Discrimination of Impurity Elements of Solids at Laser Mass-Spectrometric Analysis

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Abstract — The ion composition of a laser plasma bunch at laser mass spectrometry has been studied depending on the parameters of the laser emission. It has been demonstrated that the diameter of the focal spot plays a significant role in the formation of the ion composition of the laser plasma. In particular, at low focal spot diameters \( d \), singly and doubly charged ions prevail, while, at \( d \approx 0.4–0.6 \) mm, ions with a charge of 3, 4, and even 5 are registered. The correlation between the emission parameters and the ion composition of the plasma makes it possible to promptly predict the conditions of the exposure to the laser emissions under which ions of one or another charge are registered. It has been demonstrated that the value of the coefficient of the relative sensitivity for the impurity elements should be calculated for low \( d \), at which the relative yield of singly and doubly charged ions is 90%.

Keywords: laser mass spectrometry, discrimination of elements, ionization and recombination of ions, ion formation in plasma, coefficient of relative sensitivity

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INTRODUCTION

For understanding the ion formation processes and to provide possibilities for the quantitative mass-spectrometric analysis of solid substances, it is of interest to study the basic processes (the ionization, the ions acceleration and their recombination) that occur during laser plasma formation and spreading.

At the same time, precisely these processes, which determine the properties and composition of the ion beams obtained at the late stages of the plasma’s spreading, lead to the result that the composition of the ion beam does not always correspond to the true composition of a sample. As already been found, the causes of such inconsistency are both the differential yield of the elements of the impurities associated with the peculiarities of the ionization of the atoms of various elements and their discrimination by mass in the systems of separation and registration [1]. In this respect, the solution of the problem of the character of the quantitative relationship between the composition of the ion beam and the elemental composition of the sample reduces to the determination of the coefficients of the relative sensitivity (CRS) of the elements that are contained in the analyzed sample.

The values of the CRS, which are used for the determination of the concentration of the individual elements in relation to the internal standard, can be determined experimentally from the results of the analysis of standard samples with compositions close to the analyzed samples. This allows reducing the systematic error approximately to 0.20 on the average [2]. However, as the preparation and certification of standard samples is extremely difficult, the problem of the determination of the CRS empirically remains crucial.

The aim of the present work is the experimental study of the kinetics of the ion formation during laser mass-spectrometric analysis and an attempt at the creation of an algorithm for the calculation of the CRS values taking into account the properties of the matrix and the impurities of the elements, as well as the conditions of the action of the laser radiation on the target.

EXPERIMENTAL CONDITIONS

The experiments were performed using a laser mass spectrometer with an axially symmetric mass analyzer described in detail in [3]. A solid-state Q-switched laser (LTPICH-7) with the wave length \( \lambda = 1.06 \) \( \mu \)m and energy up to 400 mJ a with pulse duration time of \( 10^{-8} \) s was used as the emitter. To control the stability of the laser’s power, a portion of the power (up to 10\%) was diverted to a power meter (IMO-2N) using beam splitters. The energy of the acting emission was changed with the use of neutral filters in such a way that the density of the emission flux on the target changed from \( 1 \times 10^9 \) to \( 2 \times 10^9 \) W/cm\(^2\) at the spot diameters \( d \) from 0.05 to 0.4, and from \( 2 \times 10^9 \) to \( 5 \times 10^9 \) W/cm\(^2\) at the change of \( d \) from 0.6 to 1.0 mm; this
was performed by defocusing of the laser emission in such a way that the focal plane was located beyond the sample’s surface.

The studied object was stainless steel 08X18H13M3 (with known a content of impurities at the level of 10⁻²%) analyzed at a wide range of masses from P to Mo. The resolution capability of the mass analyzer was 500 at the peak height level of 0.1.

Before starting the measurements, the ion-optics system was aligned. The energy transmission of the ion optics system calculated in accordance with [4] was 1000 eV.

**EXPERIMENTAL RESULTS**

In Fig. 1, the dependence of the yield of singly and multiple charged matrix ions (Fig. 1a) and the impurity of Cr (Fig. 1b) on the focal spot diameter is shown. At the diameter of the focal spots of 0.05 and 1 mm, ions with \( z = \pm 1 \) and \( \pm 2 \) are registered, while, at the successive transition to the initial plasma sizes \( d = 0.2 \) and 0.6 mm, ions with charges of three, four, and five start to be registered. In this case, the number of ions \( \text{Fe}^+ \) and \( \text{Fe}^{++} \) reach the maximum values in the range of \( d = 0.05 \)–0.2 mm, and the ions with \( z = 3 \) and \( z = 4 \) reach the maximum values at \( d = 0.4 \) and 0.6 mm, respectively. It should be noted that, in a series of additional studies, we found that the decrease of the number of ions with the increase of \( d \) under the conditions of our experiment is not a consequence of the spreading of the ion beam, which occurs due to the intrinsic space charge at the increase of \( d \).

In Fig. 1b., we will follow with the formation of the charge composition of the impurity component with an increase of \( d \) using the example of \( \text{Cr}^+ \). In the range of the \( d \) values from 0.05 to 0.2 mm, only singly and doubly charged ions are registered, and, at \( d = 0.2 \) and 0.4 mm, triple and tetra charged ions are registered, respectively. The maximums of the multiply charged ions shift to the region of the higher \( d \) values. With the increase of \( z \), the decrease of the rate of growth of the function \( N_k(d) \) is observed, and the ratio of the maximum and minimum values \( N_{\text{max}} / N_{\text{min}} \) changes by 22 times for the ions with \( z = 1 \), while, for the higher charged ions, the change is approximately by 3, 1.4, and 1.2 times. Such dynamics of the formation of the charge’s composition is characteristic for other impurities ions as well. This indicates that the production of impurity ions with high charges (\( z = 3, 4, \) and 5) is caused by the increase of \( d \). Therefore, the initial size of the plasma bunch is an significant experimental requirement for the generation of beams of impurities ions with a specified charge.

In Fig. 2, the change of the function \( N_k(d) \) of singly charged ions of impurity elements in the matrix Fe normalized to the corresponding concentrations of