Surface characterization of stainless HP-40 steel using laser induced \(\mu\)-breakdown spectroscopy (\(\mu\)-LIBS)

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Abstract. In the present study, optical microscopy in stereoscopic mode coupled to laser-induced \(\mu\)-breakdown spectroscopy (\(\mu\)-LIBS) was applied for analysing HP-40 steel samples. microLIBS (\(\mu\)-LIBS) is a new growing area that employs low energy laser pulses for the generation of plasma emission, which allow the realization of localized microanalysis [1]. This new LIBS instrument was used for the surface characterization of the steel samples in the spectral range from 356 to 401 nm. Elements such as Cr, Ni, Fe, Nb, Pb, Mo, C, Mn and Si in the steel samples were investigated. The results allowed the construction of elemental distribution profiles of the samples. Complementarily the HP-40 steel samples were superficially characterized by Scanning Electron Microscope (SEM).

1. Introduction

Reformer tubes are commonly used in furnaces to produce hydrogen in the refining and petrochemical. Their most critical components are the radiant tubes, where extreme pressure and temperature conditions required HP grade steels [2-4], owing to their high mechanical and corrosion resistances at high temperatures. They are designed for a nominal life of 100,000h in service conditions, typically 980°C with an internal pressure of 10 to 40 bars. Nevertheless, the HP grade alloys undergo damage with time, caused by the extreme work conditions. With reference to the foregoing arises the fact analyse microstructural changes that occur in steels using laser-induced breakdown spectroscopy (LIBS). Laser-induced breakdown spectroscopy is an analytical technique where atoms and ions are mainly formed in their excited states as product of interaction between a tightly focused laser beam and the material sample. The interaction among matter and high-density photons creates a plasma plume, which evolves with time and may eventually acquire thermodynamic equilibrium. One of the main features of this technique is that it does not need any sample preparation, unlike conventional spectroscopic analytical techniques [5]. The present paper report the results of the characterization of the HP-40 steel coming from the reformer furnaces pipes out of service by the presence of cracks and structure damages. Implemented laser induced breakdown spectroscopy coupled with optical microscopy that generates a microLIBS device (\(\mu\)-LIBS). This device allowed carry out a localized microanalysis of surfaces of HP 40 steels. The HP-40 steel samples were superficially characterized by Scanning Electron Microscope (SEM).

2. Experimental description

HP-40 steels samples from tubes of reformer furnaces removed from the industry with 65000-66000 hours. Table 1 shows the elemental composition reported in accordance with global standards of steel. \(\mu\)-LIBS device was implemented as shown in Figure 1. Nd: YAG laser (Quanta-Ray INDI) with a
fundamental wavelength of 532nm, pulse width of 7ns, repetition frequency of 10Hz, is employed to generate the plasma. The laser intensity is reduced using an attenuator in a range from 50% to 60%. The size laser beam spot is reduced through an aluminium sheet with a hole of approximately 3.18mm in diameter and reflected by a triangular prism to the side entrance of the microscope SM-LUX-POL (Leitz Wetzlar, Germany), allowing to focus the laser beam perpendicularly into the area of interest, using an Olympus 10x objective. Finally, we obtain a laser beam with an intensity of 2.2mJ per pulse. The microscope was used in stereoscopic mode (i.e. with an external light source). A Shamrock spectrometer 500i (Andor Technology), coupled to a detector ICCD (intensified charge-coupled device) iStart 720 Gen II (Andor Technology) of 1024x256 pixels, with detectors of 26x26µm was used. The experimental operations were controlled by PC and carried out in air at atmospheric pressure.

![Figure 1. Experimental assembly μ-LIBS.](image)

In addition, we used a camera Guppy GF046C (Allied) on the top of the microscope to localize the microanalysis region. The elemental distribution profiles were obtained over the surface in the range 356-401nm, using a grid of 1200lines/mm. The acquisition time of signal was 1µs with a delay of 1µs after laser shooting the surface. With these times and an accumulation of 5 pulses was possible to spectrally solve, the emission lines of the elements present in the μ-plasma.

The Scanning Electron Microscopy micrographs of the HP-40 steel were obtained using a Digital Scanning Electron Microscope (FEI Quanta 650 FEG SEM), under the following analytical conditions: magnification=800-1024x, WD=9.2-10.0mm, HV=20kV, signal=Z Cont detector=ETD.

| Table 1. Elementary composition of HP-40 steel [6]. |
|-----------------------------------------------|
| Element | Composition (%) |
| Cr     | 23.5             |
| Ni     | 34.0             |
| Si     | 1.5              |
| C      | 0.37             |
| Mn     | Máx. 1.25        |
| S      | Máx. 0.003       |
| Pb     | Máx. 0.01        |
| Nb     | 0.7-1.5          |
| Mo     | Máx. 0.5         |

3. Results and discussion

3.1. Qualitative identification

The main goal of LIBS is to realize a chemical analysis at the atomic level; a key step is the appropriate identification of each emission line of a particular element in a neutral or ionized state. If the sample composition is identified approximately, the set-up can be adjusted to know the optimal spectral range where there are emission lines of the elements in analysis or to discard emission lines of elements outside the sample. Figure 2(a) shows spectrum of atomic emission in a spectral range from 356 to 401nm. Most of the lines in this region belong to transitions in neutral state (Cr, Pb, Ni, Fe, Mo and Mn), also emission lines of ionized state were identified (Si, C). All transitions are listed in the National Institute of Standards (NIST) database [7]. Laser-induced breakdown spectroscopy (LIBS) coupled with a microscope was utilized to find and focus the laser beam directly on precipitations observed in the samples (removed of service). Figure 2(b) shows spectrum of atomic emission in a spectral range from 356 to 401nm, the black line shows the spectrum of a zone of the sample without precipitations and the
blue line is the spectrum with the laser beam focus in a precipitation. It is notable in the blue spectrum a rise in signal intensities, which suggests an increase in concentration of the elements in this area.

**Figure 2.** LIBS Spectra of HP-40 steels (spectral range 356-401nm) (a) the arrows of colours indicate the location of atomic emission lines of elements in the steel. (b) Spectrum produced focusing the pulse laser in a zone affected by precipitation.

3.2. Elemental profiling

With µ-LIBS has been possible a micro-spatial analysis of steels. The distribution of selected trace element (Cr, Pb, Ni, Fe, Mo, Mn, Si, and C) was measured on 1cm² area approximately. Observed revealed similar accumulation for all the tracked elements across the scanned lines, we detected homogeneity in elemental distribution inside the sample of steel without any type of work. The opposite showed the samples extracted from the pipe (exposed to high pressures and temperatures), an elemental inhomogeneity can be clearly distinguished. The variations in composition of Pb, Ni, Fe, Mo, Mn, Si, and C were not very drastic compared with the changes in the composition of Cr. Figure 3(a) depicts chrome distribution with the more intense atomic emission (381.95nm). The Chromo content increases toward the precipitations, the results are confirmed with the observations in SEM.

**Figure 3.** (a) Distribution graph of the chrome (381.95nm) (b) Surface image of the crater of ablation produced by a pulse laser 7ns (FWHM) and 2.2mJ of energy on a sample of steel HP-40.

3.3. Superficial damage

The superficial damage of the analysed samples depends principally on the laser wavelength, the duration of the pulse and the positioning system, which will limit the superficial area of the crater produced by the ablation laser. LIBS is a technique considered practically not destructive, since the craters produced by the impacts of the pulses laser on flat surfaces of steel produce approximately craters of 200μm of diameter and a depth of penetration less than 1μm [1]. The area of approach can be diminished by the suitable optics. Spectral information of the steels was obtained producing craters of
minor area, diminishing the superficial damage in the analysed sample. The use of Objective Lenses of
microscope, an attenuator of energy and a laser beam reducer (3.18mm of diameter), it generated
diameters of superficial craters about 20µm (Figure 3(b)). With the parameters and the suitable optic, it
was achieved to obtain spectra of the zones affected by the precipitations.

3.4. Scanning electron microscopy

Figure 4 shows the SEM image of a precipitation in the HP-40 steel and the spectra overall composition
of the inclusion and surface texture. Detail of analysis show that the concentration of Cr in the two
spectra is (i) 25.84%, (ii) 62.12%; Fe is (i) 51.62%, (ii) 22.25%; Ni is (i) 20.56%, (ii) 3.46% and Si is
(i) 0.48%, (ii) 1.21%. The detailed analysis per SEM of the precipitation showed the variation in
chemical compositions in the steel HP-40, supporting the findings obtained by LIBS.

4. Conclusions

This work demonstrates of LIBS capabilities for mapping in surfaces, mainly by optimization of LIBS
ablation crater diameter. LIBS proved to be suitable for the fast analyses superficial. The measured Cr,
Pb, Ni, Fe, Mo, Mn, Si, and C profiles across the sample showed fluctuations and the agglomeration of
the elements in certain areas. We have shown that LIBS with microscope coupled can be successfully
applied as direct or complementary techniques in spatially resolved microchemical analysis of steel
samples. The sensibility, the selectivity and the versatility of this analytic technique make it ideal for
the surface characterization. The results indicate that the laser focal conditions and the energy of the
laser pulse are important parameters that determine the lateral resolution. Exist a direct correlation
between the sizes of the crater of ablation with the energy of the incident beam; craters of different sizes
for the same optical conditions can be generated.

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