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Analytical Note

An experimental observation of the different behavior of ionic and neutral lines of iron as a function of number density in a binary carbon–iron mixture

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ABSTRACT

We report on the dependence of the intensities of atomic and ionic lines emitted by a nanosecond laser-induced plasma on the atomic number densities of the constituents of a *binary* mixture formed of carbon and iron. We show that the packing density of the sample greatly affects the relative standard deviation of the emission lines. Furthermore, we show that the variation of the intensities of the C and Fe emission lines depends in a non-trivial way on the relative C–Fe concentration. The intensities of Fe neutral atomic lines behave differently than those of the ionic ones particularly at and above concentrations of 75%–80% Fe embedded in a carbon matrix. Unlike the emission from neutral Fe, those from ionic Fe yield a very sharp decrease followed by an equally strong increase of the emission lines over a relatively small range of relative concentration of C and Fe. To better investigate this effect, we have compared the results obtained with nanosecond-LIBS to those with femtosecond-LIBS and found that this phenomenon disappears. The physical interpretation of the sharp decrease followed by an equally sharp increase in the emission intensities from Fe ions as the concentration of Fe is increased requires more studies.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a well-known analytical technique that can provide the elemental composition of a sample in a solid, liquid or gaseous phase [1–3]. LIBS relies on the spectral analysis of atomic, ionic and occasionally molecular lines emitted by the plasma plume initiated above the surface of a sample to be investigated. This plasma is typically generated by focusing nanosecond long laser pulses with an optical fluence large enough to break down the matrix of the target. The photon flux heats up and vaporizes a relatively small portion of the material (typically a few hundreds of nanograms). The vaporized material contains free electrons, atoms, ions, molecules, and fragments. The free electrons gain energy by means of inverse bremsstrahlung and electron collisions, leading to avalanche ionization. As the plasma cools down, it emits characteristic light through various emission and recombination processes.

Due to its versatility and simplicity, LIBS has been used for a wide range of analytical applications [4]. These include simultaneous multi-elemental analyses of metals, and biological samples [5–7]. However, despite the widespread use of LIBS, a number of fundamental processes are still not fully explained and to some extent are at times ignored. This is in part due to the fact that high power laser–matter interaction results in numerous complex processes that take place in non-trivial conditions. To name a few, LIBS plasmas are not necessarily uniform; the plasma plume is typically influenced by the laser characteristics which are not always monitored, by sample properties which are not always fully known, and the environment surrounding the sample of interest which cannot always be fully controlled and/or monitored [8,9]. Therefore, a *quantitative* analysis of the elemental composition of a sample based on the use of such plasmas remains a challenging task. In particular, matrix effects may limit the domain of application of LIBS and our ability to provide an analysis with a very high degree of accuracy. For the purpose of this paper, matrix effects are those that yield a measurable variation of the LIBS spectra with a slight change in the composition or property of the target.

Many authors have addressed matrix effects on LIBS spectra. Wisburn et al. [10] reported on grain size effects on the measured intensities of LIBS spectra of cadmium. Such effects stem from the laser's sampling process. These authors observed that for samples contaminated with the same amount of weight of Cd relative to the weight of the solution but with grain sizes that vary from 0.38 mm, to 1.1 mm, the LIBS intensities produced are proportional to the grain sizes. Eppler et al. [11] investigated the effects of chemical speciation and matrix composition on the Pb and Ba concentrations in sand and soil matrices using LIBS. With changes of the bulk matrix from pure sand to pure soil composition, the Ba (II)/C(I) signal was found to decrease. They concluded that because of the dependence of analyte emissions on chemical speciation and matrix composition, the accuracy of LIBS measurements can be

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expected to degrade when calibrations are not compound- and matrix-specific.

Several approaches for matrix effect correction were proposed [11,12]. One of the most convenient approaches is to determine the element concentrations by the line intensity signals obtained from a standard reference having a similar matrix. Unfortunately, it is not always possible to obtain standard references and their corresponding calibration curves. Recently, an alternative approach of calibration free was proposed [13]. This method relies on the assumption that the plasma is in local thermodynamic equilibrium (LTE), and optically thin. The hypothesis of stoichiometric ablation should also be considered. However, these assumptions are not always valid particularly when experimental parameters vary largely. Another approach is to employ statistical multivariate analysis (MVA) methods. They allow signals from other emission lines at other points in the spectrum to partially correct for chemical matrix effects that may be induced by the presence of these other elements. Studies which have investigated MVA include Sirven et al. [14], Clegg et al. [15], Tucker et al. [16], Dyar et al. [17,18], and Anderson et al. [19].

In this paper, we report on the analysis of the LIBS spectra of a sample with a known and controlled ratio of concentration of C and Fe as a function of the number density of a particular element in a binary target sample. To achieve this, we recorded the LIBS spectrum of a sample with a *known and controlled* ratio of the concentrations of C and Fe. LIBS spectra are thus recorded for two types of compounds: C embedded in a Fe matrix, and of Fe embedded in a C matrix. Owing to the complexity of plasma phenomenon, care was taken to ensure that to within the experimental uncertainties, these spectra were recorded under the same experimental conditions. A careful analysis of the variation of the intensity of some of the most persistent atomic and ionic lines with the number densities of C and Fe reveals two critical observations. First, the surface morphology of the sample investigated, and more specifically the packing density of its constituents, greatly affects the relative standard deviation of the LIBS emission lines. Packing density, an empirical parameter that describes the density of solid particles obtained when they are packed closely has been studied experimentally and theoretically by many groups [20–22]. To illustrate the meaning of packing density, it is useful to note that to a higher packing density corresponds a lower free space. Second, we find that the LIBS intensities of atomic and ionic emission lines of Fe behave differently with the number density of iron embedded in carbon. Under the same experimental conditions, and for number densities of Fe embedded in C below 5.2×10^{22} atoms/cm^3 (corresponding to Fe atomic number concentration of about 75%), the LIBS spectral emission from neutral atomic and ionic Fe emission lines vary almost linearly in agreement with models that assume a state of local thermodynamic equilibrium (LTE) [23,24]. However, for the ionic emission lines and for number densities of Fe higher than about 5.2×10^{22} atoms/cm^3, the relation is no longer linear. The variation of the intensities of C (which is itself embedded in a Fe matrix) as a function of number density is rather complex. Throughout this paper, all number densities reported are the calculated concentrations in the sample and not in the plasma.

2. Experimental

2.1. Sample preparation

Pressed pellets have been investigated for a variety of reasons. For example, Borisov et al. investigated pressed pellet surrogates for Pu material disposition using laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) while Eivindson used them for X-ray fluorescence (XRF) analysis of ferrosilicon alloys by [25,26]. We prepared pellets to control the atomic number densities in the sample to be investigated using LIBS. Various amounts of graphite (C) and pure iron (Fe) were measured and mixed together to form the $C_{1-x}Fe_x$ composites using powdered graphite (Spectrum, USA) and iron (99% Powder, 325 Mesh, Acros Organics) as sources. The mixtures were hand ground thoroughly in an Agate mortar for approximately 6 min with no binder added to the mixture, then fitted in a 15 mm bore stainless steel (non-magnetic steel, 300 series) die, and pressed at 4500 psi (Benchtop shop press, Big Red). The cylindrical pellets obtained had a 15 mm diameter, thicknesses ranging from 2.75 to 4.55 mm, and concentrations that varied from 1000:1 to 1:1000 (mole ratio) of C to Fe (to within 0.1%). Fig. 1 shows high-resolution images of the pellets obtained using a field emission scanning electron microscope (JEOL JSM-7500F SEM). This Figure reveals that the sizes of the C and Fe particles are 1–10 μm and 20–200 μm respectively.

2.2. Setup and data acquisition

A typical automated nanosecond-LIBS experimental setup is shown in Fig. 2. It consists of a Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (B.M. Industries Thomson-CSF Series 5000) operating at the fundamental wavelength with a pulsed duration of 10 ns and a focal spot area of about 1.6×10^{-3} cm^2 (450 μm diameter which is large enough to include both C and Fe) which yield a typical irradiance of about 5×10^9 W/cm^2. An energy meter (FieldMaxII-TOP, Coherent Inc.) and a digital storage oscilloscope (Tektronix TDS2024B, 200 MHz) with high speed Si photo detector (DET210, Thorlabs) were employed to measure and monitor continuously shot to shot laser pulses. The laser beam was focused onto the sample surface by a 60 mm focal length fused silica Bi-Convex lens to create a plasma. A motorized stage with x–y translation was used to automatically translate the sample during the measurement. Optical emissions from the plasma plume were collected under normal atmospheric pressure by a fiber collimation lens with a diameter of 6 mm and focal length of 8.7 mm. This lens was located about 30 mm from the plasma and at 45° with respect to the laser beam and focused onto an optical fiber located at the focal plane of the collecting lens which allows the collection of the LIBS signals from the entire plasma plume volume which is estimated to reach around 15–25 mm^3. A 50 μm core diameter fiber-optic was coupled to a 50 μm slit aperture of an Echelle spectrograph with an Intensified Charge Coupled Device (ICCD) camera (iStar, Andor Technology, ME 5000, DH734-18F O3). Andor's Echelle spectrograph is designed to operate in the wavelength region ranging from 200 to 975 nm in a single acquisition, with a spectral resolution power of 4000 corresponding to 4 pixels FWHM. Emission from the plasma was collected 300 ns after the Q-switched pulse, with an integration time of 700 μs by an onboard digital delay generator (DDG) of the spectrograph. To reduce effects of air interference, LIBS spectra were collected in a helium environment.

It has been reported that quantitative and semi-quantitative analysis of LIBS suffers from poor reproducibility [27]. Many optimization procedures were proposed to improve reproducibility of the signal to noise ratio of LIBS and to minimize the fluctuations due to the non-uniformity of the sample. For our measurements, the effect due to the variation of geometrical focusing on the sample surface was controlled and reduced following three steps. First the sample surface position was set up so that the plasma emission is centered on the optical axis of the fiber collimation lens. This was achieved by optimizing the LIBS signal as the sample surface position and the focusing lens were adjusted vertically and uniformly. A LabView-based computer controlled program was used to maintain a fix distance between the sample surface and the focusing lens during this optimization step. Second, the distance between the focusing lens to the sample surface was set to yield maximum peak intensities and then the focusing lens position was slightly adjusted for a minimum spectral line broadening and least possible fluctuation of the LIBS signal. Third, the distance between the fiber collimation lens and the plasma was set to maximize the intensity of the LIBS signal and minimize its fluctuations.

Furthermore, a motorized stage was used to control the sample surface height each time a sample was replaced by another. To check for the uniformity of the distribution of C and Fe elements contained in