Rapid evaluation of the extent in micro-degradation of protective coatings using laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

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Abstract: The durability of coatings used to protect base materials can be affected by environmental factors and degradation mechanisms including thermal decomposition, catalytic decomposition, bio-disintegration, chemical corrosion and mechanical scission. LA-ICP-MS is often used for the analysis of the trace elements to understand the degradation mechanism. This article extends the use of the LA-ICP-MS for the determination of the extent of coating degradation. The method is particularly useful for the rapid evaluation of conventional overlay metal-coatings at micron and sub-micron levels in applications such as pipelines commonly found in the oil and gas industry.

Keywords: laser ablation; ICP-MS; depth-profiling; micro-degradation; protective coatings.


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1 Introduction

Coatings are commonly used to protect the deterioration of the base materials from corrosive and oxidising environments. However, protective coatings can weaken under prolonged exposure to harsh environments and the long-term inter diffusion of chemicals between coating and substrate could alter the physical and mechanical properties of the base materials. This is a serious and widespread problem in many technical applications. If left un-monitored coating degradation could lead to catastrophic failure with disastrous consequences. For example, the failure of the pipe lines in the oil and gas industry could lead to considerable financial losses and environmental damages. To overcome this problem, it is necessary not only to understand the mechanism of degradation, but also determine the extent of the coating degradation.

The durability of coatings is affected by environmental factors and degradation mechanisms including thermal decomposition, catalytic decomposition, bio-disintegration, chemical alteration and mechanical scission. Many testing methods are available for evaluating the durability of coatings (Sakumoto et al., 2001). These techniques measure the coating thickness to determine the level of degradation. However, none of these techniques can directly provide depth characteristics of the trace elements while determining the coating thickness. In the last few years, laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) has attracted wide interest in different fields of science and technology (Barca et al., 2007; Becker et al., 2007; Scarciglia et al., 2009) for the analysis of elements in solid specimens and the determination of trace and ultra-trace impurities down to the sub nano-gram per gram concentration level (Bi et al., 2000; Fernandez et al., 2007). This technique is particularly useful for the understanding of the degradation mechanism. However, LA-ICP-MS is not commonly used to determine the extent of coating degradation. Degradation at micron and sub-micron levels is almost imperceptible with most current techniques. This article extends the usage of LA-ICP-MS for monitoring the extent of the coating degradation while it is being used for analysing the mechanism of degradation from the trace elements. The advantage of such high-resolution detection is that both the mechanism and early signs of coating failure can be rapidly monitored with LA-ICP-MS. The method is particularly useful for the evaluation of conventional overlay metal-coatings in...
applications such as pipe lines (Glazov et al., 2006) commonly found in the oil and gas industry.

2 The LA-ICP-MS system (Fryer et al., 1995; Vander Putten et al., 1999; Becker, 2002; Tiepolo, 2003)

One of its practical advantages of LA-ICP-MS is that there is no need for sample preparation. Coating failure in the solid sample is examined by laser ablation. This is a simple and straightforward process. Ultra-thin coatings (a few microns thick) on suitable solid specimens can be ablated for depth-analysis to assess coating homogeneity and determine the elemental composition of major and minor trace elements in the substrate.

Figure 1 shows a schematic diagram of the LA-ICP-MS system. For ablation of most metals, it is common to use Nd: YAG laser with wavelength of 266 nm or 213 nm, operated at 5 to 10 Hz with pulse energy of about 2 mJ to 7 mJ, and pulse width of 6–8 ns. The focused spot diameter is generally about 20–60 μm. Most commercial systems allow the sampling speed of the ablated laser to be varied between 1 Hz to 100 Hz and the laser spot size to be controlled between 5 μm and 400 μm. In general, the parameters of the laser operating conditions such as beam spot size, speed, length, power and magnification should be optimised based on the coatings and the substrates.

Figure 1  Schematic diagram of the LA-ICP-MS system (see online version for colours)

Interaction between the laser beam and the solid specimen, which is normally placed on a mechanically adjustable table, occurs in the ablation chamber. The adjustable table movement is normally controlled by a computer to allow the specimen to be displaced by a few microns in the x, y, and z directions. Different tasks such as depth profiling, spatial profiling, surface and bulk analyses are performed by changing the timing between individual laser pulses and platform movements.

The intense energy delivered by the laser instantly removes and vaporises a minute finite volume of the solid specimen into an aerosol of particles. Shorter laser wavelengths generally offer higher photon energies for efficient bond breaking and ionisation of the solid specimen. However, absorption of laser energy by the target material can vary
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significantly with laser wavelength. Inert gases are used to carry the ablated aerosol into the ICP system. To accomplish this, the chamber is typically flushed with Argon or Helium. Efficient transportation of aerosol through the ablation chamber is critical to achieve reliable and timely measurement in the ICP-MS. A high carrier gas flow can reduce sample deposition in the chamber and transfer tube resulting in better transport efficiency. Nevertheless, the volume of the transport tube can also influence the sample density in the ICP. Smaller volumes may shorten the transportation time of the sample ablated aerosol.

The resulting aerosol under normal pressure is transported into the ICP-MS detection system, which measures most of the elements in the periodic table. The concept is based on the isotopic fingerprint for that element. The natural isotopes of each element have different atomic mass but the same atomic number. The ICP-MS determines the individual isotopes for each element. The signal can be further processed to give isotope ratio and isotope dilution measurements. With proper correlation with the laser sampler, the instrument can establish a time versus concentration relationship for the specimen and provide data of isotope concentration with respect to crater depth. Solid standards of matching matrix are generally not available, and the only recourse to validating the analytical performance of the laser technique was to examine an available certified standard, which in our case was a glass bead (NIST, Certificate 613). Some values linked to this standard itself were not fully certified indicating that repeatability studies with the laser tends to be tricky. Accumulation of debris in the crater formed by the laser and imperfect crater formation could affect such studies. In our case, we examined the analytical performance of the instrument by taking replicate measurements \(n = 3\) for equivalent counting times at random points on the glass standard. Relative standard deviations of less than 5% were attained (Table 1) indicating that the operational performance of the facility was acceptable.

<table>
<thead>
<tr>
<th>Measurements</th>
<th>(^{59}\text{Co})</th>
<th>(^{85}\text{Rb})</th>
<th>(^{88}\text{Sr})</th>
<th>(^{138}\text{Ba})</th>
<th>(^{140}\text{Ce})</th>
<th>(^{238}\text{U})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>503</td>
<td>718</td>
<td>3,688</td>
<td>1,618</td>
<td>1,023</td>
<td>1,805</td>
</tr>
<tr>
<td>2</td>
<td>511</td>
<td>736</td>
<td>3,672</td>
<td>1,624</td>
<td>1,141</td>
<td>1,814</td>
</tr>
<tr>
<td>3</td>
<td>491</td>
<td>735</td>
<td>3,587</td>
<td>1,620</td>
<td>1,036</td>
<td>1,792</td>
</tr>
<tr>
<td>Mean</td>
<td>502</td>
<td>730</td>
<td>3,649</td>
<td>1,621</td>
<td>1,067</td>
<td>1,804</td>
</tr>
<tr>
<td>± RSD</td>
<td>± 1.6%</td>
<td>± 1.1%</td>
<td>± 1.2%</td>
<td>± 0.15%</td>
<td>± 4.95%</td>
<td>± 0.5%</td>
</tr>
</tbody>
</table>

Laser depth-profiling is an ultra-sensitive tool that has the capability of ‘drilling’ through samples and obtaining relevant information on the distribution of trace metals. The technique is highly sensitive and can attain a limit of detection of \(10^{-6}\) mg/kg (parts per trillion) for most elements. The trace elements are important for the understanding of the mechanism of degradation. However, the trace elements would not be needed for the proposed extension of the LA-ICP-MS for the determination of the coating thickness. The key to quickly evaluate the coating degradation level using the LA-ICP-MS is to obtain the time versus substrate concentration spectrum characteristics. This semi-quantitative technique is best illustrated using the following case study.
3 A case study

Specially prepared steel plates were coated with regular acrylic-based protective coatings of uniform thickness according to the guidelines established by The Society of Protective Coatings. The coated metal plates were then separated into two sets. Control specimens were kept indoors at room temperature of 23°C and tested about two hours after the coating has hardened. This avoids the micro defects due to long-term effect of chemical alteration and allows the determination of the homogeneity of the coating thickness prior to degradation. The second set of coated metal plates was exposed to various hazardous environments. These include changing weather conditions (including intense solar radiation, sand blizzards and excess humidity), immersion in sea water and ‘acid-rain’ solution (pH = 5.5). These specimens were inspected at regular intervals to visually monitor the extent of coating damage.

The coating degradations were investigated after three months using the Perkin Elmer SCIEX DRC-e ICP-MS facility fitted with New WAVE UP-213 Nd:YAG laser ablation system. Prior to each run, the instrument underwent appropriate calibration and background correction (Jarvis et al., 1992). The specimens were placed in a special 5 cm × 5 cm sample holder attached to the adjustable table in the ablation chamber. Specimens were subjected to 213 nm Nd:YAG laser irradiation along a linear path – each point separated by a distance of about 5 mm. The level of the beam energy was 30%, with a beam diameter of 55 μm. The system was programmed to continuously ablate samples at constant depths at each point and ‘drilled’ through the coating till the substrate was reached. These operating conditions were optimised after numerous trials. The time versus substrate concentration spectra were recorded.

The objective of the study was to extend the LA-ICP-MS to determine the level of coating degradation and so the determination of the trace elements is not presented here. Laser pulses were progressively applied at a given location on the specimen surface to generate a crater and the substrate spectral signals are recorded at various depths in terms of sampling time. Since increasing the pulse number increases the crater depth, the variation of substrate spectral intensity with sampling time (or pulse number) directly correlates with its variation of concentration with depth. As the laser is penetrating the coating and before reaching the substrate, the substrate spectral intensity should remain zero. As soon as the laser reaches the substrate, the characteristic intensities of the substrate should be reflected in the spectrum. Any deterioration in the coating thickness due to harsh environmental conditions will alter the penetration depth and it will take less time to reach the substrate. In this way, the level of coating degradation can be evaluated from the time versus substrate concentration spectrum. For the purposes of comparison, all measurements were performed as a function of real sampling time. The time taken to reach the substrate for the specimens with degraded coatings can be compared with the control specimens and to determine the percentage change in coating thickness. As the approach was largely semi-quantitative, valid considerations were given to potential interferences and matrix effects. Very few contemporary instrumental methods have the capability to study metal intensity with depth. X-ray methods are useful, but lack the ability to control depth penetration. Nuclear particle irradiation, SEM, SIMS and XPS are equally useful, but such techniques tend to be limited in terms of sample preparation and handling. Dry film thickness gauges are valuable for such measurements but are not reliable for measurements within a few microns. The competence, therefore, of the laser
approach to delve to discreet depths below the surface of a sample is attractive for homogeneity studies in bulk materials.

Figure 2 shows the time versus substrate concentration spectrum of a typical control specimen. The y axis (counts/sec) in Figure 2 represents the base substrate ion intensity. The sampling time taken to reach the substrate was about 300 seconds. Several measurements were conducted on different surface points and the discrepancies in coating uniformity were small and did not exceed a relative deviation of 2%. The results indicate the homogeneous thickness of the coatings. Variation in the peak heights of the substrate trace element after 300 seconds can be due poor homogeneity in the substrate material and to deviation in the level of impurities with depth and accumulation of debris in the crater created by the laser (Robinson et al., 2005). It is envisaged that micro defects due to the long-term inter-diffusion of chemicals between the coating and substrate would not have any significant impact on the variation in substrate concentration in the control samples.

**Figure 2** Time-concentration spectrum of coated control steel specimen (see online version for colours)

![Figure 2](image)

**Figure 3** Time-concentration spectrum of coated steel specimen with weakening protective coating (see online version for colours)

![Figure 3](image)
Figure 4  Time-concentration spectrum of coated steel specimen with completely degraded protective coating (see online version for colours)

An example of specimen with coating degradation is shown in Figure 3, where the time taken to reach the substrate was about 100 seconds. Comparison of Figures 2 and 3 shows that it takes less time for specimens with weakened protective coatings to reach the substrate. Figure 4 shows the time versus substrate concentration spectrum of a completely degraded protective coating. The substrate intensity appears immediately after irradiation with no time lapse.

By comparing the time taken for the laser to reach the substrate in the control and uncontrol specimens, the percentage change in coating degradation can be determined. Table 2 summarises the variation of coating degradation of four points (i.e., points A, B, C and D) along a linear path – each point separated by a distance of about 5 mm. The results indicate that the coating thickness can degrade by 40% to 50% when specimens were subjected to harsh environment for three months. These results are comparable with those obtained using SEM. Characteristic intensities originating from the substrate of interest were measured. Variation in the peak heights was attributed to accumulation of debris in the crater created by the laser.

Table 2  Percentage of coating degradation of four points along a linear path (each point separated by a distance of 5 mm)

<table>
<thead>
<tr>
<th>Point</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>% degradation</td>
<td>46.7%</td>
<td>50%</td>
<td>40%</td>
<td>43.3%</td>
</tr>
</tbody>
</table>

4 Discussion

The simple and straightforward manner of data interpretation in Figures 2 to 4 is mainly suitable for semi-quantitative analysis of conventional overlay coating (several microns thick), where the coating and the substrate remain as two distinctly separated chemical entities. An abrupt intensity change is usually observed across the coating/substrate interface. For more complex organic coatings, detailed quantitative profile analysis may be needed to accurately determine the minor trace constituents and impurities in order to understand the mechanism of degradation at the molecular level (Riaz et al., 2009). In cases of non-uniform multi-layer composite coatings on metallic alloys, the concentrations of transition element impurities can influence the properties even at μg/g
levels. As a result damage can start at the coating-substrate interface under extreme environmental conditions (Izmer et al., 2005). To study these internal weakening and sub-surface coating instability, direct correlation of the intensity variation with the actual depth profile must be generated based on calibration curves for depth versus sampling time (or pulse number). Currently, there is no universal method of calibration for all solid specimen types. Calibration typically requires matrix-matched standards, which can be difficult to obtain or fabricate. Matrix matching is needed as the ablation rate can vary with the matrix composition. Many metal standards as well as certified reference materials for some types of solid matrices are commercially available. The standard or certified reference material must be carefully selected to match that of the specimen under investigation to minimise fractionation: a situation in which the composition of the mass analysed is not representative of the bulk sample.

Fractionation could be a significant source of error that is heavily dependent on the laser beam properties such as pulse width, wavelength, etc. In general, the shorter the laser wavelength, the higher the ablation rate and lower the fractionation. With a shorter laser pulse, less energy is lost through thermal dissipation and more energy can be utilised for ablation. The effective utilisation of energy will affect the crater depth and its aspect ratio. Although an exact mechanism for crater effects on fractionation is not established, fractionation can be significant for some elements when the depth to diameter ratio of the ablated crater was greater than six (Mank and Mason, 1999). Effective laser irradiation will also affect the particle size distribution in the sampled aerosol and lead to fractionation during the transfer to the ICP as small clusters less than 2 nm in diameter may disperse on the walls along the route, while large particles greater than 5 μm in diameter may settle due to gravitational effects. Furthermore, a typical ICP can only completely ionise particles between 10 to 20 μm and incomplete ionisation in the ICP due to inappropriate particle size could further contribute to fractionation. In the present study, these effects have not been fully considered and the experimental beam parameters were optimised through repeated trials to ensure that the depth to diameter ratio of the ablated crater is less than six.

In view of the above factors, it is essential to optimise the laser’s energy with respect to the maximum ion intensities of analyte to suit the ablation of specimen under investigation. Softer materials are generally easily ablated using laser with lower power density and increasing the laser’s energy can affect the peak intensity. Moreover, the spot size should be adjusted based on the coating thickness. For coatings of a few microns thick, it may be appropriate to use the smallest spot sizes in the laser beam to improve the measurement.

Plasma shielding is another phenomenon that needs to be considered when using the LA-ICP-MS. This occurrence is strongly dependent on the laser wavelength. The duration of the laser pulse can determine the interaction of the laser with the expanding plasma plume created during the early stage of the ablation process. Depending on the pulse duration, the plasma plume can either absorb or reflect the laser energy. The degree of plasma shielding, which reduces the laser-sample energy coupling efficiency, is dependent on the ionisation potential of the gas species. Hence, the carrier gas could affect the laser ablation and measurement performance. To make matters worse, gas with heavy atomic mass could also reduce transport efficiency due to collision of gas species and the ablated plume. Inappropriate flow rate could also cause delay in sample transportation into the ICP-MS system. The fluctuations in arrival time and size of the individual ablated particles transported to the ICP coupled with the variations of
shot-to-shot laser output energy could affect the precision of the measurements. Besides these considerations, atomic or molecular ions having the same nominal mass as the isotope of interest can interfere with the measurement accuracy. Finally, certain elements such as phosphorous can be difficult to detect. To effectively utilise LA-ICP-MS for coating degradation studies, all the above mentioned issues that can affect the measurement accuracy must be carefully taken into consideration. At the current stage it is difficult to estimate the role of these factors in the measurement accuracy. Future work will try to address this issue.

5 Concluding remarks

LA-ICP-MS is fast becoming a popular and frequently used technique in a wide range of applications in industry for fast and accurate determination of multi-elements in solid specimens at the trace and ultra-trace concentration levels. LA-ICP-MS is an excellent tool to better understand the mechanism of degradation. The article presents the extension of LA-ICP-MS for the determination of degradation levels in protective coatings. A case study on conventional overlay coating illustrates how the substrate time-concentration spectrum can be used to quickly estimate the level of coating degradation and homogeneity in coatings. The technique can be extended to complex multi-layer composite coatings on metallic alloys but factors affecting the measurements have to be carefully considered. This technique will be useful for predicting localised ‘hotspots’ of coating degradation in pipelines. Such predictions could be useful to prompt damage control, thereby saving immense costs and avoiding environmental catastrophes.

References


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