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Morphology and characteristics of laser-induced aluminum plasma in argon and in air: A comparative study☆

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ABSTRACT

In laser-induced breakdown spectroscopy (LIBS), ablation takes place in general in an ambient gas of the atmospheric pressure, often in air but also in noble gas such as argon or helium. The use of noble gas is known to significantly improve the performance of the technique. We investigate in this work the morphology and the characteristics of induced plasma in argon and in air. The purpose is to understand the mechanism of the analytical performance improvement by the use of argon ambient with respective to air ambient and the dependence on the other experimental parameters such as the laser fluence. The observation of plasma morphology in different ambient gases provides also information for better design of the detection system which optimizes the signal collection according to the used ambient gases. More specifically, the expansion of the plasma induced on an aluminum target with nanosecond infrared (1064 nm) laser pulse in two ambient gases, argon and the atmospheric air, has been studied with spectroscopic imaging at short delays and with emission spectroscopy at longer delays. With relatively low ablation laser fluence (65 J/cm^2), similar morphologies have been observed in argon and in air over the early stage of plasma expansion, while diagnostics at longer delay shows stronger emission, higher electron density and temperature for plasma induced in argon. With higher ablation laser fluence (160 J/cm^2) however, different expansion behaviors have been observed, with a stagnating aluminum vapor near the target surface in air while a propagating plume away from the target in argon. The craters left on the target surface show as well corresponding difference: in air, the crater is very shallow with a target surface chaotically affected by the laser pulse, indicating an effective re-deposition of the ablated material back to the crater; while in Ar a deeper crater is observed, indicating an efficient mass removal by laser ablation. At longer delays, a brighter, denser and hotter plasma is always observed in argon than in air as with lower ablation laser fluences. The observed different influences of the ambient gas on the plasma expansion behavior for different laser fluences are related to the different modes of laser-supported absorption waves, namely laser-supported combustion (LSC) wave and laser-supported detonation (LSD) wave.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) uses ablation plasma as a spectroscopic emission source. The analytical performance of the technique greatly depends on the properties of the plasma and the corresponding properly designed optical systems to generate the plasma and to collect the emission from the plasma. Even working under the fixed atmospheric pressure as in most of LIBS measurements, it is well known that the nature of the ambient gas (molecular or monoatomic gas, reactive or inert gas) can greatly influence the expansion behavior of the plasma and the properties of the resulted plume [1–5], thus crucially affect the analytical performance of the technique. It has been clearly established that a noble gas such as argon can lead to a dense and hot plasma and therefore stronger spectral emission from the plasma than that in the case with the atmospheric air as ambient gas. The reported results however are often based on time-resolved and space-integrated diagnostics. Observation on the morphology of the plasma, and especially over the early stage of the plasma expansion, is often absent. Such absence, of course, does not alternate the established results about the beneficial effects of the use of argon for a better LIBS performance. But it prevents from a thorough understanding of the mechanism responsible of such improvement. In addition, the morphological information of the plume, including its size, the distribution of the species and its temporal evolution, is very important for the design of a proper detection system of an optimized collection of the plasma emission. The understanding and the control of the morphology of the

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plasma are therefore important for the analytical performance of LIBS in terms of precision, repeatability and reproducibility [6]. According to the results presented in our previous works [7–11], laser-supported absorption waves (LSAW) during the post-ablation interaction, especially the laser-supported consumption (LSC) wave and laser-supported detonation (LSD) wave can greatly influence and modify the morphology of the plasma. Such influence is particularly pronounced for infrared (IR, 1064 nm) ns laser ablation at relatively high fluence (>150 J/cm^2). However up to now, the influence of the nature of the ambient gas (monoatomic or molecular) on the expansion behavior of the induced plasma remains still unclear.

In this paper, we report the results of a comparative study of the morphology and the characteristics of laser-induced plasmas in different ambient gases of argon and air at one atmosphere pressure. A simple configuration of ablation with an IR (1064 nm) nanosecond pulse of a metallic target (aluminum) was used in order to stress the behavior of the plasma during its expansion into different ambient gases. The expansion process of plasma was studied in two fluence regimes, a moderate fluence regime of 65 J/cm^2 and a high fluence regime of 160 J/cm^2. In each of these ablation regimes, the expansion behavior of the plasma was observed using fast spectroscopic imaging at short delays (0 to 200 ns) and space-resolved emission spectroscopy at longer delays (350 to 2000 ns). Fast spectroscopic imaging reveals the morphology of the plasma [12], while emission spectroscopy results in electron density and temperature profiles of the plasma. The observations of the plasma morphology in the early stage of the expansion and that of the plasma characteristics over the delay interval when LIBS measurements generally take place, are further correlated to the observation of the craters left on the sample surface with scanning electronic microscope (SEM). Such multi-time scale and multi-aspect observations enrich the obtained results for an advanced understanding of the implicated mechanisms in different ablation fluence regimes and with different ambient gases. We interpret the observed plasma expansion behaviors and the resulting plasma characteristics using the different modes of LSAW in the early stage of the plume expansion when the laser pulse is still present.

2. Experimental setups and measurement protocols

Detailed description of the used experimental setup can be found elsewhere [9,10]. A Nd:YAG laser (Quantel Brilliant) was used for ablation in two fluence regimes with pulse energy of 20 mJ corresponding to a fluence of 65 J/cm^2 (moderate fluence regime) and 50 mJ corresponding to a fluence of 160 J/cm^2 (high fluence regime). The aluminum targets used in the experiment were of two different qualities, which respectively correspond to two types of detection, the image type and the spectroscopy type, performed in the experiment. A piece of pure aluminum (Al 99.99%, Cu 0.005%, Si 0.002%, Fe 0.001%) was used for the image type measurement, while a certified reference aluminum alloy (Al 89.5%, Si 8.39%, Fe 0.999% and some traces) was used for the measurement of spectroscopy type. A pair of tubes installed above the target close to the laser ablation zone was used to deliver a stream of argon gas of a fixed flow of 8 l/min, which ensured the plasma to expand into a pure argon ambient gas at the atmospheric pressure. The tubes were removed for ablation in the atmospheric air.

In the image type measurement, a pair of achromatic lens (in BK7) was used to form plasma image on an ICCD camera (Andor Technology, iStar) along an axis perpendicular to the propagation axis of the laser beam which was focused vertical down to the surface of the target. Fast spectroscopic images were realized correspondingly for the different species in the plume with the help of narrowband filters with central wavelength and corresponding species as shown in Table 1. We can see in the table that a plume in our experiment is characterized by 4 species: neutral aluminum (Al I), ionized aluminum (Al II), neutral gas (Ar I or N I according to the used ambient gas), and ionized gas (Ar II or N II). For a given species in the plume, a pair of filters was used with one of them centered on the corresponding emission line (filter-on) and the other shifted outside but nearby the line (filter-off). Assuming that the spectral intensity of the continuum background remains almost constant in the vicinity of the considered emission line, it is possible to subtract the contribution of the continuum from the intensity recorded with the filter-on using the intensity recorded using the corresponding filter-off. After such subtraction between the images, the resulting image corresponds to the emission image of the concerned species. The Abel-inversion [13] is further applied to emission image, resulting in emissivity image of the corresponding species. In our experiment, the intensity distribution in an emissivity image is considered as representative of the space distribution of the corresponding species. This consideration obviously corresponds to an approximation, because it is well known that the emissivity of an emission line is directly related to the population of the concerned species in the up state of the corresponding transition. Such approximation is however justified when the variation of the electron temperature within the plasma remains relatively smooth. This condition will be verified in our experiment. For the image recording, each raw emission image, with filter-on or with filter-off, was the result of the accumulation of 100 laser impacts distributed over 10 craters with 10 impacts by crater.

Table 1
Emission lines chosen to represent different species in the plume and the narrowband filters used in the image type measurement to perform spectroscopic image of these species.

Element	Species	Emission line (nm)	Central wavelength of the filters (nm)
Al	Neutral (Al I)	394.4, 396.2	On: 400 Off: 380
	Ion (Al II)	358.7	On: 360 Off: 380
Ar	Neutral (Ar I)	750.4, 751.5	On: 750 Off: 720
	Ion (Ar II)	484.8, 488.0	On: 488 Off: 530
Air (N)	Neutral (N I)	746.8	On: 750 Off: 720
	Ion (N II)	500.1, 500.7	On: 500 Off: 530

In the spectroscopy type measurement, a pair of fused silica lens was used to form an image of the plasma along an axis perpendicular to the laser beam incident direction. An optical fiber of aperture of 50 μm was put in the plasma image plane to catch the emission from a given volume of the plasma. Axial profile of the plasma was thus preformed in the lateral middle of the plasma image by translating the fiber step by step along the laser incidence axis. Such detection system allowed a space resolution of 75 μm by taking into account the magnification of the used optical system. The output of the fiber was connected to the entrance of an echelle spectrometer, which was in turn connected to an ICCD camera (Mechelle 5000 and iStar from Andor Technology). Each spectrum was the result of the accumulation over 200 laser impacts distributed over 20 craters with 10 impacts by crater.

Representative lines were chosen in order to get axial profiles of the ablated aluminum plume. For aluminum ion, the line at 281.6 nm was chosen with the lower energy level of the transition of 11.8 eV, which prevents it from significant self-absorption. For aluminum atom, the resonant line at 309.3 nm (with the ground state as the lower level of the transition) was among the several lines that exhibited an enough good signal-to-noise ratio, because of the high degree of ionization of the aluminum vapor in the condition of our experiment, especially at short delays. Such high ionization reduced the self-absorption of the chosen neutral aluminum line. The electronic density was determined using the Stark broadening of the Ar I 696.5 nm line in the argon ambient, and that of the H I 656.2 nm line in the air ambient. The determination of the electron temperature needs the plasma to be in the local thermodynamic equilibrium (LTE). Our previous work shows that in the delay interval considered for the spectroscopy type measurement (350 to 2000 ns), the LTE state represents a reasonably good approximation for