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Infrared nanosecond pulsed laser irradiation of stainless steel: Micro iron-oxide zones generation

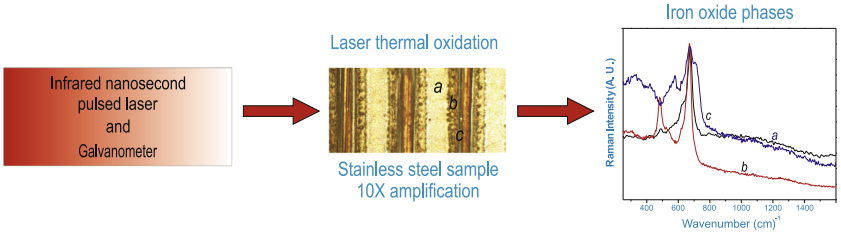
M. Ortiz-Morales [a,b,*], C. Frausto-Reyes [b], J.J. Soto-Bernal [a], S.E. Acosta-Ortiz [c], R. Gonzalez-Mota [a], I. Rosales-Candelas [a]

[a] Instituto Tecnológico de Aguascalientes, Lab. de Optoelectronica, Av. A. Lopez Mateos 1801 Ote. Fracc Bonagens, Aguascalientes 20256, Mexico
[b] Centro de Investigaciones en Óptica, A.C. Prol. Constitución 607, Fracc. Reserva Loma Bonita, Aguascalientes 20200, Mexico
[c] Lasertech, S.A. de C.V. Blvd. Olivares Santana 113, Fracc. El Dorado, Aguascalientes 20235, Mexico

HIGHLIGHTS

- Periodic patterns of different oxides zones were generated by IR laser irradiation.
- The films generated were attached to the metal by laser irradiation.
- After laser irradiation an elemental redistribution for each oxide zone was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanosecond-pulsed, infrared (1064 nm) laser irradiation was used to create periodic metal oxide coatings on the surface of two samples of commercial stainless steel at ambient conditions. A pattern of four different metal oxide zones was created using a galvanometer scanning head and a focused laser beam over each sample. This pattern is related to traverse direction of the laser beam scanning. Energy-dispersive X-ray spectroscopy (EDS) was used to find the elemental composition and Raman spectroscopy to characterize each oxide zone. Pulsed laser irradiation modified the composition of the stainless steel samples, affecting the concentration of the main components within each heat affected zone. The Raman spectra of the generated oxides have different intensity profiles, which suggest different oxide phases such as magnetite and maghemite. In addition, these oxides are not sensible to the laser power of the Raman system, as are the iron oxide powders reported in the literature. These experiments show that it is possible to generate periodic patterns of various iron oxide zones by laser irradiation, of stainless steel at ambient conditions, and that Raman spectroscopy is a useful punctual technique for the analysis and inspection of small oxide areas.

Introduction

Nowadays, iron oxides play an important role in several disciplines such as chemistry, corrosion science, geology, soil science, biology and medicine. Their applications are growing with the development of synthesis methods that allow creating iron oxides with specific characteristics; they are used as catalysts for other processes or as transport agents in medicine [1]. All iron oxides consist mainly of Fe and O but differ in composition and crystal structure. Iron oxides are of great interest for a variety of applications including opto-electronics, medicine, environmental remediation, pigments, corrosion protection, and gas sensing, among others [2–5].

* Corresponding author at: Centro de Investigaciones en Óptica, A.C. Prol. Constitución 607, Fracc. Reserva Loma Bonita, Aguascalientes 20200, Mexico. Tel.: +52 (449) 4428124; fax: +52 (449) 4428127.
E-mail address: maortiz@cio.mx (M. Ortiz-Morales).

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Laser thermal oxidation is a promising method for oxidation research and for obtaining new results about laser metal interaction and non-traditional methods such as laser synthesis from the mixture of various elements [6–16]. It has been shown that the synthesis of materials and their modification by laser radiation offer several advantages [8,14,17]. For example, Li et al. showed that UV lasers produce different colors on the surface of stainless steel that are related to the type of oxide generated [18], Adams et al. showed that it was also possible to create oxide coatings with Nd:YAG (1064 nm) and to determine the relation of these oxides to different colors [19] and Cui et al. showed that laser surface melting affects the surface morphology of the oxides formed in the heat affected zones [20–22]. Amulevicius et al. describes the synthesis of Fe–C compounds using laser irradiation on powder samples [23]. Despite numerous published papers on laser thermal oxidation of iron, to our knowledge there is still plenty of work to be done about the mechanisms and parameters that can be controlled in a laser based setup for materials synthesis and surface modification, such as atmosphere, laser wavelength, laser power, pulse width and frequency, scan speed and number of passes, to name only the most important. In addition, a focused laser spot has the advantage of generating, with the use of galvanometers, very localized oxide micro-zones, with particular forms or patterns. These complex forms and patterns can be used as small detectors or small zones for catalytic processes or in any other application that can be developed at microscale.

Raman spectroscopy has been recognized as a useful technique for the analysis of solid and powder materials, oxide films and oxide layers on metal surfaces [24–27]. In addition, this technique has the advantage that the sample to be analyzed can be as small as the laser focused spot size of the Raman system. As Raman spectroscopy uses a focused laser over the sample, the temperature of the analyzing zone may increase to such a degree that it could induce material alterations or even the destruction of the sample due to local laser heating [8,28]. Raman spectroscopy has been used to study different kinds of oxides, including iron, chromium, zinc, and TiO_2, among others, finding that it is possible to identify certain types of oxides by comparing their spectra and the position of their Raman bands [6,9,11,26,29,30].

Most of the works related to laser iron oxide generation, reported the analysis taking the average of the oxide zone in the heat affected zone and the color effect for appearance purposes, others are related to the generation and deposition of thin films over other substrates but taking into account the average oxide zone generated by the influence of laser heat. Considering the above, in this work, the main objective is to show that it is possible to generate different iron-oxide micro-zones on the surface of commercial stainless steel samples at ambient conditions using nanosecond pulsed, focused infrared laser irradiation, controlling the size and the shape of the generated patterns with a galvanometer scanning head. The oxide micro-zones generated can be precisely analyzed by Raman spectroscopy and Energy-dispersive X-ray spectroscopy; the results are compared to those reported in the literature.

Experimental

Two samples of commercial stainless steel plates AISI304 and AISI430 (1.5 mm in thickness) were used in this experiment; they were cut to 10 mm × 10 mm and cleaned with deionized water and alcohol, and dried in air.

For irradiation, the samples were mounted on a table at a distance equal to the focal length of the F-theta lens of an Ytterbium pulsed fiber laser (IPG Photonics *i*-series marker model YLP-1-100-30-30-HC) with an average power output of about 30 W and a wavelength of 1064. The laser pulse width and repetition rate used for irradiation were about 120 ns and 70 KHz, respectively. The diameter of the focused laser beam was about 55 μm, the spacing between laser scan lines was 0.2 mm, the scanning speed was 80 mm/s and three scanning cycles were performed.

The selection and identification of oxide zones to be analyzed was made with an optical microscope (Axioscope, Zeiss) with 10× and 40× objectives. The images of the selected zones were obtained using the Imagebase software and a M-PS-20 CCD camera from kappa.

The Raman spectra were measured using a micro-Raman system (Renishaw, 1000B with a backscattering geometry) with a 600 lines/mm grating, a CCD camera (Rem Cam 1024 × 256 pixels); and a laser diode at 830 nm wavelength as excitation source. The laser beam was focused onto the sample (spot-size of about 2 μm) using the 50× objective of a Leica (DMLM) microscope [29]. The calibration of the instrument was done using the 520 cm^{-1} Raman line of a silicon wafer. Grams software was used for data acquisition. Measurements were made at several points in each selected oxide zone and along several lines, although only a representative spectrum is shown. The shown Raman spectra have not been smoothed and were normalized to the most intense peak, and do not have a base line.

The elemental composition of the samples was determined with Energy-dispersive X-ray spectroscopy (EDS), which is used in a scanning electron microscope system (SEM, model JEOL JSM-5900LV). Also with this SEM equipment, the width of the oxide zones was measured. All the measurements were made at the sample surface in the selected oxide zones.

Results and discussion

Samples before irradiation

The Raman spectra of the surface of the two steel samples without laser irradiation (not shown), did not presented any Raman bands, and only the noise generated by the Raman system is observed. So far, it could be said that there was no oxide layer on the surface of the samples, or at least the oxide layer could not be detected under the measurement conditions.

Although the stainless steel type is mentioned in the experimental section, Energy-dispersive X-ray spectroscopy analysis was done to know the elemental composition of the samples. Table 1 shows the weight percent of the components with the highest concentration for samples (denoted as S1 for SE304 and S2 for SE430). The lack of oxygen is evident in both samples, which allowed us to corroborate the assumption that there was no oxide present before laser irradiation.

By analyzing the data shown in Table 1, it could be found that the ratio of Cr–Fe for S1 is 0.218 and for S2 is 0.204. This analysis allows us to observe and conclude that the samples were not of the same type of stainless steel.

Irradiated samples

Figs. 1 and 2 show the microscope images of the laser irradiated samples using the 10× and 40× objectives respectively. We identified a periodic pattern of three well defined zones, denoted as (*b*–*d*), on both sides of each marked line (zone *a*); these zones

Table 1
Energy-dispersive X-ray spectroscopy analysis for elemental composition of samples S1and S2 before laser irradiation (elements with the highest wt.%).

Sample	Elements	
	Cr (wt.%)	Fe (wt.%)
1	16.46	75.42
2	14.95	73.00