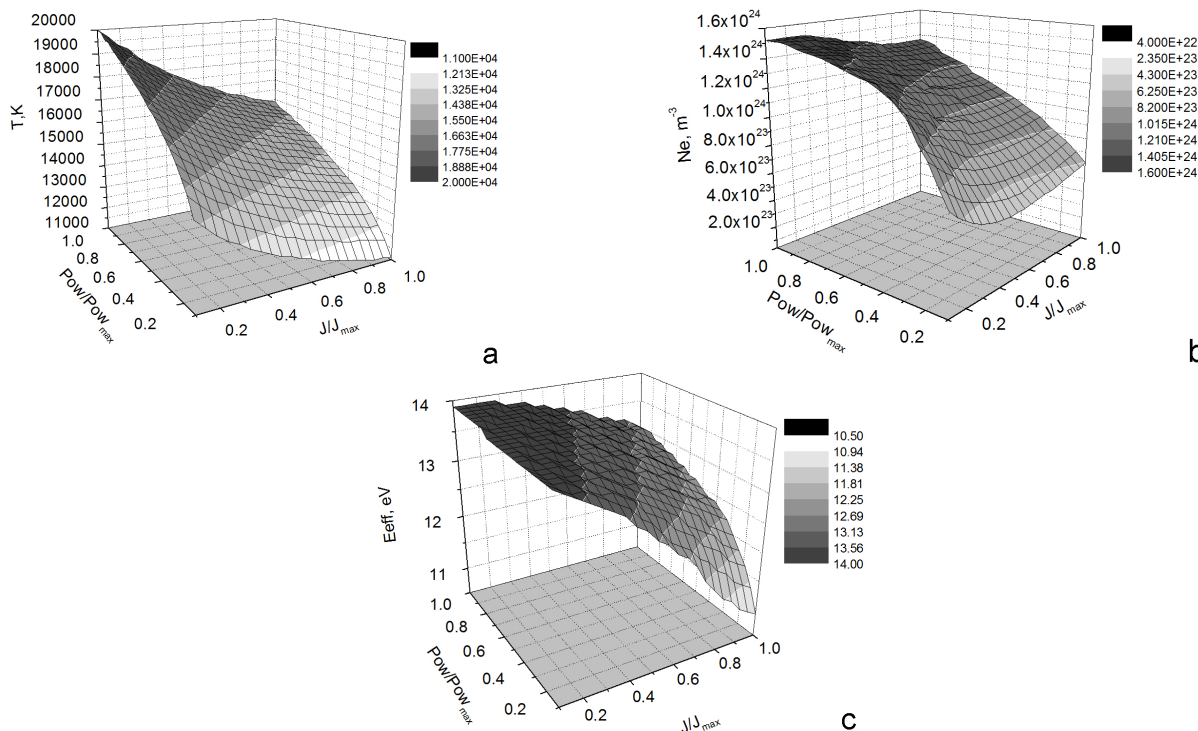


Fig.3. Temperature (a), electron concentration (b) and effective ionization potential (c) on the discharge axis as functions of discharge power density and evaporation rate of Fe electrode. Pressure 1 MPa, maximum power density $Pow \approx 4 \cdot 10^{16} \text{ Wm}^{-3}$, maximum evaporation rate – $J_{max} = 8 \cdot 10^{26} \text{ m}^{-2}\text{sec}^{-1}$.

Equation of state imposes also restrictions on the maximum value of n_e , as partial pressure of electrons cannot exceed the total pressure in the current channel. With increasing power the minimum value of n_e is shifted to the higher evaporation rates and become less distinct in curves of Fig.3b.

These results show that addition of metal vapors in the discharge does not lead to an immediate increase in electron concentration, as it sometimes assumed because of relatively low ionization potentials of metals. Moreover n_e initially may even decrease. This effect depends not only on evaporation rate and power but also on metal of matrix since frequency of inelastic collisions is dominated by exponentially decaying term with energy of excitation and ionization [14]. Growth of n_e occurs only at certain values of evaporation rate and power. The common action of complex processes in the spark plasma results in substantial stabilization of electron concentration. It varies within an order of magnitude despite wide range of variation of power and evaporation rates.

Adequacy of the model has been verified by comparing calculated and measured electron densities and temperatures using various pairs of electrodes: Fe - Me (Me = Cu, Al, Ag, Mg). Electrodes from these metals are used for carbon determination in steels using the line of the doubly charged ion CIII 229.687 nm. Temperature was measured by the lines of single charged iron ions for energies of the upper levels of 43.000–64.000 cm^{-1} using Boltzmann plot. In order to measure the temperature as close as possible to the discharge axis, the axial image of the discharge was used. Electron concentration was measured using Saha equation and lines of atomic and single charged ions of iron (FeII 245.878 - FeI 245.760). Atomic constants were taken from [18]. Due to the displacement of the discharge axis from the optical axis of spectrometer experiments yield average values over the plasma volume and time.

Relative deviation of measured and calculated values of n_e does not exceed 20–25% and temperature of 4%, which falls into error of measurements and calculations (Table 1). These results indicate that the model adequately reflects real processes in the plasma.

Table 1. Calculated and measured plasma parameters on the axis of a spark discharge in air for various pairs of electrodes Fe-Me.

Elec-trodes	Electron concentration n_e, m^{-3}		Temperature, K	
	measured	calculated	measured	calculated
Fe-Cu	$1 \cdot 10^{24}$	$1.20 \cdot 10^{24}$	15000	15000
Fe-Al	$9 \cdot 10^{23}$	$1.22 \cdot 10^{24}$	15000	14900
Fe-Ag	$1.3 \cdot 10^{24}$	$1.42 \cdot 10^{24}$	14900	14500
Fe-Mg	$1.4 \cdot 10^{24}$	$1.76 \cdot 10^{24}$	14900	14400

Discrepancies for the pair Fe-Mg is rather high and may be attributed for inaccuracy of effective energy of inelastic processes and for overestimated value of evaporation rate of Mg. Account must be taken of the rapid drop of temperature and electron concentration outside the region of current channel.

Effect of discharge power and evaporation rate on concentration of doubly-charged ions and intensity of spectral lines with high excitation potential (16.38 eV) is illustrated in Fig.4. A characteristic feature of the curves is that the maxima for intensities of spectral lines and concentration of ions emitting these lines do not coincide. The peak intensity is shifted toward lower rates of evaporation, which corresponds to the lower ion concentration, but somewhat higher temperature. Fairly sharp peak defines a narrow range of evaporation rates favorable for excitation of levels of doubly-charged ions. Outside this range sensitivity of analysis decreases rapidly.

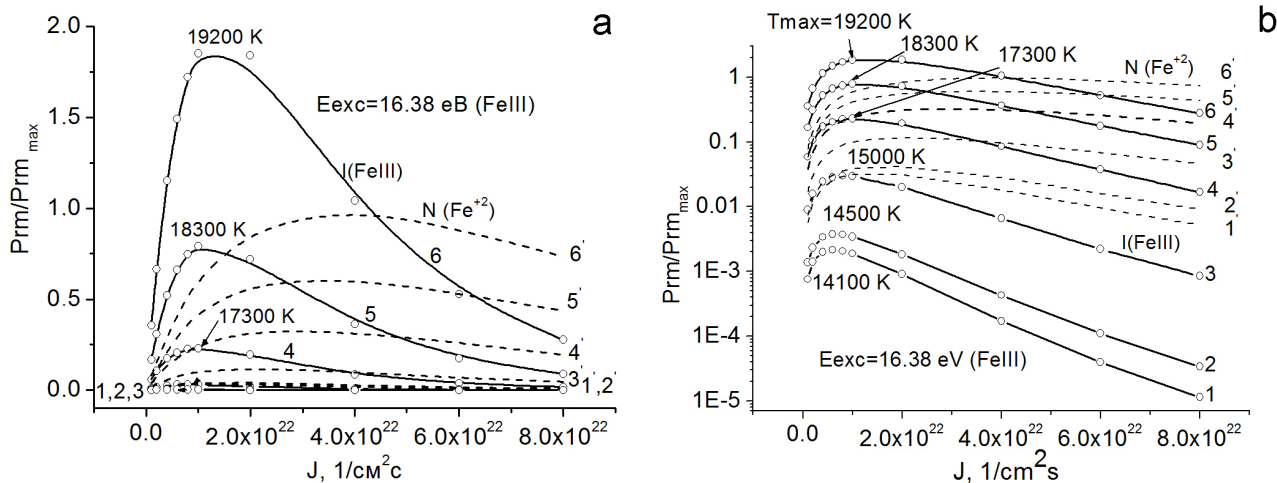


Fig.4. Concentration of doubly-charged ions of Fe (1'–6') and intensity of spectral lines of FeIII with excitation potential 16.38 eV (1–6) as functions of evaporation rate at different discharge powers. (a) – linear scale, (b) – logarithmic. $Pow_{max} = 4 \cdot 10^{16} \text{ Wm}^{-3}$, 1, 1' – $0.1 Pow_{max}$, 2, 2' – $0.125 Pow_{max}$, 3, 3' – $0.25 Pow_{max}$, 4, 4' – $0.5 Pow_{max}$, 5, 5' – $0.75 Pow_{max}$, 6, 6' – $1 Pow_{max}$.

In the Fig.5 are plotted concentration and intensity of lines of atoms, singly-charged and doubly-charged ions as functions of power density and evaporation rate. To provide insight into the nature of the link between temperature and electron concentration and intensities of lines calculations were performed for the same ranges of powers and evaporation rates as in Fig.3.

The rise of power results in increase of temperature, whereas increase in evaporation rate and concentration of atoms of the electrode leads to energy scattering on excitation of levels and temperature became lower. Intensity of spectral lines and concentrations of particles are determined by combined action of these factors that results in complex nature of the dependencies.

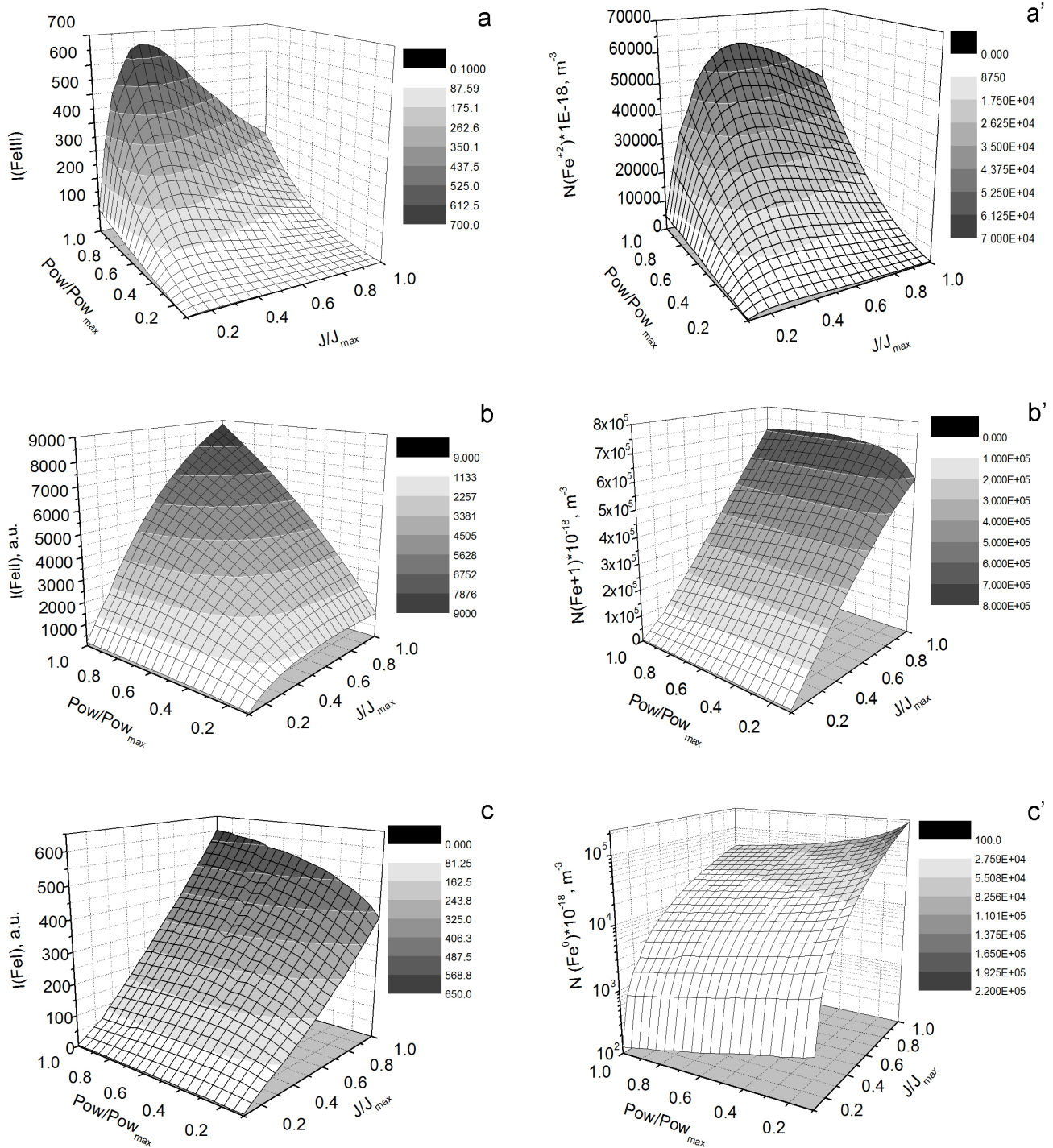


Fig.5. Intensity of lines of Fe (a, b, c) and particles concentration (a', b', c') as functions of evaporation rate and power density. a, a'– doubly-charged ions ($E_{\text{exc}} = 7 \text{ eV}$), b, b'– singly-charged ions ($E_{\text{exc}} = 7 \text{ eV}$), c, c' – atoms ($E_{\text{exc}} = 6 \text{ eV}$); $\text{Pow}_{\text{max}} \approx 4 \cdot 10^{16} \text{ Wm}^{-3}$, $J_{\text{min}} = 1 \cdot 10^{25}$, $J_{\text{max}} = 8 \cdot 10^{26} \text{ m}^{-2}\text{sec}^{-1}$.

Concentration of doubly-charged ions and the intensity of their lines with excitation potential of 7 eV have a similar dependency as for lines with excitation potential of 16.38 eV (Fig.4). Peak intensities of lines of ions are shifted to the region of smaller evaporation rates as compared to their concentration. Concentrations of doubly charged ions and intensity of their spectral lines increase with power, as it should be expected from thermodynamics, but dependencies have salient features. At low evaporation rates an increase is weak whereas for higher values intensity reaches a maximum and for higher evaporation rates it diminishes progressively.

Strong dependence of intensity of spectral lines of doubly-charged ions on evaporation rate and discharge power requires strict compliance with conditions of homology at selection of pairs of spectral lines. With imprecise these conditions variations in the rate of evaporation, such as those associated with the density of sintered powder samples, heat treatment or fluctuation of discharge power can significantly affect precision of the analysis. Normalization of the line intensity to the whole spectra, as is often the case [1] hardly could be recommended for these lines.

In contrast, concentration of singly-charged ions remains constant over a wide range of variation of power for a given rate of evaporation (Fig.5b'). However, intensity of spectral lines increases with power density, but not as strongly as for doubly charged ions. Concentration of ions increases in proportion with evaporation rate, whereas intensity of spectral lines of these ions nonlinearly depends on this parameter. Moreover, at the range of low and middle power densities intensity remains practically constant in a wide range of evaporation rates. This range of parameters helps to improve the reproducibility of the analysis because fluctuations of evaporation rates of standards and analyte weakly influence intensity of spectral lines. Increase in power density leads to improved sensitivity of the assay, but simultaneously increased requirements for selection of spectral lines of the internal standard.

There is proportionality between erosion rate of electrode and intensity of spectral lines of atoms. However, at increased power concentration of neutral atoms decreases, as it should be expected from thermodynamics, whereas intensity of spectral lines remain stable. Occurs a kind of compensation for the intensity – reducing the number of emitting atoms is balanced out by increasing of temperature of the discharge. Analysis with these lines also requires strict compliance with homology conditions provided that erosion rates of standards and samples are different.

As it is seen from calculations dependencies of spectral line intensities and particles concentration emitting these lines of discharge parameters differ widely. This effect is of importance in interpretation of radial distribution of particles or mass transfer through discharge gap using spectral lines.

Conclusions

Mathematical model developed allows understand complex relationships between intensities of spectral lines, parameters of air spark plasma at LTE conditions and erosion rate of electrodes, their composition and power density. Calculations revealed another important facet of the known from experiments dependencies of analytical lines on the “third” elements and structure of samples even at constant parameters of generator that were traditionally attributed mainly to the surface oxidation and formation of secondary structures. Lines of doubly charged ions can decrease in 3–10 times at twofold increase in erosion rate, whereas intensity of single-charged ions only weakly depends on erosion rate. These effects especially important in analysis of sintered powder samples, since erosion rate in a great extent depend on sample density. Concentration of atoms increases exponentially with increase of erosion rate, whereas Intensities of lines of atoms increase linearly, because the rise in atom concentration is balanced by the drop of temperature. Intensity of lines of double charged ions (for instance, CIII 229.687 nm) and concentration of particles emitting these lines have maxima in narrow range of erosion rates, so sensitivity of analysis strongly depend on discharge power and erosion rate. Normalization of the line intensity to the whole spectra, as is often the case, would strongly affect reproducibility and precision of analysis. Calculations show that elements with higher first and second ionization potential and lower statistical sums ensure higher temperature of plasma because of lower energy dissipation on inelastic collisions. As a consequence most suitable electrode material for such analysis is copper, besides its evaporation rate is lower than that of Ag, Al, Mg. Using the model it is possible to calculate effect of difference in composition of standard samples and samples to be analyzed on analytical results owing to the shift of ionization equilibrium. So, calculations show that addition of 8 % of Fe in aluminum alloy AL5, containing 0.3% Si decrease intensity of ion line in 1.5 times whereas the same addition of Zn practically does not change it. Calculated and measured values of temperature and electron concentration are in reasonably good agreement.

Since the model used general principles of thermodynamics and plasma physics it gives more deep insight into the interconnection between power density, concentration of vapors and parameters of other plasmas, such as LIB plasma at LTE stage.

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