Temporal behavior of a laser ablation plasma

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ABSTRACT

Time resolved emission from a plasma, induced by laser ablation of uranium samples has been studied. The temporal profile of emission is strongly influenced by the nature and pressure of the buffer gas. It displays three time scales, indicating that three different processes within the expanding plasma plume are involved. The time resolved spectra help to identify these processes.

INTRODUCTION

Laser ablation is a commonly used method of gasification of solid samples. Its applications include analysis of solids, where it serves as a sample introduction for techniques based on measurements in the gas phase /1/, as well as production of molecular species, used for spectral analysis /2/. The fundamental properties of the plasma produced by laser ablation are strongly dependent on the parameters like laser energy, laser pulse duration and pressure of the gas surrounding the solid sample. Thus the phenomenon is extremely complex and not yet fully understood.

The ablation process was studied mostly for either high (> 10 mbar, /1/) or low (< 0.001 mbar, /3/) gas pressure. Here we present the emission measurements of laser ablation plasma in the intermediate range of pressures. We try to identify the most important processes occurring during the plasma plume expansion under these conditions.
EXPERIMENTAL

Laser ablation is performed with 1064 nm radiation from a Q-switched Nd-YAG Laser (J.K. Lasers Ltd), focused on the sample. Pulse duration, pulse energy and repetition rate are 20 ns, 10 mJ and 10 Hz, respectively. The plasma radiation is collected with an optical fiber and detected either by a photomultiplier in combination with an interference filter or by a 1421 BR intensified diode array in combination with a 0.25 m Jarrel-Ash grating monochromator. The latter is a part of an OMA III system (EG&G). This arrangement allows to observe the full temporal behavior of the plasma radiation (with an accuracy of 10 ns), integrated over the band width of an interference filter (10 nm) as well as the full spectrum (200 – 800 nm), integrated over at least 100 ns (the minimal gate width of the OMA system). Figure 1 shows a cross section of the ablation chamber, which is a cylinder with 8 cm internal diameter. A metal bar is placed between the target and the observation window in order to block the radiation coming from the two lowest parts of plasma. The position of the optical fiber can be varied. The obscured part of the plasma spreads from the target surface up to 1.5 mm above for the position H, 4 mm for the position M and 7 mm for the position L.

Knowing the diameter and depth of the ablation crater we can estimate ablation efficiency and irradiance to be $10^{14}$ uranium atoms/shot and $10^{12}$ W/cm$^2$, respectively. The available energy per uranium atom is in the order of 1 keV. The ablation chamber is filled with buffer gas (argon or air), which pressure can be varied. The applied range is 0.002 – 5 mbar for air and 0.4 – 5 mbar for argon.

RESULTS AND DISCUSSION

A typical example of the temporal behavior of the plasma radiation is shown in fig. 2. It displays a characteristic shape, showing three time resolved states of plume evolution. In further description they will be referred to as the spike (1, 0 – 100 ns from the laser pulse), the first tail (2, 100 ns – 5 µs) and the second tail (3, > 5 µs). These three states can be separated only within a certain range of pressures regardless the kind of the buffer gas, observed part of the plasma plume and wavelength of the interference filter. This range is typically 0.01 to 2 mbar for the first tail and 0.1 to 1 mbar for the second tail. Outside this pressure range the maxima of these signals are not clearly pronounced and the emission intensity versus time has a single decay constant. Below we present the analysis of the three time resolved signals:

The spike (0 – 100 ns).

Its half width is typically 50 ns. Its time of arrival is independent of pressure of the buffer gas. The spectrum of the whole uranium plasma (without the metal bar) in this very period of expansion is dominated by very intense emission from the lowest parts of the plasma. For uranium it shows an irregularly shaped quasi continuum profile. However, by comparison with spectra of other elements (e.g. aluminum), recorded in analogous conditions, we can decide that the radiation in this period consists mainly of line emission of target particles.

A similar temporal profile of an ablation plasma (i.e. the existence of the spike and the first tail) was also reported by other investigators [4], who performed their measurements very close to the target surface. The spike was ascribed to continuum, while the first tail was found to be due to line emission. In our experiment we have observed this characteristic profile also for large distances from our target, where the continuum intensity is negligible. Therefore we propose the following simple mechanism of the plume expansion, involving interactions of the ablated material with the gas particles:

At low and moderate pressures practically all laser energy is coupled to the target particles. We assume a well known ablation model according to which a cloud of partially ionized target material absorbs the laser energy by inverse Bremsstrahlung and the plasma emission has just one maximum and a single decay constant. As the pressure increases, the ablated...
particles encounter a barrier and slow down. In this process an important parameter determining the rate of both momentum and energy transfer to the buffer gas is the collision frequency. According to the classical formula the frequency of ion–ion collisions, which are most effective in this process, is proportional to $n_i^2 \nu_i^2$, where $n_i$ and $\nu_i$ are ion densities and velocities. At the beginning of the expansion the buffer gas is not ionized, so the fastest particles undergo very few collisions (mainly with neutrals) and lose little energy. Therefore they can penetrate the gas further. However, the collisions they undergo are enough to ionize the gas. This is supported by the fact that the spectra, taken high above the target surface in the period of 0–100 ns show presence of both emission from the ionized gas and from the target particles.

The bulk of material, having lower velocities enters a region with high ion density. This causes the particles to undergo many collisions and to slow down quickly. It explains the time delay between the two events: ionization of the gas performed by the fastest particles (the spike) and the arrival of the majority of ablated particles (the first tail). As separate maxima in time. Consequently, the spike has always the same time of arrival, while the first tail will be controlled by the gas pressure.

This process occurs only in a limited range of pressures. At higher pressures the gas starts to absorb the laser energy as well. This changes the dynamics of the plume expansion: the ablated particles do not have that high energies and they do not penetrate the cold gas. At very high pressures the ablation process is initiated by a breakdown in the above the target and the solid is simply etched by the plasma.

The first tail (100 ns – 5 µs). In this time region we collect the emission from the target particles. Based on the mechanism presented above we expect that the shape of the first tail will depend on the pressure of the buffer gas. Indeed, a response of the time profile of radiation to varying pressure of the gas has been observed. Moreover, we have found dependencies of the time for which the first tail reaches its maximum on pressure of argon or air (figure 3a, 3b). It can be noted immediately, that these dependencies are just opposite. The explanation of this effect is based on the fact, that we can detect only radiating particles, which arrive in the observed region. The emission intensity will be proportional to the amount of particles in relevant excited states. If the interaction between the ablated particles and the buffer gas consists mainly of elastic collisions (argon), the increase of pressure will cause the particles to slow down and therefore the maximum of emission in time will appear later. On the other hand, if quenching of excited states is also important (e.g. due to electron attachment and molecules formation in air), the maximum will appear earlier for higher pressure (the quenching is more effective). The detailed explanation is presented in [6].

The second tail (>5 µs). The intensity of the second tail is very low. Its maximum can be observed only in the position M and it is most clearly pronounced in the air plasma. The presence of this maximum in time can be explained by the following effect: there is always some material, which at the very ablation event obtained only little energy (the very inner part of the ablated cloud). This material is not completely atomized and it consists of all kinds of droplets and clusters, moving much slower than the plasma plume. However, as the plasma plume is slowed down, these species eventually enter it, dissociate and get excited, thus contributing to the total radiation intensity. This mechanism can provide another local maximum in time.

The spectra, recorded in the second tail (figure 4, 5) are particularly interesting. Fig. 4 shows a smooth quasi continuum of the line emission of uranium, while fig. 5 shows both line emission (A) and an unknown band around 360 nm (B). A possible explanation of this UV band could be formation of uranium oxide(s) in the plasma afterglow.

Unfortunately, this band cannot be identified as any of the known spectra of uranium molecules.

It is remarkable that the uranium line emission profile (A) from fig. 5 is red shifted with respect to this from fig. 4. This fact makes us suspect that the wavelength for which the emission is maximal is related to temperature (in analogy to the Wien's displacement law of black body radiation). Indeed, we expect the uranium plasma to be colder in air than in argon. The rate
of energy transfer to air molecules is faster than to argon atoms, due to electron attachment: vibrational and rotational excitation and other inelastic processes.

CONCLUSION

The main difficulty in using Optical Emission Spectroscopy to study a low or moderate pressure laser produced plasma is the low intensity of radiation. It does not allow a good spatial and spectral resolution. However, even poorly resolved spectra and temporal profiles can indicate, that the plume expansion dynamics in this pressure range differs from the one found in high or extremely low pressure ablation plasmas. From our experiments we can draw the following conclusions:

* For some range of pressures the plasma radiation has three time scales.
* The first period (the spike) is in fact the ignition of the plasma above the target surface. It is clearly separated in time from the arrival of the bulk of the ablated material. The ignition is performed by the high energetic target particles, which energies can be estimated from their time of arrival at a certain place in the plasma.
* The second period (the first tail) is due to the emission from the ablated target particles. The temporal position of the maximum of intensity is determined by the kind and pressure of the buffer gas. This effect is related to influence of the gas on both velocities of ejected target particles and their radiative decay.
* The third period (the second tail) can be explained by arrival of slow particulates, which dissociate and contribute to the total amount of target particles in the plasma plume.
* The line emission of uranium forms a quasi continuum, which is red shifted as the temperature decreases. Moreover, the spectrum of air plasma shows an additional UV band, which probably can be ascribed to band emission of a uranium oxide.

REFERENCES

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