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Technical Note

Sensitive analysis of carbon, chromium and silicon in steel using picosecond laser induced low pressure helium plasma

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ABSTRACT

An experimental study has been performed on the gas pressure and laser energy dependent variations of plasma emission intensities in Ar, He and N_2 ambient gases induced by picosecond (ps) Nd-YAG laser irradiation on low alloy steel (JSS) samples. The study is aimed to demonstrate distinct advantage of using low pressure He ambient gas in combination with ps laser for the sensitive ppm level detection of C, Si and Cr emission lines in the UV–VIS spectral region. The much shorter pulses of ps laser are chosen for the effective ablation at much lower energy and for the benefit of reducing the undesirable long heating of the sample surface. It is found that the C I 247.8 nm, Fe I 253.5 nm, and Si I 251.4 nm emission lines induced by the ps laser at 15 mJ are readily detected with He ambient gas of 2.6 kPA, featuring generally sharp spectral signals with very low background. The following experimental results using samples with various concentrations of C, Si and Cr impurities are shown to produce for each of those elements a linear calibration line with extrapolated zero intercept, demonstrating the applicability for their quantitative analyses, with a preliminary estimated detection limits of 20 μg/g, 15 μg/g, and 5 μg/g, for C, Si, and Cr, respectively. The possibility of applying the same setup for concentration depth profiling is also demonstrated.

1. Introduction

The precise elemental composition of a steel product is known to be very important for its quality specification and is commonly required by the consumers or end users [1,2]. A practical, sensitive and reliable measurement technique of C (carbon), Si (silicon) and Cr (chromium) concentrations in steel is in great demand for the regular inspection and assessment of steel products and remains an important and challenging issue in steel industry. In fact, the ability to meet the industry standard of elemental analysis for various grades of steel products has often been regarded as a benchmark for evaluating the performances of laser-induced breakdown spectroscopy (LIBS) as first proposed by Radziemski et al. [1].

The sensitivity of quantitative carbon analysis needed in steel industry covers the range of C concentration from a few percents to 10 μg/g or less, depending on the steel qualities required for the intended applications and the production conditions in the steel plants. In general, elemental analysis in steel industry requires the simultaneous measurement of many elements beside the three cited above. However, due to the experimental restriction in this study, we are mainly concerned with the three elements C, Si and Cr as the representative elements for the evaluation of the technique proposed in this work. The quantitative analysis of Cr in steel is required to have the limit of detection (LOD) in the range of 0.2% to 3%, while a much lower LOD down to 10 μg/g and below is required for C. A practical low cost and even field deployable system was proposed previously employing microchip laser in combination with Ocean Optics miniature spectrometer [2]. Unfortunately the reported detection limit of 400 ppm C/Fe falls short of the technical requirement mentioned above. On the other hand using the strong vacuum, UV C I 193.1 nm emission line detected in LIBS, Aragon et al. [3] reported a LOD of around 250 ppm. Subsequent studies [4–14] reported the achievement of even lower LOD, down to a few ppm by means of multiple pulse excitation technique, and in some cases employing the detection of stronger C emission line in deeper UV region. For example, LOD of a few μg/g were reported by Peter

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et al. [6] and Sturm et al. [5,7], respectively. An unusually low LOD of about 1.2 μg/g for C was also reported as a result of comprehensive optimization of the experimental condition [4]. It is nevertheless desirable to investigate the possibility of practical application of LIBS for sensitive analysis of the three elements in steel, in particular by avoiding the need of detecting the vacuum C I 193.1 nm emission line.

It is important to recall in this connection to the previously reported advantages of using low pressure He ambient gas in LIBS for suppressing the line broadening effect and the continuum background, which was successfully applied in the detection of well resolved H and D emission lines in LIBS [15]. These advantages were explained as due to the presence of metastable excited state of He atoms in the plasma which allows, via the Penning-like collision induced energy transfer process, for the more favorable delayed excitation of the H and D atoms after the plasma has cooled down along with the disappearance of a large part of the charged particles from the plasma. The remarkable improvements of those spectral qualities were also found to be applicable to a number of light elements [15]. As a light element, C is expected to benefit from similar improvement of the spectral quality of its C I 247.8 nm emission and thereby making possible its sensitive detection with standard LIBS spectrometer.

Another important factor considered for the realization of more competitive system is the advantage of picosecond (ps) laser as proposed recently [16–18]. Firstly, the much shorter laser pulses can effectively deliver the same amount of power density with much smaller laser energy and much shorter duration of irradiation. Secondly, it is also supposed to offer the benefit of reducing the unfavorable long heating of the sample surface in the use of nanosecond (ns) laser pulses operated at relatively large ablation energy as commonly found in conventional LIBS [3–14]. This long heating process may give rise to some thermally induced complications to the sample such as the local volume expansion and the impurity migration or segregation due to accumulated local heating during the successive ablation processes on the same sample spot. These processes will in turn induce unwanted changes of local impurity distribution leading to distorted experimental data. Lastly, the ps laser is further expected to reduce the size of crater created by the laser irradiation on the sample surface.

It is the purpose of the current study to investigate the expected advantages of adopting the He ambient gas and ps laser by comparing the relative merits of using different ambient gases at various pressures for the sensitive analysis of C, Si, and Cr in low alloy steel samples using their emission line in the ordinary UV–VIS region. The most favorable experimental condition will be employed in the following experiment for the determination of calibration lines for those elements along with the associated limits of detection (LOD).

1.1. Experimental procedure

The schematic diagram of the experimental arrangement is similar to that described previously [8]. In this experiment, the 1064 nm ps laser from Nd:YAG (Ekspla, PL 2143, 20 ps, maximum energy of 30 mJ) is operated in the Q switched mode at a repetition rate of 10 Hz with the laser output energy fixed at 15 mJ yielding a power density of around 100 TW/cm^2. The laser beam is focused by a high energy lens (f = 250 mm) and sent through a quartz window onto the surface of the sample. The shot to shot fluctuation of the laser is estimated to be about 2%.

The steel sample used in the experiment is a piece of low alloy steel series (JSS produced by The Iron and Steel Institute of Japan, Otemachi, Chiyoda-ku, Tokyo, Japan) with 30 mm diameter and 8 mm thickness. It is mounted as the irradiation target in a small, vacuum tight metal chamber of 25 cm diameter, which is evacuated with a vacuum pump and subsequently filled with the selected ambient gas at the desired pressure. Three kinds of gases are used in the experiment; namely, Ar, He and N_2 (all are prepared by Air Liquids, 5N) and the gas flow through the chamber is regulated by a needle valve in the air line and another valve in the pumping line. The chamber pressure is measured and monitored with the use of a digital absolute vacuum meter. The sample together with the whole chamber and multilayer lens can be moved in the laser beam direction with a stepper motor. The whole assembly can also be moved stepwise with a micrometer in a direction perpendicular to the laser beam. The sample can either be rotated at 1 rpm or fixed at a certain position during the irradiation.

For the spectral measurement of the plasma emission, an optical multichannel analyzer (OMA system, Andor I*Star intensified CCD 1024 × 256 pixels) of 0.012 nm spectral resolution at 500 nm is attached to a spectrograph (McPherson model 2061 with 1000 mm focal length f/8.6 Czerny Turner configuration) which is connected to an optical fiber on the other end. The entrance end of the fiber is inserted through a cylindrical quartz tube well into the chamber and kept at a position 50 mm sidewise from the sample but can be placed at different distances from the sample surface, allowing the fiber to collect effectively the emitted radiation entering within 27° of solid angle. The spectral window of the detector has a width of 16 nm at 500 nm wavelength. The accumulated spectra detected from 50 successive laser shots on the same spot are monitored on a screen, and recorded to yield the averaged results presented in this report.

1.2. Experimental results and discussion

Prior to the spectroscopic measurement, a visual inspection is conducted on the plasma generated by 15 mJ laser irradiation on the JSS sample in He ambient gas at 2 kPa in tight focus optical setup. The plasma is found to exhibit a typical hemispherical shape consisting of a primary and secondary plasma regions as observed previously with ns and ps laser in He ambient gas [8,12–14]. The relatively tiny primary plasma shows a very dense white color, while the much larger secondary plasma extending far beyond the primary plasma displays a bright whitish color arising mainly from the Fe emission lines. The radius of the secondary plasma is found to increase with decreasing pressure of the ambient gas. When the He gas pressure is reduced below 600 Pa, the secondary plasma edge becomes barely distinguishable. These plasma features are basically similar to those observed in the experiments using N_2 laser [12], TEA CO_2 [13] laser, XeCl laser [14] and ns Nd-YAG laser [8].

As the first part of our experiment, a measurement is performed on the pressure dependent variation of the spatially and time integrated emission intensities of three different elements (Fe, Si and C) from the sample. This is carried out by adjusting the light collecting assembly at the proper position in order to capture effectively the desired emission intensity. Meanwhile the OMA system is operated with 10 ns gate delay and 50 μs gate width, taking into account the prior knowledge concerning the time profiles of the emission intensities in the different ambient gases. The resulted time integrated intensities obtained with 15 mJ laser irradiation at various gas pressures are presented in Fig. 1 for the cases using the different ambient gases of He, Ar and N_2. It is interesting to note that apart from some small local deviations, the emission intensities of each of the Fe I 253.5 nm, Si I 251.6 nm dan C I 247.8 nm emission lines generally experience a steep climb up to their individual maximum at roughly the low gas pressure of around 2.6 kPa, which is followed by more or less a constant trend of decline with further increases of pressure. As expected, the Fe I 253.5 nm emission line has the highest intensity simply due to the largest concentration of Fe in the sample. In addition to that, the highest maximum emission intensity is found in the case of Ar ambient gas as also observed previously [15]. However, the background emission is also seen to be significantly stronger in the case of Ar ambient gas. In terms of S/B ratio, He ambient gas at the low pressure of about 2.6 kPA appears to be the optimal choice as an ambient gas for this experiment. Particularly in view of the superior spectral quality achieved with He ambient gas as displayed in the spectra reported here and also amply demonstrated in previous works [15]. We shall therefore perform the following experiments with ambient He gas at 2.6 kPa.