Spectrochimica Acta Part B 101 (2014) 330–334

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Research note

Unexpected temporal evolution of atomic spectral lines of aluminum in a laser induced breakdown spectroscopy experiment☆

Rawad Saad [a], Daniel L'Hermite [a,*], Bruno Bousquet [b]

[a] CEA, DEN, DPC, SEARS, LANIE, 91191 Gif-sur-Yvette, France
[b] LOMA, Université de Bordeaux, CNRS, 351 Cours de la Libération, 33405 Talence Cedex, France

ARTICLE INFO

Article history:
Received 14 December 2013
Accepted 16 September 2014
Available online 22 September 2014

Keywords:
LIBS
Plasma temperature
Temporal evolution
Collisional energy transfer
Molecular recombination

ABSTRACT

The temporal evolution of the laser induced breakdown (LIBS) signal of a pure aluminum sample was studied under nitrogen and air atmospheres. In addition to the usual decrease of signal due to plasma cooling, unexpected temporal evolutions were observed for a spectral lines of aluminum, which revealed the existence of collisional energy transfer effects. Furthermore, molecular bands of AlN and AlO were observed in the LIBS spectra, indicating recombination of aluminum with the ambient gas. Within the experimental conditions reported in this study, both collisional energy transfer and recombination processes occurred around 1.5 μs after the laser shot. This highlights the possible influence of collisional and chemical effects inside the plasma that can play a role on LIBS signals.

1. Introduction

One of the most widespread rapid multi-elemental techniques for quantitative analysis is laser-induced breakdown spectroscopy (LIBS) [1–4]. It is based on the atomic emission of laser-induced plasma resulting from the laser ablation in the case of a solid sample. Moreover, liquid and gas samples can also be ionized by a laser beam and thus analyzed by LIBS. This technique has established itself as an analytical tool in different fields of applications such as the spatial application on Mars [5,6], nuclear industry [7,8], analysis of pigments [9,10], aerosols [11,12], polymers [13,14], metallurgy [15,16], environment [17], art and cultural heritage [18,19], pharmacy and biology [20,21]. This list illustrates the fact that LIBS is a very versatile analytical technique presenting high spatial resolution and possible remote measurements [22].

Different mechanisms and phenomena could affect the LIBS signal such as instrumental fluctuations, shot noise, spectral interferences, self-absorption, and matrix effects. Several research groups worked on different normalization methods to correct these phenomena. Zorov et al. have outlined most of them in a recent review paper [23]. On the other hand, physico-chemical phenomena occurring in LIBS plasma still remain less studied. The chemical reaction $Al + O_2 \rightarrow AlO + O$ was first studied by Dagdigian et al. [24] in a beam-gas arrangement in the framework of a laser fluorescence study. In their work, the state distribution, the dissociation energy and the radiative lifetime of AlO were derived. Another group studied the dynamics of the above reaction and found that the relative reactivity for $Al(^2P_{1/2})$ and $Al(^2P_{3/2})$ depend on the collision energy amount [25] and thus on the plasma temperature. Moreover, Misra and Thareja showed that aluminum reacts with nitrogen to form the molecule AlN in the framework of aluminum films deposition in nitrogen ambient atmospheres [26]. In another study, Sharma and Thareja studied the formation of aluminum nitride [27] and concluded that the ionized states of Al II and N II contributed to the formation of AlN. In addition, Dors et al. worked on the determination of the AlO spectroscopic temperature by the use of the modified diatomic Boltzmann plot and the Nelder–Mead algorithm in the fitting of the recorded spectrum [28]. After this, in a recent paper [29], Parigger showed that atomic and molecular emissions should be evaluated together and in the same time in order to overcome the occurrence of superposition spectra in the plasma decay. He suggested using spatially and temporally resolved LIBS experiments to understand the different phenomena. Within the framework of a PhD thesis in our research group [30], matrix effect was analyzed during LIBS experiment. A loss of the signal intensity was noticed but not totally explained by the self-absorption phenomena. A hypothesis of the presence of chemical reactions in the plasma was proposed. Consequently, in order to study the chemical reactions in the plasma, we choose to treat the simple case of a pure aluminum sample. In this paper, we focused on the peculiar temporal evolution of the observed Al I lines during the plasma expansion. The results presented here were obtained under air and nitrogen atmospheres and at ambient pressure. We describe in a first

☆ Selected paper from the 7th Euro-Mediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS 2013), Bari, Italy, 16–20 September 2013.

* Corresponding author. Tel.: 33 (0)1 69 08 95 04.
E-mail addresses: rawad.saad@cea.fr (R. Saad), daniel.lhermite@cea.fr (D. L'Hermite), bruno.bousquet@u-bordeaux1.fr (B. Bousquet).

http://dx.doi.org/10.1016/j.sab.2014.09.017
0584-8547/

step the experimental setup for the acquisition of time-resolved LIBS spectra. Then, we present the results and discussions related to the temporal evolution of the chosen Al I lines.

2. Experimental

The whole experimental setup is the MobiLIBS ® equipment from IVEA-Solutions, France. The plasma was generated at atmospheric pressure using a Nd:YAG laser operating at 266 nm and providing 5 ns (FWHM) pulses at 20 Hz repetition rate. A 25 cm focal length lens was used to focus the laser beam onto the sample surface. The maximum laser pulse energy was 4 mJ and the spot diameter at the sample surface was equal to 50 μm so the irradiance was approximately 40 GW cm^{-2}. The emission from the plasma was collected in the direction of the incident laser beam, and transmitted through optical fiber to the entrance slit of a high-resolution spectrometer (Mechelle, Andor Technology, resolving power $\lambda/\Delta\lambda = 4000$) equipped with an intensified CCD camera. The ICCD sensitivity was equal to 400 counts/photoelectron which corresponds to a gain of 200 set on the MCP software. In this work, a super-pure aluminum sample (198f—TechLab) with trace elements of Si (0.002%), Fe (0.001%) and Cu (0.005%), was analyzed under two different ambient gases (nitrogen and air) at atmospheric pressure. Fig. 1 displays a part of the Grotrian diagram of aluminum limited to the spectral lines of interest for this work. The Einstein coefficients (A) and the upper energy level values (E_k) of the selected Al I lines listed in Table 1 are provided by the Kurucz atomic spectral line database [31]. In order to study the temporal behavior of the spectral lines of interest, the delay time between the laser pulse and the signal acquisition was tuned within the range of 0.2–15 μs. At earlier delay times, namely before 0.2 μs, the atomic lines were hidden under the well-known continuum signal due to the bremsstrahlung and to recombination effects. For the longest delay times of this study and to improve the signal-to-noise ratio, the temporal gate width of the ICCD was increased in order to allow the detection of the low intensity LIBS signal. As a consequence, the measured signal was divided by the temporal gate width, in order to obtain comparable intensities for different delay times. Delays used in this paper correspond to the center of the temporal gate. Each spectrum resulted from the accumulation of 25 measurements at different locations onto the sample surface. For each measurement, 50 laser shots were applied to obtain the resulting spectrum. In addition, two pre-pulses were used in order to remove the oxide layer (Al_2O_3) that was naturally formed at the sample surface.

Table 1
Wavelengths (λ), degeneracies (*g*), Einstein coefficients (*A*) and upper energy level values (E_k).

λ (nm)	*g*	*A* (s^{-1})	E_k (cm^{-1})
305.7144	6	7.50E + 07	61,843.54
305.0072	6	3.21E + 07	61,843.54
305.4679	4	4.49E + 07	61,747.56
306.6144	4	4.77E + 07	61,747.56
305.9030	4	1.41E + 07	61,747.56
305.9924	2	1.82E + 07	61,691.46
306.4290	2	8.91E + 07	61,691.46

3. Results and discussions

At first, Al I lines were examined at two different delay times and two different ambient gases. Fig. 2a displays the comparison between the LIBS spectra of the ultra-pure aluminum sample under air (plain) and nitrogen (dashed) at a delay time of 0.8 μs. The two spectra reveal no significant differences. On the other hand, at a delay time of 4.5 μs, Fig. 2b reveals a peculiar and significant difference between the recorded spectra since under nitrogen atmosphere, two Al I lines (305.007 nm and 305.714 nm) were still visible while those under air atmosphere had vanished. These persistent Al I lines were related to two transitions with the same upper energy level $E_k = 61844\ cm^{-1}$.

3.1. Temporal evolution under nitrogen atmosphere

Fig. 3 shows the temporal evolution of four Al I lines selected in the spectral range displayed in Fig. 2, in the case of plasma expansion in nitrogen atmosphere. The red curves are related to two transitions with the same upper energy level $E_k = 61844\ cm^{-1}$, the blue ones to $E_k = 61748\ cm^{-1}$ and the orange ones to $E_k = 61691\ cm^{-1}$. In order to compare the temporal evolutions of these Al I transitions, all the intensities were normalized to 1 at the delay time of 0.2 μs. The error bars

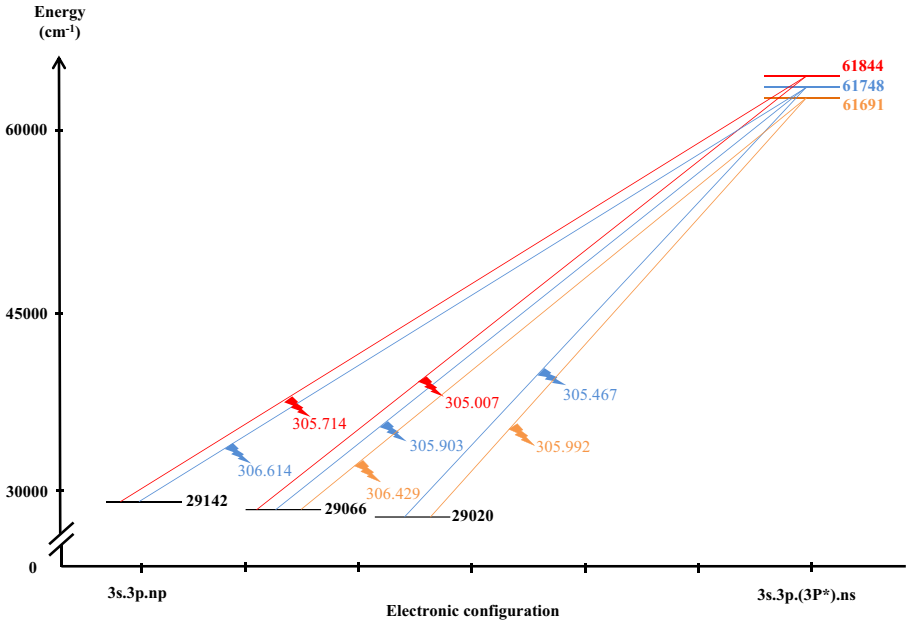

Fig. 1. Part of the Grotrian diagram of aluminum related to the observed spectral lines.