Full Survey Chemical Analysis of Thin Films With Pulsed Fast Flow Glow Discharge Mass Spectrometry

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Overview

Purpose: General investigations on the feasibility of the microsecond pulsed GD-MS technique based on the very efficient fast-flow source (µs-FF-GD-MS) for chemical analyses of thin engineering coatings and films. Several important characteristics, such as the coating layer thickness, element mass per unit area or volume, the exact chemical composition or distribution of elements including trace elements in these systems are compared to GD-OES, which is currently one of the most common analytical techniques in this field.

Methods: µs-FF-GD-MS; GD-OES.

Findings: The µs-FF-GD-MS results on engineered coatings are in excellent agreement with GD-OES measurements. In addition, the µs-FF-GD-MS technique is several orders more sensitive and significantly more robust compared to the GD-OES technique.

Introduction

High resolution glow discharge mass spectrometry is broadly recognized as one of the most sensitive and robust analytical techniques for direct bulk trace element determinations. However, due to the nature of the magnetic field, scan speed is traditionally considered to be a limiting factor for depth specific measurements and thus unsuitable for thin film or layer analysis.

The fast flow Thermo Scientific™ ELEMENT GD™ equipped with a microsecond-pulsed power supply feeding its DC ion source provides the means to overcome these limitations. In pulsed mode, the source of the ELEMENT GD is running at much lower nominal power conditions (typically 3-4 W) as compared to standard continuous DC modes, but does not compromise the inherent high instrumental sensitivity. The combination of significantly reduced sputter rates with very high sensitivities provides the analytical prerequisites for performing full survey analyses even at nanometer scale depth resolution.

In pulsed mode it is possible to achieve a depth resolution of <10 nm whilst still achieving trace to ultra-trace level detection power. For the analysis of major components in layered systems, the GD power can be further decreased to give even greater depth resolution at a lower overall sensitivity.

Methods

Test Specimen

Iron based substrates with a variety of technologically important thin surface layers or coatings (Figure 1).

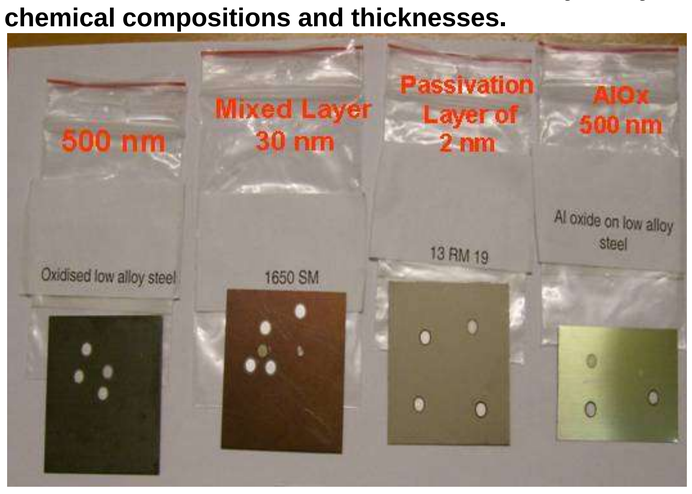
Mass Spectrometry

Thermo Scientific ELEMENT GD equipped with a µs-pulsed control of the DC-GD ion source.

Data Analysis

Spectroscopic Data Analysis software (optional).

FIGURE 1. Iron based substrates with a variety of layer chemical compositions and thicknesses.



Layer Analysis on Low Alloy Steel

Quantitative Multi-elemental Measurements with High Sensitivity

A well-characterized low-alloy steel sample with a 500 nm thick oxidized layer has been measured using the new pulsed source on the ELEMENT GD instrument (Figure 2). A comparison of the obtained results with those from the international round-robin studies related to ISO 25138:2010 GD-OES Test Method confirm that the µs-FF-GD-MS results are in excellent agreement with the GD-OES test results (Figure 3).

In addition, the µs-FF-GD-MS results in analyte responses that can be several orders of magnitude more sensitive than an optical emission technique. Figure 4 shows that even features at the low ppm range can now be distinguished in the depth profile.

FIGURE 2. Multi-element determination on oxidized low-alloy steel sample; 100 points for 14 elements; data frequency around 10 nm. Profiles in rows 1 and 5 correspond to analytes measured by GD-OES (Fig. 3). In the spectra, numbers indicate ppm concentrations at arbitrarily selected measurement times.

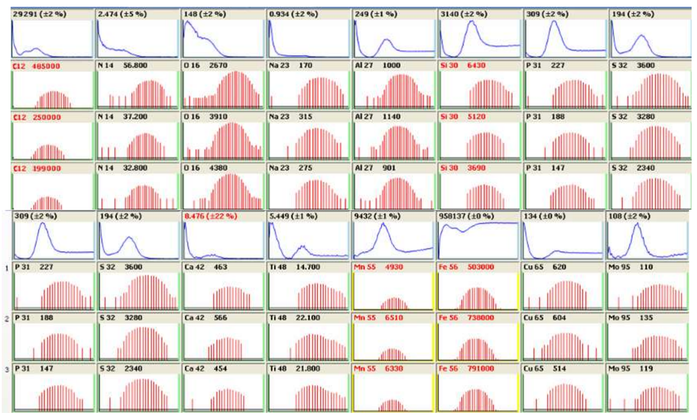


FIGURE 3. Typical GD-OES depth profiling results of oxidized layer on low-alloy steel (Results from ISO 25138:2010 International Test Method).

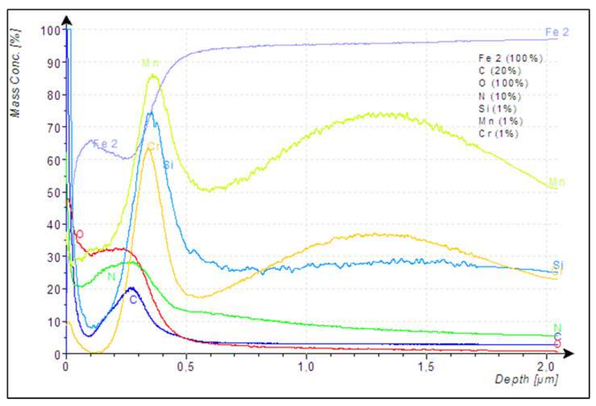
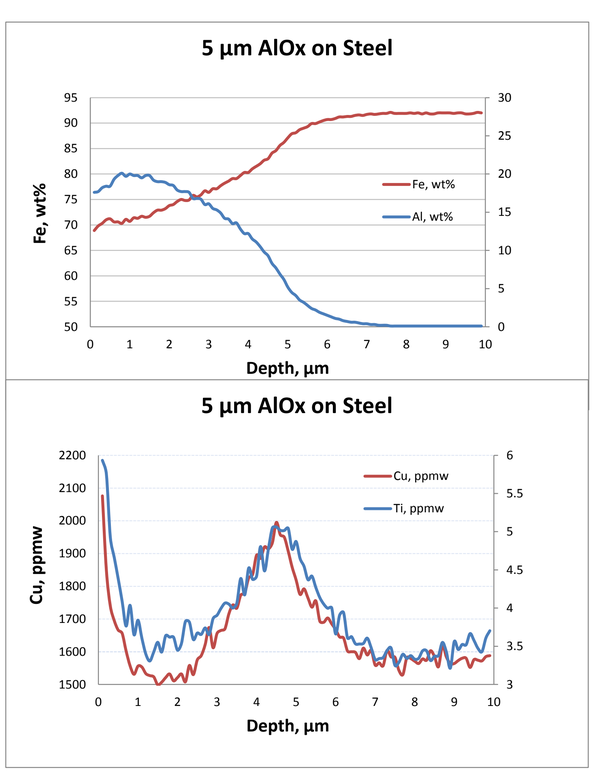


FIGURE 4. µs-FF-GD-MS results illustrating the distribution of Cu and Ti at the ppm level in the interface regions between the alumina coating on high-alloy steel. Alumina coating on HA steel: 5 µm; 50 points for 16 elements; data frequency ~ 100 nm



Sensitivity Versus Anode Orifice Diameter

µs-FF-GD-MS measurements are feasible with a range of anode orifice diameters. This provides multiple options for adjusting the source to specific analytical measurements. Table 1 illustrates how the sensitivities are inter-related for the orifice diameters mainly used in FF-GD-MS.

TABLE 1. Intensities for standard anode orifices tested on Nickel alloy CRM BAS346A in Medium Resolution.

Element	8 mm Anode Cap		4 mm Anode Cap	
	Standard Mode [cps] / ppmw	Pulse Mode [cps] / ppmw	Standard Mode [cps] / ppmw	Pulse Mode [cps] /ppmw
Mg	33000	3600	210	92
Al	48000	32200	290	130
Ti	33800	31000	260	37
V	42500	41000	380	70
Cr	15900	11000	140	51
Co	25200	21000	370	76
Ni	15500	13200	220	64
Ga	11500	9700	81	16
Mo	6100	4000	37	14
Sn	1200	740	10	3
Sb	2700	4900	73	4
Pb	8700	3800	50	6
Bi	10100	2000	29	2

Robustness

The robustness of the µs-FF-GD-MS has been studied and shows that:

A. The technique is generally applicable to rough surfaces. Figure 5 implies that the atomization occurs layer by layer, since the initial roughness is maintained throughout the GD-MS run.
B. Pulsed and continuous modes can be combined for profiling thick engineering coatings, such as Zn plated steel (Figure 6).
C. The smooth transition of the profiles in Figure 6 also indicate that calibration factors are not affected significantly if the source is running in pulse or continuous mode

FIGURE 5. Roughness of sample surface (top figure) and of the bottom of a 4 mm diameter sputter crater (lower figure). Note that crater side walls are not shown.

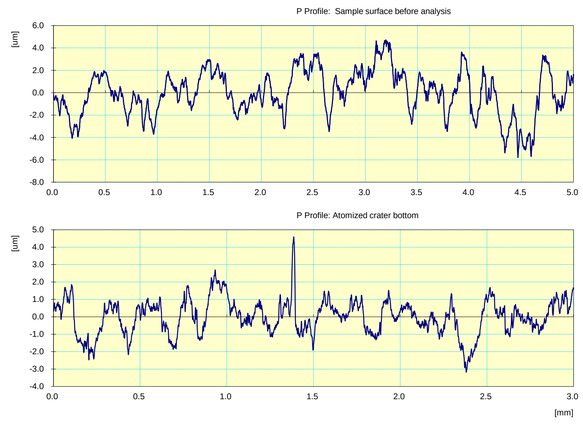
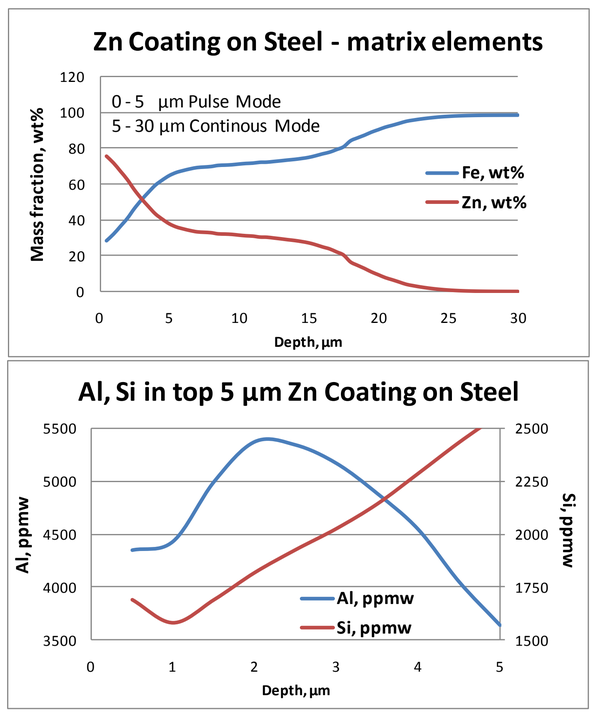


FIGURE 6. Combination of Pulse mode with continuous mode for extended depth profiling of (top) matrix elements and (bottom) minor elements in a zinc coated steel. For matrix elements the distribution from top to 30 µm depth is shown; for minor elements only the pulsed mode profile of the top 5 µm layer is shown.



Conclusion

- µs-FF-GD-MS is the most sensitive analytical technique today for determining the full chemical composition and trace element distributions in engineering coatings or thin films.
- The simple adjustment of the source components results in easy user handling.
- The µs-FF-GD-MS results are in excellent agreement with GD-OES test results, which is still the most common analytical technique today for chemical analyses of coatings or thin films.
- The application field of this new approach is exceptionally broad and will likely impact many new research areas.

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