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Analysis of magnesium and copper in aluminum alloys with high repetition rate laser-ablation spark-induced breakdown spectroscopy

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A B S T R A C T

In order to improve the analytical speed and performance of laser-ablation based atomic emission spectroscopy, high repetition rate laser-ablation spark-induced breakdown spectroscopy (HRR LA-SIBS) was first developed. Magnesium and copper in aluminum alloys were analyzed with this technique. In the experiments, the fundamental output of an acousto-optically Q-switched Nd:YAG laser operated at 1 kHz repetition rate with low pulse energy and ~120 ns pulse width was used to ablate the samples and the plasma emission was enhanced by spark discharge. The spectra were recorded with a compact fiber spectrometer with non-intensified charge-coupled device in non-gating mode. Different parameters relative with analytical performance, such as capacitance, voltage, laser pulse energy were optimized. Under current experimental conditions, calibration curves of magnesium and copper in aluminum alloys were built and limits of detection of them were determined to be 14.0 and 9.9 ppm by HRR LA-SIBS, respectively, which were 8–12 folds better than that achieved by HRR LA under similar experimental condition without spark discharge. The analytical sensitivities are close to those obtained with conventional LIBS but with improved analytical speed as well as possibility of using compact fiber spectrometer. Under high repetition rate operation, the noise level can be decreased and the analytical reproducibility can be improved obviously by averaging multiple measurements within short time. High repetition rate operation of laser-ablation spark-induced breakdown spectroscopy is very helpful for improving analytical speed. It is possible to find applications in fast elements analysis, especially fast two-dimension elemental mapping of solid samples.

1. Introduction

In the past decades, laser-induced breakdown spectroscopy (LIBS) has acquired significant development on both theories and applications [1,2]. However, most of the conventional LIBS studies are based on electro-optically (EO) Q-switched Nd:YAG laser operated at low repetition rate (usually at 5–10 Hz). The pulse energies are usually hundreds of micro joules and the pulse widths are usually several nanoseconds. EO Q-switched Nd:YAG laser usually has larger volume and is hard for building portable LIBS system. When the laser unit operates at low repetition rate, only 5–10 laser pulses act on the sample surface and generate plasma emission thus the repetition rate of data acquisition is limited to 5–10 Hz, leading to a relatively lower analytical speed if considering the possible data acquisition and processing speed of modern electrical instruments. Therefore, it is potentially to increase the analytical speed of LIBS by utilizing high repetition rate (HRR) laser sources. This will not only be able to speed up the analytical speed, but also be able to introduce several other new aspects for LIBS technique. First, HRR laser sources are usually compact, which is helpful for building portable LIBS system. Not considering femto-second pulsed laser, HRR laser sources have been used in LIBS include compact diode-pumped EO [3–7] or acousto-optically (AO) Q-switched Nd:YAG laser [8], microchip lasers [9–12] and fiber lasers [13–16]. Second, due to the low pulse energy of the laser, continuum background of the plasma was usually weak. The spectrum was possible be recorded with compact fiber spectrometers with non-intensified charge-coupled device in non-gating mode [6,9–11,13,14,16]. This is also helpful to reduce the whole size of the LIBS system; Third, HRR operation is very helpful for improving mapping speed while using LIBS to realize two-dimension (2D) elemental mapping of solid samples [4,5].

However, the pulse energy of the lasers operated at high repetition rate is usually low. This will generate weak plasma and lead to low analytical sensitivity. Therefore, it is necessary to find new approaches to enhance the signal and improve the analytical sensitivity of LIBS while using HRR laser sources.

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Several approaches have been used to enhance the signal intensity and improve the analytical sensitivity of LIBS operated at low repetition rate, such as double-pulse LIBS (DP-LIBS) [17,18], laser-induced fluorescence (LIF) combined with LIBS (LIBS-LIF) [19–21] and spark discharge assisted LIBS, including microsecond spark discharge [22,23] and fast spark discharge [24–28] depending on the time constant of the discharge circuit which was determined by capacitance of the capacitor and resistor used in the discharge circuit. Due to the low pulse energies of high repetition rate laser sources and lack of high repetition rate tunable laser source with high peak power except femto-second laser systems, it is hard to conduct DP-LIBS or LIBS-LIF measurements based on nanosecond laser systems. However, the circuit of spark discharge is relatively simple than laser system, and the spark discharge can be operated at high repetition rate provided that suitable electric parameters, such as capacitance, resistance, time constant and discharge voltage have been selected.

Spark-induced breakdown spectroscopy (SIBS) is another analytical atomic spectroscopy technique. In this technique, a high voltage spark discharge is used to ablate and break down the samples and the plasma emission is analyzed for elemental analysis of the samples [29]. In the past decades, SIBS has also been developed to analyze toxic metals or total carbon in soils [30–32], dust [33], industrial emissions [34], cement [35], fuel [36] and bio-aerosols [37]. In above-mentioned spark-discharge assisted LIBS or fast discharge assisted LIBS, if the laser pulse energy was low, sample could be ablated but might not be thoroughly broken down to atoms or thoroughly atomization. In this case, the spark discharge plays a major role to break down the ablated samples, thus it is more suitable to be termed it with laser-ablation (LA) spark-induced breakdown spectroscopy (LA-SIBS). Further, if the laser and the spark discharge are operated at high repetition rate, it is suggested to be termed with HRR LA-SIBS.

This article will report a first study on HRR LA-SIBS. A HRR LA-SIBS spectral analysis system has been established in our laboratory. The effects of different parameters on the signal intensities were studied to find the optimal experimental condition. The spectral analytical performance of HRR LA-SIBS on the magnesium and copper analysis for aluminum alloy was evaluated and discussed.

2. Experimental

2.1. Experimental setup

A schematic diagram of experimental setup of HRR LA-SIBS is shown in Fig. 1. The fundamental output of a compact diode-pumped AO Q-switched Nd:YAG laser (Changchun New Industries optoelectronics Tech. Co. Ltd. Model: HPL-1064-QM) at 1064 nm was utilized as laser source for the laser–ablation. The laser worked at 1 kHz repetition rate with pulse energy of <13 mJ and pulse width (full width at half maximum, FWHM) of ~120 ns. The diameter of the laser beam was ~8 mm after beam-expanding. The laser was focused on the sample surface with a spherical lens L1 (f = 60 mm) to ablate the sample and produce a plasma at the same time. The aluminum alloy sample was mounted on an x-y motion platform which kept moving at 2 mm/s speeds during all the experiments. The sample was electrically insulated from the platform by inserting a piece of ceramic plate between the sample and the platform.

A direct current (DC) high voltage power supply (4 kV, 50 mA) was used to charge a high voltage capacitor C *via* a current -limiting resistor R1 (R1 = 80 kΩ). A tungsten needle was selected as the anode for the spark discharge. The diameter of the tungsten needle was 2 mm, and the tip was tapered to cone shape. The tungsten needle was placed horizontally with a tilt angle of 45° in respect of the sample surface and the perpendicular distance from the needle tip to sample surface was fixed at 3 mm. A 4 Ω current-limiting resistor (R2) was added in the discharge circuit to limit discharge current. The cathode of the discharge circuit was the aluminum sample itself. Once plasma was produced by the ablation laser, the air gap between the anode and cathode became conductive and a spark discharge was triggered immediately.

The emission from the laser-induced plasma and spark discharge was collected and collimated by quartz lens L2 (f = 150 mm) and

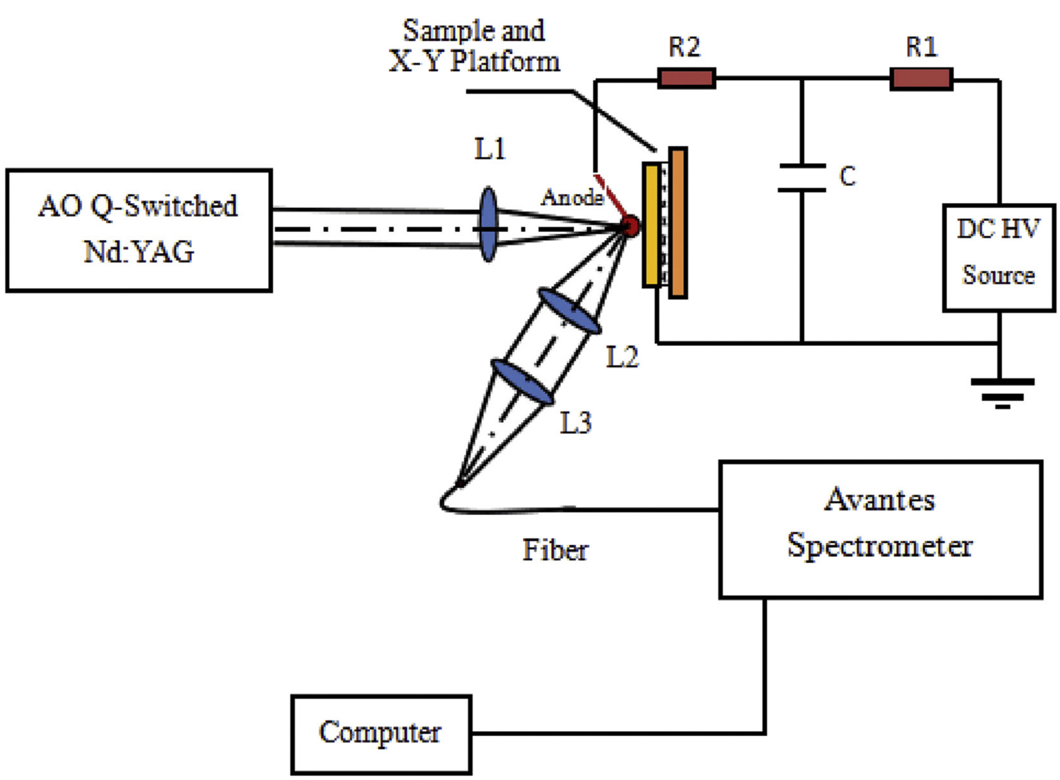

Fig. 1. Schematic diagram of experimental setup of HRR LA-SIBS.