Plasma-laser radiation interaction during dual-pulse laser ablation of metals and alloys

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It was determined that the transition from single-pulse to double-pulse laser ablation at constant energy and radiation power leads to a significant increase in the analytical signal, plasma temperature and the speed of thermal motion of copper atoms, both when exposed to pure copper and copper-based alloys. From the obtained values we can conclude that the different temperatures and thermal velocities of particles for samples of copper, bronze and brass, we can say that the plasma has spatial and temporal inhomogeneity. From this we can conclude that the heterogeneity of a multicomponent plasma leads to a violation of local thermodynamic equilibrium, which in turn can affect the error of quantitative analysis, especially when using calibration-free methods.

Keywords: laser ablation; dual-pulse laser induced breakdown spectroscopy; multicomponent ablative plasma.

Взаимодействие плазмы с лазерным излучением при двухимпульсной лазерной абляции металлов и сплавов

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Установлено, что переход от одноимпульсной к двухимпульсной лазерной абляции при постоянной энергии и мощности излучения приводит к значительному увеличению аналитического сигнала, температуры плазмы и скорости теплового движения атомов меди как при воздействии чистой меди и сплавы на основе меди. Из полученных значений можно сделать вывод, что при различных температурах и тепловых скоростях частиц для образцов меди, бронзы и латуни можно говорить о том, что плазма обладает пространственной и временной неоднородностью. Отсюда можно сделать вывод, что неоднородность многокомпонентной плазмы приводит к нарушению локального термодинамического равновесия, что в свою очередь может повлиять на погрешность количественного анализа, особенно при использовании бескалибровочных методов.

Ключевые слова: лазерная абляция; двухимпульсная лазерная атомно-эмиссионная спектроскопия;многокомпонентная абляционная плазма .

Introduction

Laser atomic emission spectroscopy (LAES) is a method of qualitative and quantitative analysis of objects, which differs from standard methods of elemental analysis in that the substance evaporates (laser ablation) and the emission spectra of an atom are excited by laser radiation. This method allows you to quickly determine the main components of raw materials and finished products (for example, for the control and analysis of surface layers, analysis of bronze and copper alloys). Currently, LAES is being developed in connection with the possibility of carrying out multicomponent analysis with

high spatial resolution over the surface, and the destruction of the sample is not large (the diameter of the crater on the surface is up to 1 mm, the depth is several tens of microns), without any sample preparation (chemical and mechanical), with a small amount of substance necessary for analysis (~10^{-10}–10^{-11} g).

Laser atomic emission spectroscopy provides high sensitivity, efficiency and the possibility of studying samples with a spatial resolution limited by the size of the focused laser beam on the sample.

LAES is mainly used for elemental analysis of massive samples, when there are no strict requirements for minimizing surface destruction and reducing the thickness of the evaporated layer during layer-by-layer analysis.

However, in some cases, it is necessary to significantly reduce the thickness of the evaporated layer (up to the submicron range). One of the most suitable approaches for this purpose is to reduce the power density of laser radiation on the sample surface.

When controlling the power density, it is necessary to control the analytical signal (the signal-to-noise ratio for the recorded relative intensities of the spectral lines compared to the background), both for the main components of the alloys and for the "third" elements, the concentration of which in the sample and in the ablation, plasma does not exceed units are tenths of a percent.

Single laser pulses are used as sources of excitation of emission spectra in qualitative and quantitative analysis. To increase the sensitivity of the analysis and reduce the error, dual laser pulses (SLP), shifted relative to each other in time, are used as a spectrum excitation source.

The purpose of this work is to study the effect of laser radiation power density on two-pulse laser ablation of metals and multicomponent alloys.

To achieve this goal, it was necessary to solve the following tasks:

• To study the possibility of applying the method of defocusing laser radiation relative to the surface of the sample to control the power density;

• Determine the effect of changing the laser radiation power density on the magnitude of the analytical signal and the signal-to-noise ratio during two-pulse laser ablation;

• Determine the optimal parameters of laser radiation for two-pulse laser atomic emission analysis of thin metal samples (~5–50 μm) and protective and functional multicomponent coatings.

Subject of study: a method of defocusing laser radiation (pulse duration 15 ns, wavelength 1064 nm) on the surface of the test sample to control the power density.

The objects of study were samples of pure metals (copper, zinc, lead, iron, aluminum) and multicomponent alloys (special multicomponent brass of the LS type).

1. Dual-pulse laser atomic emission spectrometer

To study the features of laser ablation of metals by double pulses shifted relative to each other in time, and to create analytical methods for the quantitative analysis of multicomponent alloys, as well as layer-by-layer analysis of thin coatings, a LAEMS double-pulse laser atomic emission spectrometer (manufactured by the Department of Laser Physics and Spectroscopy, Faculty of Physics, BSU) was used (fig. 1).

Main parameters of LAEMS:

• Plasma excitation source – two-pulse diode-pumped Nd:YAG laser with pulse repetition frequency f_l = 10 Hz and wavelength λ = 1064 nm.

• Pulse duration $\tau_l \approx 10$ ns.

• Interpulse interval $\Delta t = 0 \div 100$ μs (step 1 μs).

• Range of analyzed wavelengths Δλ = 260–760 nm.

• Laser pulse energy $E_{imp} = 10 \div 100$ mJ.

Fig. 1. External view of the LAEMS spectrometer

The specialized software of the LAEMS spectrometer allows you to set the following parameters:

• Mode of single (time shift between pulses is 0 μs, i. e. both pulses act on the sample surface simultaneously) and dual laser pulses (the time interval between pulses can vary from 1 to 100 μs in 1 μs increments). It should be noted that when using LAEMS, the transition from single to double laser pulses occurs without changing the total energy and radiation power.

• The number of pulses per point, while you can additionally set the number of pre-firing pulses - pulses that act on the surface before the main ones, but the spectrum from them is not recorded. The use of pre-firing pulses is necessary when examining samples whose surface is covered with visible contaminants, oxides, rust, and patina.

• Energy of dual laser pulses and frequency of their repetition.

• The software allows you to move the subject table with a fixed sample in two planes (up-down, left-right). The "microscope" mode in combination with LED illumination and an aiming laser allows you to accurately determine the method of laser radiation exposure to a sample, which is necessary when examining finished industrial products, art objects and artifacts, jewelry, samples whose dimensions do not exceed a few mm.

To study the effect of laser radiation power density on two-pulse laser ablation of metals and multicomponent alloys, it is necessary to choose the parameters of laser radiation so that the following conditions are simultaneously met during the ablation process: minimum layer thickness; uniform evaporation from the entire irradiated surface without ejection of droplets, the dimensions of which are larger than the layer thickness;

the maximum intensity of the spectral lines of the elements, exceeding the background level by several orders of magnitude. It was experimentally determined that the following parameters will be optimal for the task:

- wavelength – 1064 nm;
- laser pumping energy – 20 J;
- laser pulse duration – 15 ns;
- frequency – 10 Hz;
- time interval between double laser pulses – 10 μs;
- number of impulses per point – 10;
- energy of dual laser pulses – 65÷75 mJ;
- the measurement was carried out in an air atmosphere at normal pressure.
- analytical spectral range 400–530 nm – in this spectral range there are the most intense spectral lines of the elements of all studied samples of pure metals and special brass components.

2. Study of the Effect of Changing the Laser Radiation Power Density on the Value of the Analytical Signal and the Signal-to-Noise Ratio in Dual-Pulse Laser Ablation

With the selected parameters of laser radiation and using the selected method, a number of experiments were carried out, during which graphs of the dependence of the intensity of the spectral lines of the elements on the wavelength were obtained for focusing (0 mm) and two defocusings (5 and 10 mm) for the samples under study.

The analysis of the obtained spectra is presented in the form of tables (table 1 for pure metals, table 2 – for an alloy), which contain data that mostly demonstrate a decrease in the relative intensity of the analytical spectral lines of the elements during defocusing of laser radiation (a decrease in power density and, accordingly, the thickness of the evaporated layer) . For radiation focused on the surface (0 mm), the value of the relative intensity of the analytical spectral line of each element is taken as 100 %.

Table 1

Data for pure metals

Metal	Change in intensity, %			Signal/noise		
	0 mm	5 mm	10 mm	0 mm	5 mm	10 mm
Zn	100	80	40	88,5	72,1	87,4
Al	100	101	58	43,4	59,2	37,8
Pb	100	135	70	42,5	54,2	60,4
Fe	100	52	56	47,2	27,8	67,8
Cu	100	89	51	142,5	139,7	105,8

Based on the data in tables 1 and 2, one can judge the applicability of defocusing for the spectral analysis of pure metals and alloys.

For pure metals (zinc, copper, lead, iron, aluminum), it is possible to conduct a spectral analysis for any defocusing, since the intensity drop occurs by no more than 2.5, 2.0, 1.4, 1.9, 1.7 times, respectively (compared to the line intensity when focusing), the signal level exceeds the noise level by more than 20 times.

Table 2

Data for brass components

Metal	Change in intensity, %			Signal/noise		
	0 mm	5 mm	10 mm	0 mm	5 mm	10 mm
Zn	100	74	22	74,7	89,2	32,3
Al	100	56	6	21,0	19,2	2,7
Fe	100	67	14	9,7	10,4	2,5
Pb	100	50	15	25,3	20,8	7,8
Cu	100	74	32	64,1	77,4	40,6

For an alloy, the intensity of lines for all metals drops: for defocusing up to 5 mm, the maximum drop in intensity occurs by a factor of 2; from 5 to 10 mm – no more than 7 times (with the exception of aluminum, whose intensity dropped by 16 times). The signal level exceeds the noise level for metals by 20 times. It is preferable to carry out analysis with defocusings from 0 mm to 5 mm and the proposed parameters of laser radiation.

Despite the general trend of falling intensities and signal-to-noise ratios, even with a 10 mm defocus, it is possible to carry out quantitative analysis for pure metals. When defocusing in alloys, the intensity of all lines decreases (faster for the components of zinc, iron and aluminum, slower for copper and lead), and it is very important to control the signal-to-noise ratio so that the line intensity does not fall to the background level, which will then make the spectral analysis little effective. Powerful laser radiation acting on an object leads to heating of near-surface regions to critical temperatures. As a result, the diffusion rate of elements increases. This circumstance can be ignored in the spectral analysis of one-component metals; however, in samples of multicomponent alloys, the processes occurring on the surface lead to a change in the composition of the laser plasma. From the foregoing, we can conclude that with a decrease in power density, pure ablation may not be observed, for example, the process of melting, evaporation will occur, and when performing spectral analysis for alloys, one should not rely on the spectral data of pure metals. It is necessary for each alloy to reduce the power density by defocusing to at least control the intensities of the incoming components and the signal-to-noise ratio.

3. Conclusions

Double-pulse laser atomic emission spectroscopy is an advantageous method of direct low-destructive analysis of metals and alloys, since it allows measurements to be made at a specific point on a surface in air without preliminary chemical and mechanical surface preparation. The optimal parameters of laser radiation for two-pulse laser atomic emission analysis of thin metal samples (~5-50 μm) and protective and functional multicomponent coatings were determined. The method of SLR defocusing with respect to the sample surface makes it possible to control the power density of laser radiation, as a consequence, and the thickness of the evaporated layer. In this case, the destruction of the surface under the action of dual laser pulses is minimal compared to other sources of atomic emission analysis (the thickness of the evaporated layer is from 0.2 to 3 μm, depending on the thermophysical properties of the material and the defocusing parameter *f*, the diameter of the crater is ~ 100–250 mm).