SENRA Academic Publishers, Burnaby, British Columbia
Vol. 3, No. 2, pp. 821-825, 2009
ISSN: 1715-9997

Canadian Journal of pure&applied sciences

MONITORING INTERFACIAL DEGRADATION IN METAL-COATINGS USING LASER-ABLATION TECHNOLOGY (ICP-MS)

*AE Pillay[1], S Fok[2], S Stephen[1] and A Abd-Elhameed[1]
[1]Department of Chemistry, [2] Department of Mechanical Engineering
The Petroleum Institute, PO Box 2533, Abu Dhabi, UAE

ABSTRACT

Degradation of protective coatings on metal surfaces is a common problem, especially in the oil and gas industry, where enormous metal structures have to be shielded. Predicting the extent of coating failure is useful to pre-empt damage to the metal substrate, and save costs. This paper explores the use of laser ablation technology to monitor the level of wear in protective coatings after subjection to severe environmental conditions such as sand blizzards, intense solar irradiation, excessive humidity and rain. Specially coated metal samples were prepared for investigation. Samples were exposed to inclement weather conditions and the level of deterioration to the coating was monitored using the laser ablation technique. The laser penetrated the coating and the time taken to reach the substrate was recorded. If the coating underwent degradation, less time was taken to reach the substrate. Depth profiling in this way made it possible to monitor attenuation of the coating. The laser was part of a high resolution ICP-MS instrument, and irradiations were conducted with a 213-nm beam of 30% total energy and 55 µm diameter. Prior to each run, the instrument underwent appropriate validation and correction for background interference. Detailed analysis of different spots on the sample also provided information on the evenness of the coating. Investigating coating performance linked to interfacial degradation is relatively novel, and our work would be of considerable interest to research in environmental and materials science.

Keywords: Metal coatings, interfacial degradation, laser ablation, ICP-MS

INTRODUCTION

Coating failure on metal structures especially in the petroleum industry, could lead to considerable financial losses (Pomeroy, 2005; Meier and Cheng, 1989; Pennefather and Boone, 1996). The ability to forecast early deterioration of protective coatings would thus be highly beneficial and could lead to massive savings. High resolution laser ablation technology (ICP-MS) uses a micro beam to 'drill' through the coating and provide information on the level of attenuation. This is generally called depth profiling, and such depth analysis can be studied horizontally and vertically across a sample surface. If the coating is completely eroded at certain points, the technique will detect the composition of the substrate. In our case the substrate was steel. Our laser facility used a solid state laser with UV-radiation, and from such irradiation it was possible to predict coating instability by accumulating a relevant spectrum of a control sample (undegraded sample) measured as a function of time - and comparing it with spectra of degraded samples. If the coating underwent deterioration or attenuation, less time will be taken to reach the substrate. The level of coating damage was monitored in this way. Any interfacial degradation or variation in the physical or chemical stability of the protective coat would alter this time-spectrum. Since the altered spectra are relative to that of the undegraded material, absolute standardization of the technique was unnecessary. A laser ablation study of this nature, therefore, could provide an insight into the emaciation of surface coats, and a timely warning to ensure that adequate damage-control measures are taken to save the substrate.

The novelty of our research involved the competence of the laser ablation technique (Arrowsmith, 1987; Hager, 1989; Stix *et al*., 1995; Perkins *et al*., 1993) to predict the onset of damage by monitoring the gradual emaciation of the coating. Under certain conditions protective coatings could undergo loosening and weakening at the metal-coat interface, while the surface looks seemingly intact (Pomeroy, 2005). Our particular interest was to explore the extent of breakdown at interfacial levels. Due to invasive corrosion of certain substrates, such as steel, possible breakdown of the protective coating could commence at the metal-coat interface (Pomeroy, 2005). Clearly, attenuation from the bottom of the coating (touching the substrate) outwards to the coating surface would lead to more internal than surface damage. Such internal damage could occur uniformly or intermittently, at "hot-spots," and may be invisible to the naked eye. The significance of our study therefore, was to explore the merits of the laser technique to predict the level of interfacial damage, and this could have a significant impact on materials science and environmental research.

*Corresponding author email: apillay@pi.ac.ae

MATERIALS AND METHODS

Sample treatment

Specially prepared steel samples were coated with standard protective coatings (acrylic-based) of uniform thickness. The samples were exposed to the atmosphere (on the roofs of the north and south wings of our building) for a period of 2-3 months, and subjected to changing weather conditions including intense solar radiation, sand blizzards, rain and excessive humidity. The exposed samples were checked at regular intervals to ensure they were not disturbed. In all cases degradation was visible, and depending on the stringency of the environmental conditions and the point of exposure some coated samples displayed more damage than others. For example, figure 1 is an image of a coated sample showing early stages of degradation. It depicts degradation moving inwards from the top edges, with much of the remainder of the sample seemingly intact. On the other hand, figure 2 represents advanced deterioration, displaying severe deterioration around some edges, indicating that the damage could be quite extensive. Control specimens, prepared in identical fashion, were kept in a closed container indoors in an appropriate ambient environment.

Fig. 1. Coated steel sample showing early stages of degradation.

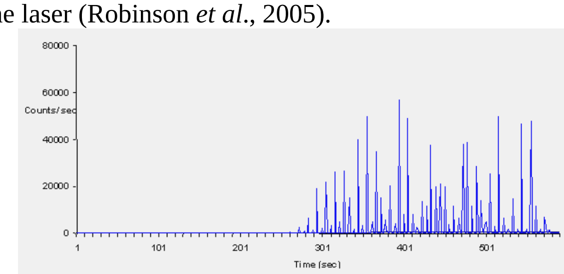
Fig. 2. Coated steel sample showing advanced deterioration around some edges.

ICP-MS laser ablation technology

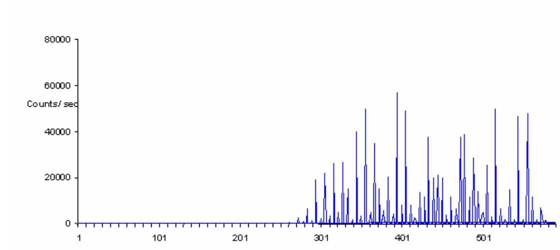
Samples were irradiated in a Perkin Elmer SCIEX DRC-e ICP-MS facility fitted with a New Wave UP-213 laser ablation system (Robinson *et al*., 2005; Jarvis, Gray and Houk, 1992). The coated plates were placed into a special sample holder. No pre-treatment was necessary prior to irradiation. Samples were subjected to 213-nm laser irradiation along a 16-point grid - each point separated by a distance of about 3-4 mm. The beam diameter was 55 µm and the level of the beam energy was comparatively low, 30%, with a dwell time of 1 second. The laser was programmed to continuously ablate constant depths at each point and penetrated the coating till the substrate was reached. Time-related spectra corresponding to the substrate (iron) were recorded for each measurement. Control specimens were irradiated under identical conditions.

Spectral analysis

Characteristic intensities originating from the substrate of interest were measured; and valid considerations were given to potential interferences and matrix effects. Prior to each run, the instrument underwent appropriate calibration and correction for background (Jarvis *et al*., 1992). The study was conducted in the absence of standardization, and for purposes of comparison, all measurements were conducted as a function of real time. Following depth profiling, the laser penetrated the coating and an appropriate time-spectrum was recorded. If the coating underwent deterioration or damage, less time was taken to reach the substrate, compared to the control. In this way the level of coating performance was evaluated. Figure 3 shows time-spectra for a typical control specimen. As shown the time taken to reach the substrate was roughly 5 minutes (290 seconds). A sample with coating failure will take less time. Variation in the peak heights was due to variation in the level of impurities with depth and accumulation of debris in the crater created by the laser (Robinson *et al*., 2005).



(a)



(b)

Fig. 3. (a) & (b) Time spectra recorded at two different spots on the control. The time taken to reach the substrate in each case was about the same thus indicating uniformity of the coating.

RESULTS AND DISCUSSION

Coating uniformity

The ablation technique can provide both spatial and depth information. Spatial studies can reveal unevenness of the coating by measuring the composition of the coating itself at different points on the surface. The penetration of the laser through the protective coating using a grid pattern distributed both horizontally and vertically across a sample surface was used to determine the quality of the coating over an area. The laser basically ‘drilled’ through the coating and the time taken to strike the substrate was recorded. Essentially, this is the time recorded from commencement of irradiation to the moment the substrate spectrum appeared. Any unevenness in the coating at different points on the surface of the control was expected to alter the penetration depth, leading to variation in the recorded time for appearance of the substrate spectra. In this way uniformity of the coating was tested at several points on the surface. Figures 3 (a) and (b) represent typical time-spectra recorded at two different spots on a control sample. It is clear that the time taken to reach the substrate in the undegraded coating of the control was about 290 seconds, which represented our ‘benchmark’. If the coating underwent any form of attenuation we expected a time of less than 290 seconds to be recorded to reach the substrate. In this way the level of coating damage could be monitored. Several measurements were conducted on different unattenuated surface points and discrepancies in coating uniformity were small and did not exceed a relative standard deviation of 2% (Table 1). This indicated that the coating application was relatively uniform and satisfied our needs. Minor irregularities arose possibly from slight unevenness or microscopic imperfections on the surface of the metal plate.

Table 1. Coating uniformity is indicated by constant times taken for the laser beam to reach the substrate, after penetrating different spots on the undegraded coating.

Random points on undegraded surface	Time taken to reach metal substrate (sec)
1	285
2	290
3	290
4	295
5	280
6	295
Mean ± RSD	289 ± 2.0%

Factors linked to coating degradation

As previously stated, samples were exposed to the atmosphere under desert conditions. The overall performance of the coating, therefore, depended on a range of environmental effects under these conditions such as sand storms, intense heat, strong winds, rain and excessive humidity (Fifield and Haines, 2000). Of significance is that some damage to these samples also arose from the impact of unfriendly environmental contaminants, such as air pollutants, abrasive chemicals (sea air) and acid rain. Corrosion of the metal was a direct result of exposure to the environment, but indirectly contributed to invasive coating damage in a mechanism which is not entirely clear. As depicted in figures 1 and 2, coating failure can be spotted at a glance, in some cases. In the cases where the coating was completely worn away at certain points, the laser technique immediately detected the composition of the substrate. Complete degradation of this nature is represented by the spectrum in figure 4, where the substrate intensity appears immediately after irradiation with almost no time lapse – thus indicating that the coating was completely worn away. A point to note is that the theory of interfacial coating abrasion or erosion is relatively underexplored for the simple reason that there is currently no existing technique (apart from laser ablation) that can adequately monitor it. An observed feature of the coated steel surfaces was that points at the edges of the sample, where corrosion set in, tended to result in more invasive interfacial damage than at points where corrosion was lacking. This suggested that corrosion contributes significantly to interfacial attenuation by somehow weakening the coating internally. Laser ablation depth-profiling technology is perhaps the only technique that can predict invasive coating failure by monitoring internal weakening, whilst the surface remains ostensibly intact.

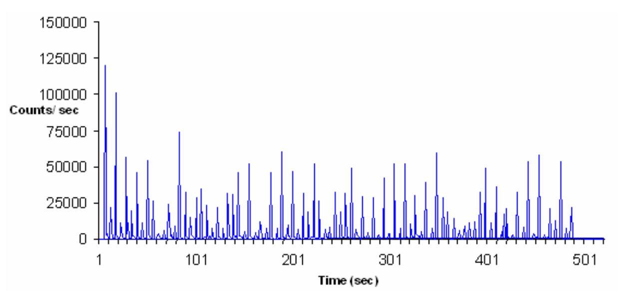


Fig. 4. Time spectrum of a sample corresponding to a completely degraded area on the sample. This is clear from the time taken to reach the substrate, which is about 2 seconds.

Interfacial attenuation

Clearly, if the coating incurs partial deterioration or damage, this would be reflected in the time-spectrum. Figure 1 delineates surface peeling around some edges. It is surmised that ‘flaking or peeling’ of this nature could be due to some form of sub-surface attenuation accompanied by a loosening of the protective coating. At this stage the only evidence to support this comes from laser irradiation of the spots on the surface in close proximity to these areas of instability. Such irradiations produced diminished times to reach the substrate. A typical spectrum depicting such attenuation is presented in figure 5, where the time taken to reach the substrate was roughly 100 seconds, signaling that roughly 67% (or two-thirds) of the protective coating sustained damage (compared to an unattenuated coating (Fig. 3) which takes about 290 seconds to reach the substrate). In some cases it is easy to say, by simple inspection, whether damage arose from the outside and consumed the coating material towards the substrate. It is more difficult to predict if the failure started invasively from the interface and thinned the coating from the interface outwards. Depth profiling is useful to investigate instability immediately beneath the coating surface; and depth analysis of this nature can be used to predict early coating failure.

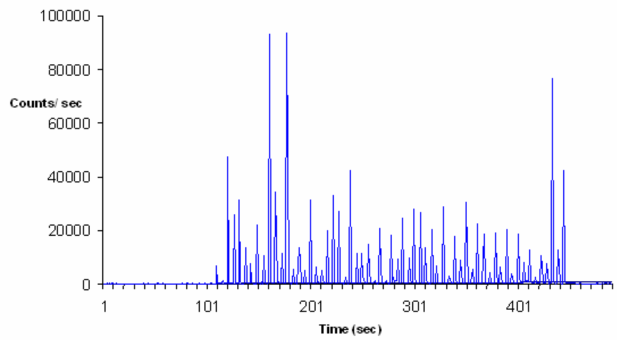


Fig. 5. Time spectrum of a coated steel sample where the protective coating is weakening. This is evident from the shorter time taken to reach the substrate - just over 100 seconds.

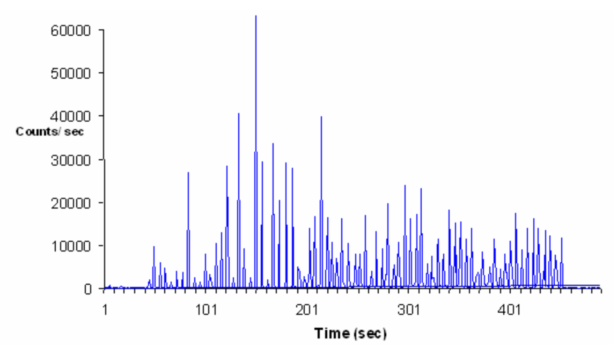


Fig. 6. Time-spectrum corresponding to a coated steel sample where the protective coating was considerably attenuated. The time taken for the laser to reach the substrate was about 45 seconds.

Another example of more advanced coating breakdown is displayed in figure 6, where the time taken to reach the substrate was about 45 seconds and demonstrated marked deterioration, which could eventually reach a state of chronic instability and expose the substrate if remedial measures are not taken. Clearly, the advantage of the laser technique is that it possesses the unique capability of locating points below the surface where the coating has weakened, thus alerting the need for damage control. Such damage control could be cost-effective by simply applying a more robust layer of protective coating, rather than replacing the metal itself.

CONCLUSIONS

This investigation revealed that the laser ablation technique (coupled to ICP-MS) is capable of predicting interfacial damage to protective coatings on metal surfaces resulting from environmental degradation. Such predictions could be valuable to corrosion engineers and used to prompt damage control, thus saving immense costs of replacing the metal itself. Our study could lead to a deeper insight into coating-life and produce a more advanced theory on the mechanism of invasive attenuation and interfacial degradation. The results indicate that such coating weaknesses would depend on several factors such as the severity of the environmental conditions, nature of the metal itself and its predilection for corrosion. Damage of this nature would probably be linked to all these factors, but it is not clear at this stage exactly what role each factor plays. It would be useful to implement laser technology on a wider scale for such purposes; and future work would involve the effect of different types of coatings and the impact of coating thickness as a function of time.

ACKNOWLEDGEMENTS

The authors would like to thank The Petroleum Institute for financial assistance and use of their premises.

REFERENCES

Arrowsmith, P. 1987. Laser ablation of solids for elemental analysis by inductively coupled plasma mass spectrometry. Analytical Chemistry 59:1437-1444.

Fifield, FW. and Haines, PW. 2000. Environmental Analytical Chemistry, Blackwell Science, Oxford, UK.

Hager, JW. 1989. Relative elemental responses for laser ablation-inductively coupled plasma mass spectrometry. Analytical Chemistry 61:1243-1248.

Jarvis, KE., Gray, AL. and Houk, RS. 1992. Handbook of ICP-MS, Blackie Publishers, London.

Meier, GH. and Cheng, C. 1989. Diffusion chromising of ferrous alloys. Surface & Coatings Technology 39/40:53-64.

Pennefather, RC. and Boone, DH. 1996. Mechanical degradation of coating systems in high temperature cyclic oxidation. Int. J. Pres. Ves. & Piping. 66:351-358.

Perkins, WT., Pearce, NJ. G. and Jefferies, TE. 1993. Laser ablation inductively coupled plasma mass spectrometry: a new technique for the determination of trace and ultra-trace elements in silicates. Geochemica et Cosmochimica Acta 57:475-482.

Pomeroy, MJ. 2005. Coatings for gas turbine material and long-term stability issues. Materials & Design 26:223-231.

Robinson, JW., Skelly Frame, EM. and Frame, GM. 2005. Undergraduate Instrumental Analysis, Marcel Dekker, New York, USA.

Stix, J., Gauthier, G. and Ludden, JN. 1995. A critical look at quantitative laser-ablation ICP-MS analysis of natural and synthetic glasses. Canadian Mineralogist 33:435-444.