Spectrochimica Acta Part B 116 (2016) 1–7

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Laser-induced breakdown spectroscopy on metallic samples at very low temperature in different ambient gas pressures

R.H. El-Saeid, M. Abdelhamid, M.A. Harith *

National Institute of Laser Enhanced Science (NILES), Cairo University, Egypt

ARTICLE INFO

Article history:
Received 31 May 2015
Accepted 17 November 2015
Available online 28 November 2015

Keywords:
LIBS
Liquid nitrogen temperature
Vacuum
Plasma parameters

ABSTRACT

Analysis of metals at very low temperature adopting laser-induced breakdown spectroscopy (LIBS) is greatly beneficial in space exploration expeditions and in some important industrial applications. In the present work, the effect of very low sample temperature on the spectral emission intensity of laser-induced plasma under both atmospheric pressure and vacuum has been studied for different bronze alloy samples. The sample was cooled down to liquid nitrogen (LN) temperature 77 K in a special vacuum chamber. Laser-induced plasma has been produced onto the sample surface using the fundamental wavelength of Nd:YAG laser. The optical emission from the plasma is collected by an optical fiber and analyzed by an echelle spectrometer combined with an intensified CCD camera. The integrated intensities of certain spectral emission lines of Cu, Pb, Sn, and Zn have been estimated from the obtained LIBS spectra and compared with that measured at room temperature. The laser-induced plasma parameters (electron number density N_e and electron temperature T_e) were investigated at room and liquid nitrogen temperatures for both atmospheric pressure and vacuum ambient conditions. The results suggest that reducing the sample temperature leads to decrease in the emission line intensities under both environments. Plasma parameters were found to decrease at atmospheric pressure but increased under vacuum conditions.

1. Introduction

LIBS has been widely tested in different fields of applications, for instance, environmental monitoring [1,2], engineering [3,4], cultural heritage analysis [5–7], underwater analysis [8,9], aerosols [10–12], and detection of energetic materials [13,14]. Numerous factors affect and have a key role in the plasma formation and consequently on the analytical performance of the LIBS technique [15,16]. Such factors include laser parameters such as wavelength, pulse energy, pulse duration, and irradiance; sample physical properties such as boiling point, melting point, and thermal conductivity as well as the environmental conditions such as ambient air pressure and sample temperature.

During the last few years, the effect of the environmental conditions, namely, the ambient gas pressure and the sample temperature, on LIBS analytical performance has been studied by different research groups [17–21]. The ambient gas pressure is one of the most important parameters that affect the spatial expansion of the plasma. Electron densities and excitation temperatures of aluminum laser-induced plasmas produced in different ambient gases (Ar, N_2, and He) at different pressures were examined [17]. It was found that the plasma emission intensity is strongly dependent on the plume confinement, which is affected by the nature of ambient gas and its pressure.

A comparison between LIBS spectra taken at atmospheric conditions and that taken at pressure of about 10^{-5} Torr was performed by Cowpe and Pilkington [18]. They found that, although the intensity of the LIBS spectrum taken at vacuum was less intense than that taken at atmospheric conditions, it was clear that the LIBS spectrum at vacuum is of higher resolution. This improvement in resolution was likely due to the decrease in the electron density which results in less line broadening. Moreover, different laser regimes were applied for investigating the plasma emission from brass using ns and fs laser pulses under both vacuum and atmospheric conditions [19]. Higher emission intensities were seen in the atmospheric case due to plasma plume confinement by the ambient gas, however in vacuum fast expansion of the emitting species was significant.

Another important parameter that influences the LIBS signal and plasma parameters is the sample temperature. Tavassoli et al. [20] showed that heating an aluminum sample in air at atmospheric pressure up to 150 °C leads to an increase in the spectral line intensities and the limits of detection (LOD) have been also improved. Similarly, Eschlböck-Fuchs et al. [21] found that the intensity of the emission lines increases with increasing the sample temperature for various solid materials. Nevertheless, the plasma parameters T_e and N_e were independent of temperature for slag samples.

During the first decade of the present century, LIBS under particular environmental conditions (very low temperature) has been adopted in space exploration. The main goal of this research was to study comets,

* Corresponding author. Tel./fax: +20 2 35675335.
E-mail address: mharithm@niles.edu.eg (M.A. Harith).

http://dx.doi.org/10.1016/j.sab.2015.11.004
0584-8547/

Table 1
Elemental composition in (%wt) of quaternary, ternary investigated bronze alloy samples.

Sample code	Cu %	Pb %	Sn %	Zn %
S1	85	6.5	6.5	2
S2	86	4	4	6
S3	93	2	5	-
S4	92.5	0.6	6.9	-
S5	88	2	2	8
S6	90.8	2.36	3.7	3.14

asteroids, the moon, and Mars [22–24]. Some of these missions involved landing on the body and conducting different types of analyses.

This paper proposes the investigation of different LIBS parameters of bronze alloy samples under extreme conditions of very low sample temperatures and low ambient pressure using nanosecond laser regime. Experimental LIBS parameters, including spectral line intensity of the main alloy elements Cu, Pb, Sn, and Zn, and plasma parameters (electron number density and electron temperature) were investigated at room and liquid nitrogen temperatures under both atmospheric pressure and vacuum.

2. Experimental

2.1. Samples

Six bronze alloy samples with slightly different compositions were used in the whole study. Table 1 summarizes the elemental composition in % wt of the certified bronze samples used throughout the present study. The sample was cooled down to liquid nitrogen temperature (77 K) by fixing it on a holder attached to the liquid nitrogen container (LNC). LNC is then filled by liquid nitrogen and is placed in a specially designed vacuum chamber as shown in Fig. 1. After fixing the sample, the chamber is evacuated by means of an oil free rotary pump to 10^{-2} Torr. In case of measurements in air at atmospheric pressure; the samples were also placed in the same vacuum chamber to just keep the experimental conditions similar.

2.2. LIBS arrangement

The schematic diagram of the experimental setup is shown in Fig. 1. A Q-switched Nd:YAG laser (Brio, Quantel, France) operating at its fundamental wavelength (λ = 1064 nm) is used to generate plasma onto the target surface. The laser pulse energy was fixed at 65 mJ with a pulse duration of 5 ns (FWHM) at 20 Hz repetition rate. The laser pulse energy was monitored by a Joulemeter (SCIENTECH, model AC5001, Boulder, CO, USA). The laser beam was focused using a plano-convex lens (f = 7.5 cm) onto the sample surface through a quartz window of the vacuum chamber. The light emitted from the plasma plume was collected via another plano-convex lens (f = 5 cm) and fed via a fused silica optical fiber with a diameter of 600 μm to an echelle spectrometer (Mechelle 7500, multichannel, Sweden). The echelle spectrometer has a focal length of 17 cm with f-number of 5.2. It provides a constant spectral resolution of 7500 corresponding to 4 pixels FWHM, over a wavelength range 200–1000 nm, displayable in a single spectrum. The spectrometer was coupled to an ICCD camera (DiCAM-PRO, PCO-Computer optics, Germany) for detection of the dispersed light. The overall linear dispersion of the Mechelle spectrometer–camera system ranges from 0.0078 (at 200 nm) to 0.032 nm pixel^{-1} (at 700 nm) with a high-resolution sensor of 1280 × 1024 pixels (9 × 9 μm^2). The ICCD was triggered optically, at a typical delay time of 1500 ns and gate width 2500 ns for measurements performed in air at atmospheric pressure. In case of vacuum measurements, the delay time and the gate width were changed to 50 and 1500 ns, respectively, due to the fast expansion of plasma plume in this case. The ICCD camera control was performed via special multichannel instrument software.

Each LIBS spectrum is the average of 5 spectra taken at five different positions (10 shots at each position) after two cleaning shots. The obtained spectra have been analyzed using the LIBS^{++} software [25]. The lens-to-sample surface distance is controlled by a micrometer translation stage in order to achieve precise focusing inside the target and avoid breakdown in air and/or defocusing on the surface.

3. Results and discussion

3.1. Dependence of LIBS signal on the sample temperature

3.1.1. Measurements in air at atmospheric pressure

The intensity of the emission lines in laser-induced plasma is strongly affected by the sample temperature. It has been established in previously published work that with increasing the sample temperature, the emission intensity of the spectral lines increases [21]. The integrated intensity (peak area) for certain spectral lines of Cu, Pb, Sn, and Zn elements was

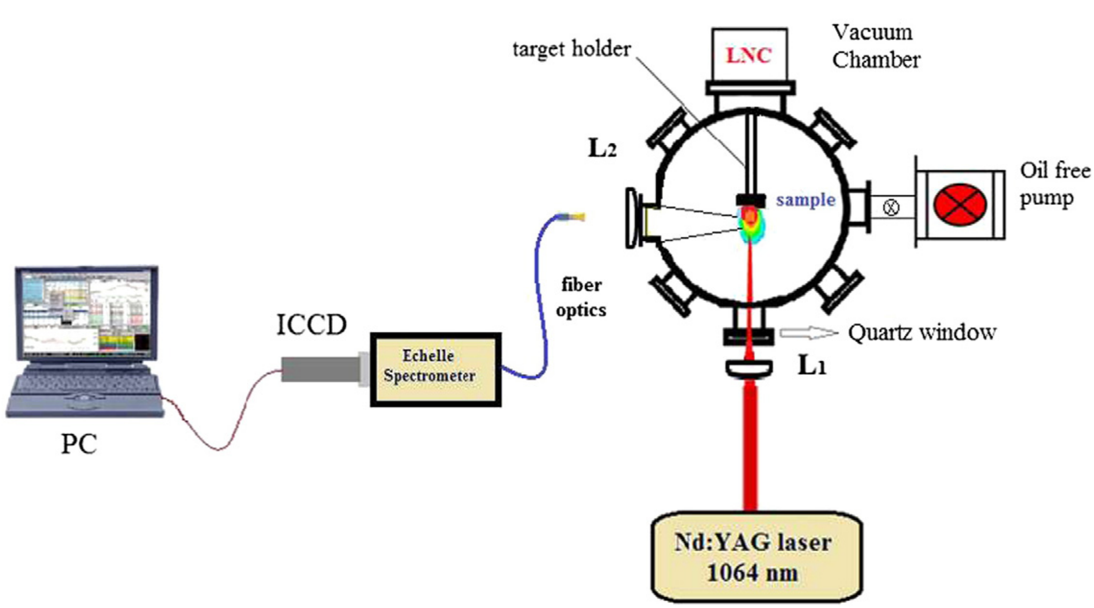

Fig. 1. Schematic diagram of the experimental setup [LNC, liquid nitrogen container, L_1 (f = 7.5 cm); and L_2 (f = 5 cm) are plano-convex collimating lenses].