Real-Time Monitoring of High-Temperature Corrosion in Stainless Steels by Open-Path Laser-Induced Plasma Spectrometry

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Open-path laser-induced plasma spectrometry (OP-LIPS) represents an appealing alternative for the real-time monitoring of high-temperature processes due to its inherent non-invasive and remote capabilities. In this work, stainless steel samples have been analyzed at 10 meters from the laser source. The effect of the high-temperature conditions to the protective anti-corrosion layer have been analyzed, as well as additional factors such as the type of steel and the exposure time. The number of pulses required to ablate the alteration layer has been found to follow a linear relationship with the square root of the exposure time, in excellent agreement with the off-line thermogravimetric measurements described in the literature.

Index Headings: Laser-induced plasma spectrometry; LIPS; Remote analysis; Stainless steel; Real-time analysis; Laser plasmas.

INTRODUCTION

Stainless steel is a high-technology material with a diverse range of compositions, typical mechanical properties, and applications. Their wide variety of mechanical properties combined with excellent resistance to corrosion make stainless steels very versatile in their applicability. The addition of Cr in high concentration (over 10%) introduced excellent resistance to corrosion that fits most of their conventional applications. Further alloy modifications can be made to tailor the chemical composition to meet the needs of different corrosion conditions, strength requirements, or to improve weldability, machinability, work hardening, and formability.

Despite the above-mentioned properties, stainless steels in the presence of oxygen and at high or moderate temperature lose their protective oxide layer and experience superficial oxidation (scaling process). The result is the growing of a thin layer composed of a mixture of iron and chromium oxides in variable proportion and thickness depending on steel composition, sample temperature, environmental conditions (mainly humidity), and exposure time. Although oxidation is seldom the main cause of high-temperature corrosion failures, the oxidation performance is of primary interest because the properties of any formed oxide layer will determine the resistance to other aggressive elements in the environment and the morphological appearance of the steel.

The scaling process has been studied by several techniques, namely Raman spectroscopy, scanning electron microscopy, and secondary ion mass spectrometry. While Raman spectroscopy does not provide pure elemental information, the last two techniques are not capable of analyzing the sample while exposed to high-temperature conditions. Possible alternatives such as thermogravimetric techniques do not provide elemental information, limiting its use to calculations of mass and estimations of scaling thickness in samples of a restricted weight (typically a few milligrams). Regardless of the technique, the analysis must be done at the expense of extensive and tedious sample preparation.

Laser-induced plasma spectrometry (LIPS) represents a simple and contactless way to generate a population of gas-phase excited atoms from any condensed phase and pick up compositional information about the sample in the area affected by the laser radiation. As every individual laser pulse removes a certain amount of material from the sample surface, the spectroscopic information from a number of subsequent pulses on the same sample location will provide information about compositional changes along the sample thickness. In the absence of an internal standard, care must be taken as the ablation rate and the crater aspect ratio may change with depth.

The only requirement to generate a laser plasma from a solid sample is reaching a certain ablation threshold (variable with the material) easily achievable by tightly focusing the laser with the proper set of optics. In the most common situation, this is achieved by focusing the laser beam with single lenses with focal lengths under 100 cm. Needless to say, this situation does not apply when the samples are at very high temperature. Under these circumstances, a different approach based on the remote focusing and collection of the laser and plasma light by means of telescopic optics may be used. This instrumental variation, called open-path LIPS (OP-LIPS), keeps intact the inherent advantages of LIPS in terms of easy sampling, no sample preparation, and real-time data acquisition.

The present work goes deeper in the use of OP-LIPS as a technique to monitor the compositional changes occurring in stainless steels when subjected to high-temperature processes. Different samples were exposed to temperatures ranging from to 20 °C to 1200 °C while continuously analyzed by OP-LIPS. The real-time multielemental analysis of each generated plasma allows us to monitor changes in the Fe and Cr content as a function of temperature and exposure time in samples of variable composition.

EXPERIMENTAL SETUP

The spectrometer developed for this application is schematically depicted in Fig. 1. The flat beam from a
Nd:YAG laser (Spectron, Spectron SL854, pulse width: 12 ns, maximum output: 1500 mJ, beam diameter: 10 mm) operating in its fundamental wavelength was focused by means of a ×9 galilean telescope (beam expander). The telescope comprises a pair of lenses with focal lengths of −22 and −200 mm, respectively. The distance between lenses may be easily modified by means of a PC-controlled linear micrometric stage, resulting in accurate modification of the focus of the system. When the stage is placed in its arbitrary zero position, the focal length of the galilean telescope is 10 meters. As the laser exits the last lens of the beam expander, the 70 mm beam passes through the 110 mm aperture of a 300 mm diameter pierced mirror tilted 45° with respect to the laser path. Once the laser plasma was remotely generated, the laser light is collected by the reflective face of the mirror and focused by means of a newtonian telescope to the entrance slit of the spectrograph (Acton Research Inc., 0.275 m, f/3.8). Typically, an 1800 grooves mm⁻¹ grating was used to disperse the incoming light, which was detected with an intensified charge-coupled detector (Andor Technology, Instaspec IV). A pulse and delay generator (Stanford Research Systems, Mod. 535) triggered by a fast photodiode was used to control the delay and opening in the detector electronic shutter. In order to help in the alignment and positioning of the laser beam, a HeNe laser collinear with the Nd:YAG was introduced in the system through an aperture in the rear side of the Nd:YAG case and delivered through the rod in the Nd:YAG amplifier. This configuration did not affect the beam profile of the ablation beam.

Stainless steel probes supplied by ACERINOX S.A. (5 mm × 35 mm × 40 mm) were used as samples. Three different steel characterized steel grades were supplied: AISI 316L (16.705% Cr, 10.287% Ni, 2.204% Mo, 1.1% Mn), AISI 430 (16.155% Cr, 0.206% Ni, 0.021% Mo, 0.08 Mn), and AISI 304 (18.352% Cr, 8.211% Ni, 0.229% Mo, 1.8 Mn). Samples were placed on a holder specifically built to allow easy sample exchange in the vicinity of the oven as well as repetitive positioning at a fixed distance from the focusing system.

The spectral region between 536 nm and 564 nm was chosen to perform the real-time monitoring due to the possibility of the simultaneous presence of emission lines from Fe, Cr, Mo, and Ni with low spectral interferences. The emission lines for Cr(I) at 540.99 nm, Ni(I) at 547.69 nm, and Mo(I) at 550.65 nm were used. An additional line of Mo(I) at 553.30 nm and an Fe(I) line at 561.63 nm were used as well. After optimization using the signal-to-noise ratio of the Cr(I) line at 540.99 nm, spectra were recorded 2 s after the firing of each laser. The acquisition time for each spectrum was 2 s. Although no evidence of plasma shielding was observed, the laser energy per pulse was set at 900 mJ, corresponding to an energy density in the sample of 114 J cm⁻² (irradiance: 9.5 × 10⁹ W cm⁻²). Under these conditions, single-shot stainless steel spectra from samples placed 10 meters away from the laser source with signal-to-noise ratio (SNR) values of 109, 39, 21, and 34 for Cr, Ni, Mo, and Fe, respectively, were easily obtained. The relative standard deviation (RSD) of the absolute intensity signals for 50 consecutive laser shots was 7%, 8%, 11%, and 10% for Cr, Ni, Mo, and Fe, respectively.

The analysis of stainless steel samples at high temperature was performed in a laboratory oven placed 10 meters away from the laser source as this is the maximum distance available in the laboratory and represents a good approximation for the remote analysis in real scenarios.
such as steel-making companies. During the analysis time, a set of security interlocks and solid barriers were used in order to prevent accidental injuries. The analysis routine called for sample thermal stabilization for 10 minutes at a selected temperature, the opening of the oven door to allow optical access of the laser, and data acquisition. A specific holder was designed to keep the samples in the geometrical center of the oven, where the thermal stability is higher. During the analysis time (less than 60 s), the drop in the oven temperature does not significantly affect the sample temperature due to the low thermal conductivity of stainless steel (~12.9 W m$^{-1}$ K$^{-1}$).

RESULTS AND DISCUSSION

The OP-LIPS laser spectrometer described allows the follow up of the oxidation process in real time as long as the optical emission spectra from different laser shots (i.e., sample depth) exhibit qualitative or quantitative differences. Figure 2 shows two single shot spectra corresponding to the 5th (solid line) and 400th (dotted line) laser shots in an AISI 316L sample exposed at 1200 °C for 10 min. The spectrum corresponding to the scaled layer (solid line) mostly consists on an Fe rich scale layer with low levels of (a) Cr, (b) Ni, and (c and d) Mo when compared with the corresponding intensity in the non-scaled steel (dotted line). The explanation for this fact is well known, and it is based on the volatility of the Cr oxides at high temperature, enhanced by the presence of water vapor, which destroys the protective steel oxide layer by chemical etching of the oxide.$^{21}$ Under these conditions, the anti oxidation Cr$_2$O$_3$ layer follows the thermodynamically favored ($\Delta G = -83.1$ kJ/mol) reaction:

$$\frac{1}{2}\text{Cr}_2\text{O}_3(s) + \frac{3}{4}\text{O}_2(g) + \text{H}_2\text{O}(g) \leftrightarrow \text{Cr}_2\text{O}_3(\text{OH})_2(g)$$

being in effect the substitution of the Cr$_2$O$_3$ layer by a (Cr,Fe)$_2$O$_3$ layer (still keeping some anti-oxidation properties) that evolves into an Fe rich (Cr,Fe)$_2$O$_3$ layer without protective effect. This effect has been experimentally tested by auger electron spectroscopy (AES) analysis in 304L steel and depth profiling and chemical information about the process can be found in the references.$^{21}$ Once this scaled layer has been depleted (i.e., after 400 laser shots), the LIPS spectra obtained are identical to those obtained from the non-thermally treated samples.

The in-depth profile of Cr (as the key element in the scaling process) as a function of temperature is shown in Fig. 3. An AISI 316L was analyzed. The experiment was performed under identical conditions to those above, including the residence time of the samples at the selected temperature. A sample at room temperature was also analyzed as a control. The Cr signal was sum-normalized with respect to Fe. As observed, and up to 1000 laser pulses, the value remains constant in the vicinity of 0.8 for the control sample and the samples at 800 °C and at 900 °C. When the experiment was performed at 1000 °C, the first 100 spectra exhibited a marked decrease in Cr signal. Beyond this range, the signal went back to the normal value found when ablating a non-affected sample. The raising of the temperature up to 1200 °C produced a similar trend that lasted longer, about 400 laser pulses. This fact is explained as the monitoring of the progressively growing scaling layer and the concomitant Cr impoverishment of the outermost layer of the steel. It is worth noting that the described impoverishment starting at 1000 °C may take place even at lower temperatures as it depends critically on the flux of water/oxygen and the presence of other species in the surrounding atmosphere such as chlorides.$^{22}$ Our experimental setup did not allow for control of the mentioned parameters, however, and all the measurements were done under the laboratory conditions (constantly about 80% humidity and 25 °C). It is also important to stress that the possibility of analyzing the samples after cooling was ruled out because the scaling layer at room temperature is very brittle and exhibits very low adherence to the steel matrix. As a consequence, it cracks and flakes off very easily, making analysis difficult. Different attempts to decrease the laser energy.

![Fig. 2. Spectral differences between the spectra recorded in the scaled layer (solid line) and the one in the non-altered steel matrix (dotted line). (a) Cr(I) at 540.98 nm; (b) Ni(I) at 547.69 nm; (c) Mo(I) at 550.65 nm; and (d) Mo(I) at 553.31 nm.](image1)

![Fig. 3. In-depth profile of the Cr sum normalized intensity in an AISI 316L stainless steel at different temperatures.](image2)
were tried, but in all the situations the steel matrix was reached after a few shots.

One of the primary concerns relative to the scaling process is the rate at which the reaction progresses. Inasmuch as the oxide scale reaction product remains on the surface, the rate of reaction may be determined by measuring off-line the weight per unit area as a function of time.\textsuperscript{3,5,6} In order to check the capability of our OP-LIPS system for on-line following of the scaling process with time, an AISI 316L sample was subjected to a thermal treatment at 900 °C for 550 min while being analyzed at different times. This temperature was chosen because it represents the lower limit of many procedures related to steel-making (slab cutting, hot rolling, and others). The results, shown in Fig. 4, evidence how the sample starts to exhibit the scaling process within the first hour of residence within the oven. From this point, five measurements were taken at different time intervals. In all situations, 1000 single shot spectra were acquired. Again, the sum normalized Cr signal with respect to Fe was plotted. As shown, when the non-altered steel matrix was ablated, the value remains around 0.7 regardless of the number of shots and exposure time, while in the scaled zone the value drops to lower values. In general, the longer the exposure time, the lower the values. The hump observed in the scaled region corresponds to local accumulation of chromium oxides in the metal–scale interface while they migrate to the outer layers.

Kinetic law studies for the oxidation of 316L stainless steel\textsuperscript{23} have shown a $t^{1/2}$ dependence of the scale layer growth with time. Again, the studies had to be done by off-line measurements. Based on our data presented in Fig. 4, it was possible to obtain information about the dynamic growth of the scale layer in a quantitative way by determining the number of laser shots required to reach the non-affected steel matrix. The plot of this value versus the square root of residence time of the samples in the oven exhibits a linear trend as observed in Fig. 5. The fitting line exhibits a correlation coefficient of 0.995, indicating excellent correlation between these variables. The experiment was performed at 600 °C as well. The spectra obtained, as expected, did not differ from the one of the non-affected steel regardless of the exposure time (at least up to 550 min) and just a slight change in the surface color was in evidence.
The anti-oxidation properties of stainless steel do not come exclusively from its Cr content, but from a correct balance with other elements (mainly Ni and Mn) that confer any steel-grade-specific properties. In general, AISI 316L and AISI 304 as typical austenitic steels do not differ in terms of high-temperature corrosion capabilities due to their high chromium content and the nickel addition, which make them very corrosion resistant. 

However, AISI 430 is a ferritic steel with Cr concentration identical to its austenitic partners. In order to check the effect of the composition on the scaling process, the three mentioned steel grades were analyzed under identical conditions (1200°C, 1000 laser shots). The results are shown in Fig. 6. As expected, AISI 304 and AISI 316L have a similar trend: the corresponding region of low Cr content and the progressive increase in the ratio as the laser ablates non-scaled regions. After 400 laser shots, the ratio remains constant as the non-affected matrix is reached. The ferritic steel starts to exhibit a similar trend, but there is an abrupt change in the transition between the scaled and non-scaled zone due to the very low adherence of this scale layer, which flakes off. However, as the thickness is considerable, it takes several laser shots (in this case about 125) to remove the layer.

The capability of our system to perform direct sorting of steel grades exposed at high temperatures was checked as well. As observed in Fig. 7, the spectral features are identical for the three grades analyzed. The Fe lines dominate each spectrum, and some weak lines corresponding to the emission lines of Cr(I) at 540.99 nm, Ni(I) at 547.69 nm, and Mo(I) at 550.65 nm (marked with dotted lines to help in their identification) are visible. However, taking into account the differences in composition of the samples and the identical y-axis scale of the graph, it is clear that the variations do not correspond with the stoichiometry in the sample. Once the scale layer has been removed, sorting out is possible, as has been previously reported.

CONCLUSION

By means of an OP-LIPS system, real-time analysis of steel samples at high temperatures has been successfully performed. In particular, this work has emphasized the real-time capabilities of the technique to follow the compositional changes that take place during the exposure of stainless steel to high-temperature conditions. To our best knowledge, OP-LIPS is the only technique with the capability to kinetically follow the scaling process in any sample regardless of its size and shape. The technique opens new possibilities for chemical analysis in production plants where contactless, real-time data acquisition means considerable time savings and a major reduction in risk and human effort. The possible extension of our method to the monitoring of kinetic measurements has yet to be checked, but these preliminary results are rather encouraging about the future possibilities of the OP-LIPS approach.

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