Laser-induced fluorescence applied to laser welding of austenitic stainless steel for dilute alloying element detection

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Abstract
Optical spectral analysis of the laser weld plume is a common technique for non-contact, in situ weld plume analysis. However, the low sensitivity of optical emission spectroscopy limits the available information during 1070 nm wavelength laser welding, which is becoming the standard in many industrial operations. Here we demonstrate an improved sensitivity of optical spectroscopy by applying laser-induced fluorescence (LIF) for probing the hot gas plume induced during fiber laser welding of 304L austenitic stainless steel. As a proof-of-principle, we show that LIF is capable of resolving a spectral signal from silicon being emitted during welding. Optical detection of such a low concentration alloying element has not previously been reported and shows the capability of LIF for increased sensitivity. Silicon atoms in the weld plume were excited in the ultraviolet at 221.09 nm and detected at 221.64 nm. We demonstrate the detection of silicon LIF down to laser welding powers of 600 W (210 kW cm$^{-2}$) making this technique applicable even in low-power laser welding or additive manufacturing scenarios.

Keywords: laser welding, laser-induced fluorescence, spectroscopy

(Some figures may appear in colour only in the online journal)
In situ measurement techniques of alloy element vaporization are desirable so that real-time information can be used for process control feedback as well as to confirm model predictions. Optical emission spectroscopy (OES) is appealing in this regard as it is non-contact and non-destructive, and indeed, numerous groups have characterized vaporization losses with OES [18–23]. However, OES is most useful for understanding the interaction of the weld laser with the plume during CO2 laser welding due to inverse bremsstrahlung absorption of the 10 µm wavelength light [24]. However, recent advancements in robust high-power fiber and disc lasers have allowed them to supplant CO2 lasers for many industrial processes like laser welding. These systems operate at a wavelength of 1070 nm that is negligibly absorbed by the weld plume [25, 26], even at very high irradiances [27, 28]. At this wavelength, OES spectra typically only show emission peaks from un-ionized major alloy elements superimposed on a broad blackbody emission [29]. For instance, a comparison of CO2 and Nd:YAG (1064 nm) laser welding found that the latter produced plume temperatures nearer the melting point of steel (2000–3000 K) with CO2 welding plumes 3–4 times higher [26].

Due to its limited sensitivity, OES has not proved useful for detecting trace alloy elements, which can play a large role in determining mechanical and corrosion properties of important weld metals. In the specific case of continuous-wave 1070 nm laser welding of stainless steels, OES has identified only the larger concentration elements of Fe, Cr, Ni, and Mn [28, 30]. The spectroscopic emission of alloying elements like Si, C, N, and P escape detection because of their limited presence in the plume resulting from inherently lower concentrations and typically lower vapor pressure relative to Fe (P is a notable exception). Additionally, their strongest atomic emissions tend to be in the vacuum ultraviolet spectral regime (<192 nm) meaning only weaker emissions can be seen during non-vacuum welding operations.

In this work, we employ laser-induced fluorescence (LIF) to target dilute species by exciting their unique atomic absorption lines. This increases their excited state population well beyond its thermal equilibrium value and thus the optical emission from these excited states is significantly enhanced. LIF has been used to explore the chemical composition in combustion flames [31] and plasmas [32], and has been combined with laser-induced breakdown spectroscopy for enhanced chemical identification in steels [33, 34]. LIF was previously applied to gas tungsten arc welding of 304 stainless steel [35], but only to look for Mn. Although Mn has low abundance in stainless steel (1–2% by weight), it has a relatively high vapor pressure making it readily seen by OES alone. This is the first attempt to use LIF during laser welding for studying element vaporization and to increase spectroscopic sensitivity.

2. Experimental design

2.1. Instrumentation

Figure 1 shows a diagram of the experimental arrangement. An optical parametric oscillator (OPO) provides the fluorescence excitation light whose peak emission can be tuned with 0.01 nm resolution. The OPO has a spectral full width at half maximum of 0.08 nm, pulse duration of about 5 ns, and delivered 3.7 mJ per pulse. The experiments were performed inside a commercial weld booth. A series of highly reflective UV mirrors (R > 90%) steered the OPO laser pulses into the weld booth where a single, uncoated, 50.8 mm diameter planoconvex lens (f = 100 mm) focused the pulse 6 mm beyond the central line of the weld laser beam at a height of 1 mm above the weld metal surface. The focus of the OPO pulse was moved behind the plume in order to avoid spectral artefacts from the OPO heating the plume. It was important that the OPO beam was parallel to the weld sample surface (perpendicular to the weld beam) so that very little OPO light scattered from the metal surface into the spectrometer. Four-millimeter-thick uncoated fused silica windows protected the OPO delivery and collection optics from weld spatter. A pair of uncoated, planoconvex, 50.8 mm diameter (f = 100 mm) lenses collected light from the weld plume and focused it onto the tip of a 1 m long, non-solarizing fiber optic cable (1 mm diameter, numerical aperture 0.22). The optical axes of the collection and OPO focusing optics were perpendicular to one another as in figure 1. A Czerny–Turner style spectrometer with a fixed 3600 line mm\(^{-1}\) grating and a 10 µm slit resolved the incoming light with 0.08 nm resolution. We used the shortest integration time available for the charge-coupled device (CCD) detector (1.05 ms) as only the emission during and shortly after the excitation (on order of 10 ns) contained a LIF signal. Spectrum collection was triggered by the 10 Hz flash lamp from the OPO pump laser with 30 spectra averaged together to improve the signal-to-noise ratio.
Table 1. Composition of the 304L stainless steel sample measured by a commercial lab with direct-reading atom emission spectroscopy. Uncertainties are ±1% for Cr; ±5% for Ni; ±10% for Mn, Si and C; and ±25% for S and P.

| Element | Cr | Ni | Mn | Si | C | S | P | Fe | Balance |
|---------|----|----|----|----|---|---|---|----|---------|
| Concentration (mass %) | 18.4 | 8.0 | 1.14 | 0.33 | 0.05 | 0.026 | 0.035 |

In order to calibrate the wavelength of our spectrometer, we performed a separate laser-induced breakdown measurement on a pure silicon wafer. Laser pulses from the OPO were focused at the wafer surface in order to cause ablation and optical emission from the hot Si atoms. The OPO wavelength (350 nm) was tuned far from the detection range of the spectrometer so as not to saturate the CCD detector. Five Si atomic emission peaks from 220 nm to 222 nm were then compared to data in the NIST atomic spectra database [36] in order to create a calibration curve. This yielded an uncertainty in the wavelength in this range of \( \Delta \lambda = \pm 0.05 \) nm, and has the advantage that it is a local calibration over the narrow range that is of interest to our experiment.

Welding was performed by a ytterbium-doped fiber laser operating at 1070 nm and capable of 10 kW CW maximum output. The weld beam was focused to a 6 mm diameter, roughly flattop profile, spot with a \( f = 200 \) mm focusing lens mounted inside a water-cooled weld head assembly. The weld laser power was measured to within a 1.3% uncertainty (coverage factor of 2) using a NIST-traceable calibration. The material welded was 304L stainless steel pipe with the composition listed in table 1, a 102 mm outer diameter, and a 6.35 mm wall thickness. The pipe was mounted in a weld positioner and rotated at 700 degrees per minute. No shield gas or specific sample preparation was used.

2.2. Emission spectra and LIF excitation

For LIF, the choice of which spectral transitions to excite is very important. The emission spectra in figure 2 are calculated from the NIST atomic spectra database [36] and can be used to give a sense of the relative strength of atomic emission lines as well as overlapping spectral lines that could lead to ambiguous result interpretation. To generate figure 2, three input parameters are assumed: electron density, electron temperature, and the relative composition of the plume. We assume a very low electron density \( 10^{14} \) cm\(^{-3} \) and a steady-state temperature of 2500 K, which are consistent with the ranges found during 1064 nm laser welding [26]. The relative concentration of the elements in the plume will be slightly different than the composition of the base metal due to vapor pressure differences of each element and therefore, a slightly more complex analysis is required.

According to the Langmuir equation, the evaporation flux of an element \( i \), \( J_i \), from the weld pool is

\[
J_i = \frac{\alpha P}{\sqrt{2 \pi M_i R T}}
\]  

Although the Langmuir equation has been shown to overestimate the absolute amount of element loss at atmospheric pressures [10, 15], we seek only a relative value for the vapor concentration which eliminates this problem [37]. In this equation, \( P \) is the vapor pressure of element \( i \) over the alloy, \( \alpha \) is a unitless parameter between 0 and 1 that accounts for redeposition and is independent of species type [15], \( R \) is the gas constant, \( T \) the temperature, and \( M_i \) the relative molecular mass of the element. The vapor pressure of the element over the alloy can be calculated from the vapor pressure over the pure liquid, \( P_i^0 \), using Raoult’s law and the element’s relative mole fraction within the alloy, \( X_i \). The vapor pressures of Fe, Cr, Ni, Mn, and Si over their pure liquid as a function of temperature were calculated from Antoine coefficients [38]. Equation (1) now becomes

\[
J_i(T) = C * \left( \frac{X_i P_i^0(T)}{\sqrt{M_i}} \right) \equiv C * K_i(T)
\]  

where \( C \) includes all constants that are independent of element type. The relative mass of elements in the weld plume is then found by integrating equation (2) over the weld pool area and dividing that value by the sum of values from all elements. In this way, the constants, \( C \), will cancel and the only temperature dependence is from the Antoine coefficients. Therefore, the relative mass of each element in the vapor, \( M_i^{\text{vapor}} \), can be calculated according to

\[
M_i^{\text{vapor}} = \frac{\int J_i(T) \, dA}{\int \sum_i J_i(T) \, dA} = \frac{K_i(T)}{\sum_i K_i(T)}
\]  

We assume a uniform temperature distribution so that the integrals over area in equation (3) cancel. \( M_i^{\text{vapor}} \) values are then used in the NIST atomic spectra database [36] to calculate the relative intensities seen in figure 2.

Table 2 shows the values used to calculate the vapor concentration in equation (3). From these data, one sees that the vapor pressure of Mn is significantly higher than the other alloying elements, which leads to a significantly larger presence of Mn in the vapor. Indeed, a depletion of Mn from the welded region in stainless steels has been documented by several groups [6, 7, 9, 11]. Furthermore, the results in figure 2 qualitatively confirm our own spectroscopic observations. If the vapor pressure differences were not accounted for, the Mn emissions at 280 nm would appear to be well below the neighboring Fe peaks. However, experimentally we see that the emission from these three peaks is far more intense than the surrounding emissions matching the results in figure 2.

The spectral region of LIF operation was chosen above the vacuum ultraviolet threshold of 192 nm and below 400 nm since this is where dilute species (e.g., Si) have the strongest emissions that are also not strongly absorbed in air. As expected, the most intense lines in figure 2 are from the higher concentration elements (solid symbols) like Fe, Ni, Cr, and Mn. Of the dilute species, Si (open symbols) has the
next brightest lines near 250 nm and 220 nm. Therefore, as a proof-of-principle experiment we will show that LIF can target these Si lines and record their emission. The measurement of Si in the weld plume is also potentially important for joining processes as it plays an important role in the weld as a de-oxidizer, a ferrite phase stabilizer, and a solid solution stabilizing element.

Figure 3 shows the atomic energy diagram for the Si transitions targeted for fluorescence. This involves a near ground state excitation from $3s^23p^23P_1$ to the $3s3p^3D_{3/2}^0$ excited state with 221.089 nm photons. From there, a collision process further excites the Si atom such that 221.667 nm photons are emitted ($3s3p^3D_{3/2}^0 \rightarrow 3s^23p^23P_2$). Initially, we investigated higher intensity emissions involving $3s^23p^23P \leftrightarrow 3s3p^4s^1P^0$ transitions. However, significant interference with atomic Fe transitions in the 250–253 nm range made spectral interpretation here ambiguous (see figure 2(b)).

3. Results and discussion

Figure 4 shows the detected OES and LIF ultraviolet spectra during stainless steel welding with 800 W (280 kW cm$^{-2}$) laser power. These spectra were taken under the same experimental conditions and the apparent shift in the baseline is due to leakage of the OPO laser across pixels in the CCD. The OES spectrum reveals limited information with only a few Fe peaks appearing above the noise level near 250 nm. The presence of these peaks also defines an approximate noise floor for our OES measurements (see figure 2(b)). The inset then compares the OES signal to the LIF signal excited at 221.09 nm. The excited spectrum shows a strong fluorescence peak at 221.64 nm. This emission is in good agreement with the absorption and emission process shown in figure 3 within the uncertainty of our measurement. Under our measurement conditions, this peak was visible down to a weld laser power of 600 W (210 kW cm$^{-2}$). This does not necessarily represent a lower bound as an increase in signal integration and realignment of the optics to account for a changing plume dimension could further improve the detection limit at lower welding power.

To confirm that the signal at 221.64 nm is a resonant signal from the excitation of Si, we performed a sweep of excitation wavelength in 0.01 nm intervals. These data are shown in figure 5. These show that the maximum emission intensity at 221.64 nm occurred most strongly when excited at 221.09 nm. The excited spectrum shows a strong fluorescence peak at 221.64 nm. This emission is in good agreement with the absorption and emission process shown in figure 3 within the uncertainty of our measurement. Under our measurement conditions, this peak was visible down to a weld laser power of 600 W (210 kW cm$^{-2}$). This does not necessarily represent a lower bound as an increase in signal integration and realignment of the optics to account for a changing plume dimension could further improve the detection limit at lower welding power.
Other Si resonances were found in this spectral range. Sweeping the OPO wavelength between 221.75 nm and 221.85 nm revealed a resonant emission at 221.08 nm when excited at 221.83 nm. These peaks correspond to a resonant excitation of Si from the 3s23p2 3P2 state to the 3s3p3 D2 state, and an emission from this excited state to the 3s23p2 3P1 state. Database values [36] for the absorption and emission wavelengths are 221.806 nm and 221.089 nm, respectively, which agree with our measured results within the uncertainty of $\Delta \lambda \approx \pm 0.05$ nm. The intensity of this signal was found to be about three times smaller than the LIF signal shown in figure 4. It does, however, reaffirm the presence of Si in the weld plume.

Element detection via OES during stainless steel laser welding has been performed by several groups. Of particular note, is a measurement during very high power fiber laser welding. Kawahito et al used tightly focused 10 kW fiber laser light to achieve very high irradiances of 900 MW cm$^{-2}$ for welding of 304 stainless steel [39]. This work is relevant since spectral emission intensity increases with laser welding power density [18] so if one were to see more faint emission signals it would be at these very high irradiances. Under these intense conditions, OES revealed only neutral atoms of Fe, Cr, and Mn with no reported emission from lower concentration alloying elements.

An estimate of the improvement of sensitivity due to LIF can be made using the relative intensities Fe peak detected at 248.8 nm (see figure 4) by comparing the relative signal strengths calculated for figure 2(b). This Fe peak, which is seen in the OES measurement, corresponds to a relatively strong emission from the 3d6(3D)4s4p(1P0) $\times$ 5F4 to the 3d4s3 a5D3 state [36], and has an intensity in figure 2(b) of $3.8 \times 10^{-2}$ arbitrary units (a.u.). The relative intensity of the Si peak at 221.67 nm from figure 2(b) is $3.6 \times 10^{-6}$ a.u. Therefore, since LIF produced a signal from the 221.67 nm peak that was measured to have a 3.8 times greater signal-to-noise than the 248.8 nm Fe peak, it has improved the spectral sensitivity by a factor of $4.0 \times 10^4$.

Furthermore, using the calculated Si concentration values in the plume (table 2) and the weld pool composition (which we assume to be equal to the alloy composition), we estimate that our minimum level of detection for Si in stainless steel is 0.04% by mass. This is determined from the signal-to-noise value of the 221.64 nm peak trending to one and corresponds to a level of detection for Si in the plume of 190 $\mu$g g$^{-1}$.

Besides the large sensitivity improvement, LIF offers several other advantages over standard OES. It permits elemental specificity as only a narrow range of possible excitations exist within the bandwidth of the excitation source. Additionally, the LIF signal is localized in both space and time. The majority of collected LIF photons are from the area of spatial overlap of the excitation photons and the optical path of the collection optics, allowing for spatially-resolved elemental analysis. Furthermore, the very short excitation pulse and radiative lifetime of the LIF emission (about 5 ns and 10 ns, respectively) enables one to probe weld plume behavior temporally on a very short timescale. Future work will explore these possibilities as well as work towards increasing sensitivity further to detect even more dilute alloying elements like P, C, and S.

4. Conclusion

We have used LIF to measure optical emission from silicon atoms in a fiber laser weld plume. This demonstrates the effectiveness of LIF for in situ measurement of low concentration alloy elements during laser welding. We used an optical excitation of 221.09 $\pm$ 0.05 nm and recorded an emission at 221.64 $\pm$ 0.05 nm, which agree with the predicted values of absorption and emission of Si atoms at 221.089 nm and 221.667 nm, respectively. We estimate the minimum detectable Si concentration in 304L stainless steel for an applied laser weld power of 800 W (280 kW cm$^{-2}$) to be 0.04% by mass. The LIF signal was visible down to a weld laser power
of 600 W (210 kW cm$^{-2}$). We have estimated that LIF provides a sensitivity increase of optical detection of 10$^4$ times greater than can be achieved by OES alone.

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