INVESTIGATION OF PARAMETERS OF A Q-SWITCHED LASER PRODUCED PLASMA USED IN LASER SPECTRAL ANALYSIS

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The utilization of the experimental setup built for purposes of semiquantitative laser spectral analysis (LSA) without the secondary excitation of the laser produced plasma has been investigated. Experiments have been carried out on samples with various chemical composition. Provided the local thermodynamic equilibrium in the laser produced plasmas occurred, electron temperature and electron density have been estimated using time integrated spectra of plasma regions that can directly be used in LSA.

I. INTRODUCTION

Laser spectral analysis (LSA) utilizes the ability of the focused laser radiation to evaporate a solid sample. LSA is usually used in two variants:

— the direct spectral analysis using the radiation of laser produced plasma as a spectral emission source for spectrochemical analysis,

— the two-step analysis with the auxiliary excitation by the electric discharge across the laser plasma.

The commercial devices for the laboratory use of LSA [1, 2, 3] have been applied to the rapid analysis of the multielement chemical composition of solids, mainly for purposes of the semiquantitative analysis. Most experimental devices for LSA incorporate systems for the additional excitation of the evaporated sample, so that the function of the laser is reduced to the sampling for LSA with the auxiliary electric discharge. The auxiliary excitation is not necessary if a Q-switched laser is used. The laser analyser without the auxiliary excitation of the laser plasma offers improvements such as a higher reproducibility of the analysis [4, 5], a simple apparatus as well as a simple analytical procedure.

II. EXPERIMENTAL

This article deals with the use of the experimental setup built for LSA without the auxiliary excitation of the laser plasma. The work described here is based on the investigation of three samples with various chemical composition. Spectroscopic diagnostics of a homogeneous zone of the LSA plasma has been used for the determination of laser plasma parameters.

The experimental setup built for LSA with directly applied laser plasma emission and for laser plasma spectroscopis diagnostics is shown in Fig. 1. The ruby laser TKG 101 (Tesla Vakuová technika, Praha) operating in the system with a passive Q-switch (a solution of vanadyl phtalocyanine dissolved in nitrobenzene) was employed to create the laser plasma. The pulse duration was ~40 ns, the energy of a giant pulse ~200 mJ with a reproducibility of ±10 % monitored by the laser pulse relative energy meter EM 10 (VEB Carl Zeiss Jena).
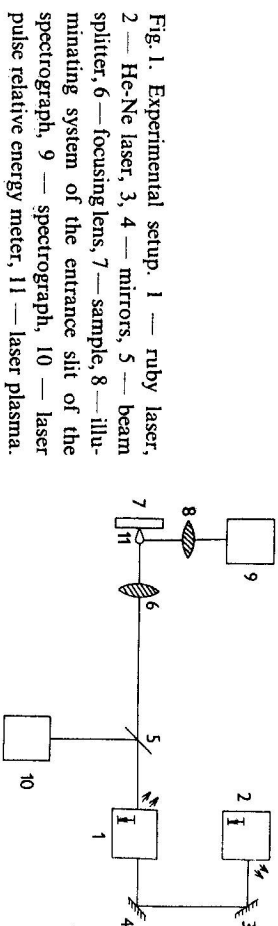

Fig. 1. Experimental setup. 1 — ruby laser, 2 — He-Ne laser, 3, 4 — mirrors, 5 — beam splitter, 6 — focusing lens, 7 — sample, 8 — illuminating system of the entrance slit of the spectrograph, 9 — spectrograph, 10 — laser pulse relative energy meter, 11 — laser plasma.

The laser radiation was focused on samples in three ways:

A) by a microscope lens objective with the focal length $f = 20$ mm and the diameter $D = 10$ mm,

B) by a lens with $f = 20$ mm and $D = 20$ mm,

C) by a lens with $f = 40$ mm and $D = 20$ mm.

The conditions of the ruby laser beam focusing on samples and the pre-choice of the sampling region were examined by a He-Ne laser beam.

Irradiances of the focused ruby laser beam were ~10^{10} W/cm².

We used the following samples: a boron ceramic wafer, an aluminium foil and refined aluminium of 99.9999 % Al.

The laser plasma emission light was relayed to the entrance slit of the spectrograph ISP 28 (the spectral range of 200—600 nm) by a single-lens illuminating system. The spectrograph axis was perpendicular to the direction of the

incident laser beam and the entrance slit parallel to the sample surface. A photographic recording of the laser plasma spectra was used. For purposes of the qualitative spectral analysis of samples and the spectroscopic diagnostics of the laser plasma, the time integrated radiation of the laser plasma homogeneous zone parallel to the sample surface and about ~1.5mm above it was investigated.

To produce a simple spectrogram a multiple exposure (about 10 times) of spectra in the same place of the photographic plate ORWO WU I was used. The plates were processed in the standard way. Spectrograms were evaluated by the microphotometer MF 2 with a chart recorder.

III. RESULTS

III.1. Laser spectral analysis

Samples with a known chemical composition were used as calibration standards in order to estimate detection limits of the experimental setup shown in Fig. 1. Differences in detection limits in the range of 10^{-2}—10^{-3}% among various chemical elements were observed, which were approximately the same as in other analytical methods using optical emission spectroscopy. The analysis of the laser plasma spectra of the three mentioned samples showed that aluminium foil (Al-foil) contained several percent of Mn and Mg as impurities. The boron ceramic wafer (produced by Owens — Illinois, Inc. as a boron planar diffusion source for microelectronics) was composed of stable oxides of Ba, Mg, Al and B. In the ceramic spectra we identified impurities of Sr and Ca, which occurred in the sample according to the listed data of the producer in amounts of ~10^2—10^3 ppm.

III.2. Laser plasma parameters

The spectroscopic diagnostics of a selected laser plasma zone was chosen as a convenient way of determining the electron temperature and the electron density.

The electron densities in the laser plasma homogeneous zone of the three mentioned samples were determined by measurements of the broadening of the neutral atom Al I spectral lines (256.80 nm, 257.51 nm, 265.24 nm and 266.04 nm). As can be seen from Fig. 2 representing the spectral line Al I 257.51 nm selected of the Al-foil spectrum the spectral line shapes were dispersive. This implied that the quadratic Stark effect was the dominant mechanism of the spectral line broadening.

Fig. 2. Spectral line profile for the Al I 257.51 nm line of the Al-foil spectrum, focusing by the lens with $f = 20$ mm. The rings are experimental points, the full line is the fitted dispersive profile. I represents the relative intensity of the spectral line, I_{max} its maximum value. $\Delta\lambda/\Delta\lambda_{0.5}$ is the ratio of the spectral line width and the full width at half maximum (FWHM).
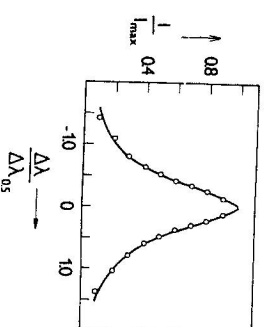
The measured values of full widths at the half maximum of the spectral lines (FWHM) $\Delta\lambda_{0.5}$ for the three samples as well as focusing methods are given in Tab. 1. $\sigma\Delta\lambda_{0.5}$ are mean-root-square (mrs) errors of these values.

Table 1

Average values of the Al I spectral line widths $\Delta\lambda_{0.5}$ (FWHM) and electron densities n_e of the laser plasma calculated from the quadratic Stark effect broadened spectral lines. $\sigma_{\Delta\lambda_{0.5}}$, σ_{n_e} are mrs errors of the values $\Delta\lambda_{0.5}$, n_e respectively. Laser light focusing methods are denoted in agreement with section II as follows: A — focusing by the objective, B — by the lens with $f = 20$ mm, C — by the lens with $f = 40$ mm. Refined aluminum of 99.9999 % Al is denoted as Al 6N.

sample	focusing method	$\Delta\lambda_{0.5}$ [nm]	$\sigma_{\Delta\lambda_{0.5}}$ [nm]	n_e [m^{-3}]	σ_{n_e} [m^{-3}]
boron ceramic	A	0.16	0.02	1.9×10^{23}	0.3×10^{23}
	B	0.19	0.03	2.1×10^{23}	0.4×10^{23}
	C	0.22	0.04	2.5×10^{23}	0.5×10^{23}
Al-foil	A	0.16	0.02	1.8×10^{23}	0.1×10^{23}
	B	0.21	0.01	2.3×10^{23}	0.1×10^{23}
	C	0.22	0.02	2.3×10^{23}	0.1×10^{23}
Al 6N	A	0.17	0.01	2.0×10^{23}	0.3×10^{23}
	B	0.21	0.03	2.3×10^{23}	0.1×10^{23}
	C	0.18	0.01	1.9×10^{23}	0.1×10^{23}

The electron densities n_e were determined from the spectral lines widths $\Delta\lambda_{0.5}$ according to Griem [6] for the electron temperature of the laser plasma $T_e \sim 10^4$ K deduced from the similarity between the spectra of the laser plasma and those of the electric arc. The spectral line broadening depends on T_e slightly, so that we can use the method of the n_e-determination [6] also when the temperature T_e is known only approximately.

The values of n_e (evaluated by mrs errors σ_{n_e}) are listed in Tab. 2.

The electron temperatures T_e of laser plasmas were determined from the relative intensities ratios of the neutral atom Al I lines and the ion Al II spectral

Table 2

Electron temperatures T_t of the laser plasma calculated from the relative intensity ratios of spectral lines. σ_T are mrs errors of the T_t values. The denotation of the laser beam focusing methods is the same as in section II and Tab. I.

sample	focusing method	T_t [K]	σ_T [K]
boron ceramic	A	15 100	360
	B	14 400	370
	C	14 300	520
Al-foil	A	16 300	570
	B	15 400	400
	C	15 500	230
Al 6N	A	16 300	400
	B	14 300	440
	C	15 800	380
			280

line 281.62 nm. Provided the local thermodynamic equilibrium (LTE) in the laser plasma occurred, the following equation is valid for the optical thin plasma [7]

$$\frac{I_i}{I_a}\left(\frac{\lambda_i}{\lambda_a}\right)^3 \frac{n_e h^3}{2(2m_e k\pi)^{3/2}} \frac{f_a g_a}{f_i g_i} = T_e^{3/2} \exp\left(-\frac{E_j + E_r - E_m}{kT_e}\right),$$ (1)

where the index i is valid for the ion, the index a for the neutral Al atom. λ is the wavelength of the transition, n_e, T_e the electron density and the electron temperature respectively, m_e the electron mass, f the oscillator strength, g is the statistical weight, E_j the ionization energy of Al, E_r, E_m the excitation energies of the ion and the neutral atom lines respectively. h is Planck's constant, k Boltzmann's constant. The calculated values n_e of electron densities (Tab. I) and the spectral line parameters tabulated in [8] enabled us to determine the electron temperature. The average values of T_e evaluated by the mrs errors σ_T are given in Tab. 2.

For the calculated values of n_e, T_e both the McWhirter criterion of the LTE existence in plasma and the condition of quasi-neutrality of the laser plasma [7] were satisfied. The character of the laser plasma spectra as well as the parameters of the laser plasma implied its similarity to the electric arc plasma and its suitability for the direct application in the spectral analysis with the use of standard spectral lines tables.

As can be seen from Tab. 1—2, focusing by three selected methods did not radically change the laser plasma parameters. Focusing systems properties influenced the resultant irradiance of the laser beam incident upon the sample surface which caused the evaporation. Slight differences of values T_e, n_e for various focusing methods show in any investigated samples (although outside

the range limited by experimental errors) that a radiation of approximately equal irradiances struck the samples. In spite of different focal lengths and diameters of the lenses, similar irradiances implied that spherical aberrations (in the case of the lens with $f = 20$ mm), respectively laser diameter limiting (in the case of the objective) influenced the laser spot size and consequently the possibility of reaching higher irradiances on sample surfaces.

IV. CONCLUSION

Results reported here demonstrate that the experimental setup described in section II. can be used for producing laser plasmas suitable for the multielement spectral analysis without the auxiliary plasma excitation. The laser plasma of the analytical zone is specified by electron temperatures of $\sim 10^4$K and electron densities of $\sim 10^{23}$ m^{-3} and satisfied the LTE criterion.

The experimental setup is suitable for the registration of chemical elements in trace concentrations in the range of 10^{-1}% down to about 10^{-3}%.

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ИССЛЕДОВАНИЕ ПАРАМЕТРОВ ПЛАЗМЫ, СОЗДАННОЙ ЛАЗЕРОМ С МОДУЛЯЦИЕЙ ДОБРОТНОСТИ И ИСПОЛЬЗОВАННОЙ В ЛАЗЕРНОМ СПЕКТРАЛЬНОМ АНАЛИЗЕ

В работе рассмотрено использование экспериментальной установки, созданной для по-лучения количественного лазерного спектрального анализа (ЛСА) без дополнительного возбуждения лазерной плазмы. Эксперименты выполнены с целью исследования образцов с различным химическим составом. В предположении локального термодинамического равновесия в лазерной плазме определены температура и плотность электронов на основании интегрированных по времени спектров области лазерной плазмы, непосредственно используемой в ЛСА.