Note

Analysis of Scrapped Materials by Low-pressure Laser-induced Plasma Spectroscopy

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1. Introduction

The desire to effectively utilize natural reserves and to protect the environment from ever increasing nuisance city scrap has compelled human beings to adopt recycling option. This has helped much in saving the energy and resources required in massive initial mining, processing, transportation and smelting operations. One major concern regarding the recycling process is the inclusion of impurity elements, called tramp elements (Cu, Zn, Cr, Sn, Pb, Ni, *etc.*) which degrade the quality of final product. If any simple and rapid technique is available, then scrap material may be checked before melting and undesired components may be separated. Laser-induced plasma spectroscopy (LIPS) is a technique which can be very effectively utilized for this purpose.

Laser ablation is a process in which a surface is irradiated by an intense pulsed laser. The impact of the laser pulse leads to ejection of atoms and molecules from the surface, which is followed by laser breakdown plasma appearing as a bright plume. By monitoring of emission signals from this plasma certain atomic and molecular species can be detected. This technique has been applied for the direct qualitative and quantitative determination of composition of different matrices such as solids, liquids and gaseous samples.^{1–3)} Among many of its applications metallurgical sample analysis⁴⁾ has got significant popularity in the recent years due to its direct sample introduction capability.

LIPS is a promising analysis method and use of low pressure conditions has resulted in unique features as low fluctuation of the emission intensity as well as the high signal to background ratio.

In the present study, low pressure (LP)-LIPS has been utilized for the surface and depth profiling of model scrap materials.

2. Experimental

Schematic diagram of the experiment is shown in Fig. 1. Laser is irradiated in the upper port of the chamber and optical emissions from the plasma can be monitored by the side port. The bottom of the chamber is fitted with special

Fig. 1. Schematic experimental setup.

silicon gel sheet (GELTEC θ -5) which sticks to the rough sample surface and also helps in maintenance of vacuum.

Nd:YAG laser (LOTIS TII LS-2135) was used for ablation at the wavelength of 532 nm (SHG). The laser energy of 50 mJ/pulse was used to achieve sufficient metal ablation. A pulse duration of 10 ns and repetition rate of 10 Hz were employed. Gas pressure was adjusted with high purity argon (99.9995%) and helium (99.9999%), after evacuation of chamber below 4 Pa. The pressure was measured with a Pirani gauge (ULVAC WP-01) and a capacitance manometer (ULVAC CCM-1000 and GM 2001) placed between an evacuation port and a rotary pump (ALCATEL SD 2010). Energy of the pulsed laser was measured using a 3A-P-Cal thermopile absorber head and a Nova laser power/energy monitor (OPHIR OPTRONICS). Emission spectra were measured using a spectrograph (RITSU OYO KOGAKU MC-25N) with a CCD detector (HAMAMATSU M 6296).

3. Results and Discussion

In order to find the optimum operating conditions of LP-LIPS, pressure dependence of the emission intensity of Fe I 357.01 nm [$4p\ ^3G_5$ (4.39 eV)– $4s\ ^5F_4$ (0.91 eV)] was examined in Ar and He atmosphere. Obtained results are shown in Fig. 2. Optimum pressures for this setup are found to be 5 Torr and 4 Torr for Ar and He respectively. Since intensity of emission spectra in Ar was stronger than that of He, Ar was used as the buffer gas for further experiments.

In order to check the utility of this new chamber for the analysis of scrap steels, gray painted steel, green painted steel, and Zn plated steel plates were used as examples of scrapped steel materials. Since impurity elements (especially so-called tramp elements, such as Zn, Sn, Pb, Cr *etc.*) may be present in a surface layer of the sample, analytical

Fig. 2. Pressure dependence of the emission intensity of Fe I 357.01 nm in argon and helium atmosphere.

Fig. 3. Spectrum of gray paint coated steel sample in argon atmosphere.

method for scrap materials should have the depth profiling capability.

In case of the gray painted steel sample, accumulative spectrum of first 9 laser shots was recorded as shown in Fig. 3. In that spectrum, distinct Ti atomic emission lines were observed. Assignments of the observed Ti emission lines are listed in Table 1. After additional 100 shots, weak Ti emission lines were still observed, reflecting that Ti is contained in the gray painted layer and the thickness of the gray painted layer is roughly equal to the crater depth of 100 laser shots. Gray color is produced by the mixture of

Table 1. Observed Ti, Cr and Zn emission lines and their assignment.

Emission Lines (nm)	Assignment ⁵⁾	
	Upper Level (eV)	Lower Level (eV)
<i>Titanium</i>		
Ti I 335.83	4p ³ D ₂ (3.69)	4s ³ F ₂ (0.00)
Ti I 336.90	4p ⁵ D ₄ (3.73)	4s ³ F ₄ (0.05)
Ti I 337.92	4p ³ G ₄ (3.72)	4s ³ F ₄ (0.05)
Ti I 338.87	4d ³ H ₆ (5.70)	4s ⁵ G ₆ (2.04)
Ti I 339.26	4p ¹ F ₃ (5.16)	4s ¹ G ₄ (1.50)
Ti I 339.86	4p ³ D ₁ (4.69)	4s ³ P ₀ (1.05)
Ti I 344.66	5p ³ G ₄ (5.48)	4s ³ G ₄ (1.88)
Ti I 346.15	4p ⁴ G _{9/2} (3.72)	3d ⁴ F _{7/2} (0.13)
Ti I 347.89	4p ³ P ₁ (4.61)	4s ³ P ₀ (1.05)
Ti I 349.32	4p ⁵ F ₄ (3.57)	4s ³ F ₃ (0.02)
Ti II 350.54	4p ⁴ G _{7/2} (3.69)	3d ⁴ F _{9/2} (0.15)
Ti I 351.16	4p ⁵ F ₂ (3.55)	4s ³ F ₃ (0.02)
Ti I 353.60	4p ³ D ₁ (4.40)	4s ¹ D ₂ (0.90)
Ti II 368.51	4p ² D _{3/2} (3.94)	4s ² F _{5/2} (0.57)
Ti I 374.10	4p ³ F ₃ (3.33)	4s ³ F ₃ (0.02)
Ti II 375.93	4p ² F _{7/2} (3.90)	4s ² F _{7/2} (0.61)
<i>Chromium</i>		
Cr I 335.64	4d ⁷ D ₃ (6.61)	4p ⁷ P ₄ (2.91)
Cr I 336.75	4p ⁵ G ₄ (6.22)	4s ⁵ G ₃ (2.54)
Cr I 337.92	4p ⁵ F ₃ (6.21)	4s ⁵ G ₂ (2.54)
Cr I 338.65	4p ³ F ₃ (7.22)	4s ³ D ₂ (3.56)
Cr I 368.37	5p ⁵ D ₃ (7.21)	4s ³ D ₃ (3.84)
<i>Zinc</i>		
Zn I 328.23	4d ³ D ₁ (7.78)	4p ³ P ₀ (4.00)
Zn I 330.29	4d ³ D ₁ (7.78)	4p ³ P ₁ (4.03)
Zn I 334.56	4d ³ D ₂ (7.78)	4p ³ P ₂ (4.08)

Fig. 4. Spectrum of green paint coated steel sample in argon atmosphere.

black and white pigments. Since TiO₂ is a well known white pigment, the observed Ti emission lines seem to be originated from TiO₂.

In case of the green painted steel sample, atomic emission peaks of Cr were observed in the accumulative spectrum of first 9 laser shots as shown in Fig. 4. Assignments of the observed Cr emission lines are listed in Table 1. Such CrI emission lines disappeared in the accumulative spectrum of next 9 laser shots. One of the well known green colored pigment is Cr₂O₃; therefore, the observed CrI lines seem to be due to Cr₂O₃. In this case, CrI emission lines disappeared within 18 laser shots, so the thickness of the

Fig. 5. Spectrum of zinc coated steel sample in argon atmosphere.

green painted layer is very thin compared with the gray painted layer mentioned above.

In case of the Zn plated steel sample, observed emission spectra are shown in Fig. 5. After accumulation of 100 laser shots, very prominent Zn atomic lines were identified. Assignments of the observed Zn emission lines are listed in Table 1. Since weak Zn atomic emission lines were still observed in the accumulated spectrum of next 100 laser shots, the Zn layer was found to be thick.

In this experiment, a CCD detector was used to measure emission spectra of the samples. Since the detector sensitivity in ultra violet region is poor, accumulation of the spectrum is needed to improve the signal-to-noise ratio (S/N). Such accumulation requires the data integration over the

large number of laser shots; therefore, the ability of depth profiling is degraded. If an intensified CCD (ICCD) is available, emission spectrum with a sufficient S/N could be obtained even for one laser shot, which enables the rapid analysis as well as better depth resolution to be attained.

4. Conclusion

With the help of this simple arrangement, qualitative information about the surface coatings of the steel plates can be obtained in a short time. The impurity elements which degrade the quality of commercial steels can be identified by just placing this chamber on the surface and by irradiating the laser beam.

The design of chamber is being improved by replacing the optical path consisting of mirrors with an optical fiber and reducing the size further for more convenient utilization.

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