



## GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY (GDOES), AN EFFECTIVENESS METHOD FOR CHARACTERIZING COMPOSITION OF SURFACES AND COATINGS

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### ABSTRACT

*Within the frame of this work, the technical procedures and real advantages of using Glow Discharge Optical Emission Spectroscopy (GDOES) for establishing depth concentration profiles of surfaces are presented. GDOES can detect low concentrations with high accuracy. It can be used for either quantitative bulk analysis (QBA) or quantitative depth profiling (QDP) in the nanometer to micron range. Non-conductive and conductive samples can be analysed.*

*The main applications of this spectral method are related to different technology fields such as: heat treatment processes, casting, heat and cold forming processes, thermochemical treatments, electro-chemical processes (galvanic coatings), chemical and physical vapour depositions (CVD, PVD), thermal oxidation processes and anodizing, thin-films and others.*

KEYWORDS: glow-discharge, deep-profile composition, spectrometry

### 1. Introduction

The increase of requirements for process control, quality assurance and documentation of product quality has led to an increased interest in the Glow Discharge Optical Emission Spectroscopy. Major organisations linked to the steel manufacturing industry, work for the establishment of an international standard for Zinc coating analysis by GDOES, where the technique is well established. The standard is currently being discussed in ISO TC 201, and in various European committees.

GDOES has various acronyms: GD-AES, GDOS, SDL, GDA, GDS. The GD source (or GD lamp) used in most commercially available GDOES instruments is based on the original design of the Grimm source. GDOES is an analysis technique used to determine the elemental composition of solids. A plasma is created by applying high voltage over an anode and cathode (the sample), thus igniting the argon gas in the analysis chamber. The argon gas is ionized and the ions are accelerated towards the sample, sputtering the sample surface. The sputters atoms from the sample are excited within the plasma to give optical radiation. Since each element has a unique radiation pattern and the intensity can be measured using photon detectors, the concentration of the

elements can be determined by comparison to known standards.

Glow Discharge Analysis (GDA) made its first appearance in 1968 and was designed primarily for bulk spectrochemical analysis of various metals and their alloys. Since its introduction, this method has been steadily developed and has excelled in the areas of surface and coating analysis as well. Compared with conventional excitation techniques, the striking feature of Glow Discharge technology is the ability to discern defined surface layers in the material being examined. In the field of metal analysis the GDA is ideal for concentration profile analysis and surface analysis. All kinds of surface treatment processes as well as surface coating processes can be monitored by analyzing the surface and near-surface areas of the treated material. Coating thickness and chemical composition can be accurately measured using the technique of depth profile analysis. Glow Discharge Spectroscopy is the preferred method of analysis for materials that were previously impossible to analyze by traditional methods. Non-conductive materials and coatings such as glass, ceramics, varnish and paint layers can be analyzed using the optional Radio Frequency source.

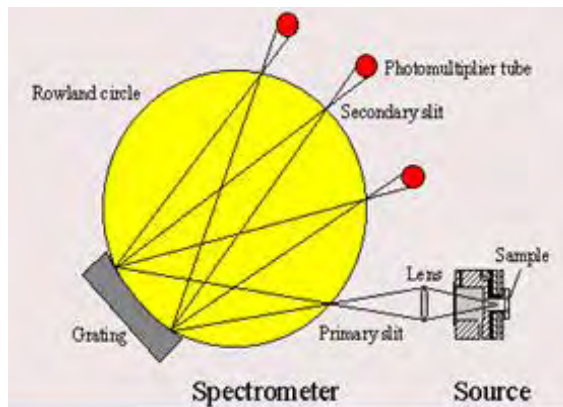
Generally, the fields of application are: Heat treatment processes – in particular treatment of

ferrous and non-ferrous alloys, casting, heat and cold forming (forging, milling, drawing, deep-drawing) steel and non-ferrous alloys, electro-chemical (galvanic coatings), chemical and physical vapour-phase deposition (CVD, PVD), thermal oxidation processes and anodizing (anodizing process), thin-film technologies (ion implanting), thick-film technologies (plasma-powder polymer coatings).

- GD-OES is capable to analyse solid material with only little sample preparation;
- Due to the multi-matrix calibration GD-OES is a versatile tool for depth profiling on such materials;
- The analysis time is short compared to other depth profiling techniques;
- Low consumption of resources (Ar < 0.5 l/min);
- Easy operation of the equipment. The majority of the instruments are working in industrial labs or close to the production line.

## 2. Theoretical Background

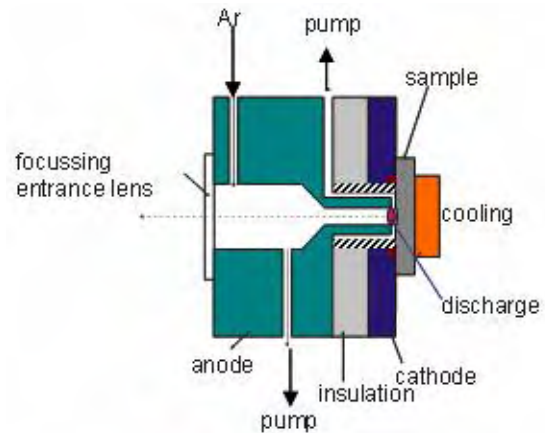
In terms of GD-OES basic design, a hollow anode glow discharge chamber serves as the light source for the spectrometer. The two electrodes of the discharge cavity are designed as a tubular grounded copper tube and the flat sample to be analysed. In fact, the sample closes the discharge cavity: sample introduction is therefore extremely simple. The electrical power is supplied directly to sample. The spectrometer displayed here uses a concave grating in the Rowland circle or Paschen-Runge configuration and photomultiplier tubes (PMT) for the light detection. The use of solid state detectors, CCD's and photo diode array's have become a common alternative for PM Tubes. These detectors allow the acquisition of the entire spectrum, or at least a large portion of it, but are usually slower than PM Tubes and therefore not suitable for very short acquisition times used in thin film analysis. A schematic layout is given in figure 1.



**Fig. 1.** The schematic layout of GD-OES design

After calibration, glow discharge optical emission spectroscopy can provide a quantitative depth profile (QDP) or compositional depth profile (CDP) of materials.

The glow discharge source (figure 2) is constructed by the so called Grimm type design with the sample acting as electrode and simultaneous sealing the source. The instrument can be equipped with anodes of 2.5 mm, 4 mm, and 8 mm inner diameter defining the size of sputter crater and the required sample surface.



**Fig. 2.** The schematic layout of Glow Discharge Source (Grimm type)

Thus, the detector systems used in GD-OES could be: GD – PMT (High sensitivity / High speed), GD - CCD (High sensitivity / Channel flexibility), GD - PMT/CCD (High sensitivity, speed and flexibility).

## 3. Experiment

The paper presents some experimental data of GD-OES analytical possibilities. For the experimental program, a performing **GDA-750 Spectruma – Analytik Spectrometer** (manufactured by Spectruma – Analytik GmbH, Germany) was used.

With over 60 analytical element channels available, the GDA-750 Glow Discharge spectrometer is perfect for demanding applications requiring high resolution and analytical precision. Coatings can be analyzed down to a depth of 200µm, with a resolution of one atomic layer on the surface and 10% relative in deeper regions. The analytical software is powerful and flexible; chemical composition can be determined along with other characteristics such as density or mass distribution in the area of the layer being examined. Comparison of the surface characteristics before and after the technical coating process (CVD, PVD) ensures that the production process is being optimized and that

costly mistakes are avoided. The GDA 750 is also capable of bulk analysis (chemical composition of materials) providing superior linearity of calibration for complex matrices. Using the optional Radio Frequency Glow Discharge Lamp, the GDA 750 is proficient in analyzing non-conductive materials such as ceramics, glass and paint layers. GDA automation: automation of sample handling tuned to customer requirements (to/from conveyor belt-magazine-tipping pallet) by means of robotics is also possible. GDA 750 is used for the direct analysis of solids; two modes of operation are possible: Bulk mode (integrated intensities/conc), and DPA mode (time resolved intensities/conc). All elements of the periodic system detectable from 0,1ppm - 100% in a depth range: <10nm - >100µm.

In terms of GDA-750 RF excitation equipment, formerly, an impedance matching device ("matchbox") was used to adapt the plasma impedance to the output of the RF generator. At present, it will be replaced by the newly developed.

Spectruma RF generator. With this, instability of the RF power after switching on is reduced to a minimum. This makes possible the analysis of thin layers. Capacitors, which have to be adjusted according to the plasma impedance and which often have caused a second analysis, are no longer present.

The optical detection system is designed as a polychromator based on the Paschen-Runge mount.

The polychromator is equipped with a 2400 grooves/mm master grating with a focal length of 750 mm offering a resolution of 20 pm. Up to 64 emission lines can be detected with selected PM Tubes (PMT). The polychromator vessel is evacuated to extent the spectral range into the deep VUV region allowing the observation of wavelength down to 120 nm. Elements of interest like Nitrogen, Carbon, Sulphur and Phosphorous are easily detected using their most sensitive first order spectral lines. A set of CCD detectors can be added covering the spectral range from 200 nm to 800 nm. Another option is a monochromator with a spectral range of 200 nm to 730 nm. This adds flexibility in the choice of elements to be analyzed and spectral lines to be used without technical changes.

#### 4. Results

For the beginning is given an example of an Aluminum clad material.

Usually this material is used in the automotive industry for radiator tubes, condenser tubes etc.

The defining characteristic of this type of product is that the material is actually two different aluminum alloys bonded together in the manufacturing process by heat and pressure.

This creates a multi-layer system, which at first glance may seem to be one solid piece.

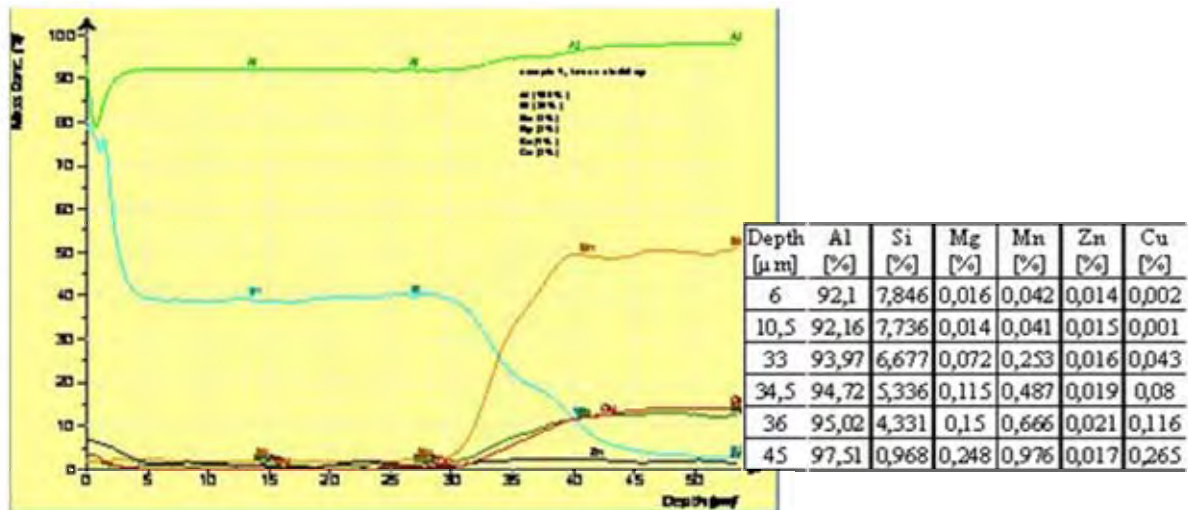


Fig. 3. Aluminum cladding GD-OES analysis results

Producers of this material must control not only the thickness of the clad, but also the possibility for surface or clad contamination coming from elements migrating from the core to the outer layers. The clad material analysed in Figure 3 consists of a 4043 aluminum alloy bonded to the core material, which is

a 3005 alloy type. The thickness of the clad material is 30 microns as seen by the graph and the following data table (figure 3). Secondly, it is presented an example of analysis of zinc coatings. This analysis gives the possibility to know integration of the Zn-concentration or total concentrations versus depth



delivers the coating weight and to control the important elements in the coating like Al, Pb (figure 4). Figure 5 presents the results of GD-OES analysis in the case of a thin - film, CrNiAl type, deposited on a super-alloy used for turbine blade manufacturing.

Figure 6 presents a wire spectral analysis, using an USU adaptor for wires, which offers an easy

sample exchange, a defined sample position and is flexible in sample diameter. Next figure (7) shows the analysis results for a semiconductor layer (GaN) on a saphir base containing a Mg enriched zone of some nm. The maximum Mg-concentration is 250ppm.

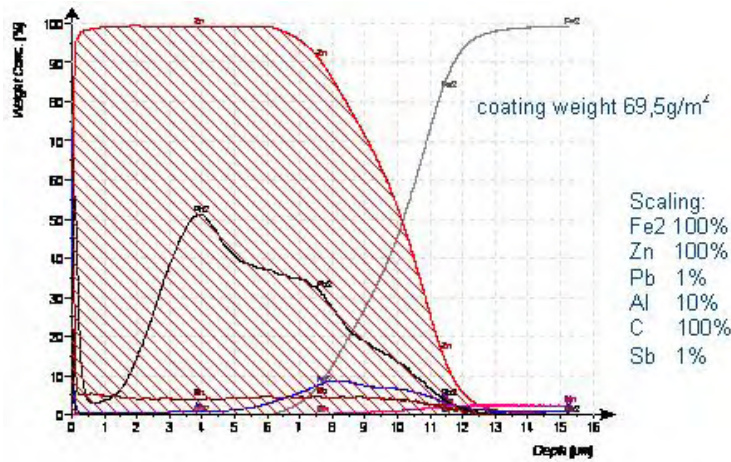


Fig. 4. Zn coating GD-OES analysis results (including the coating weight)

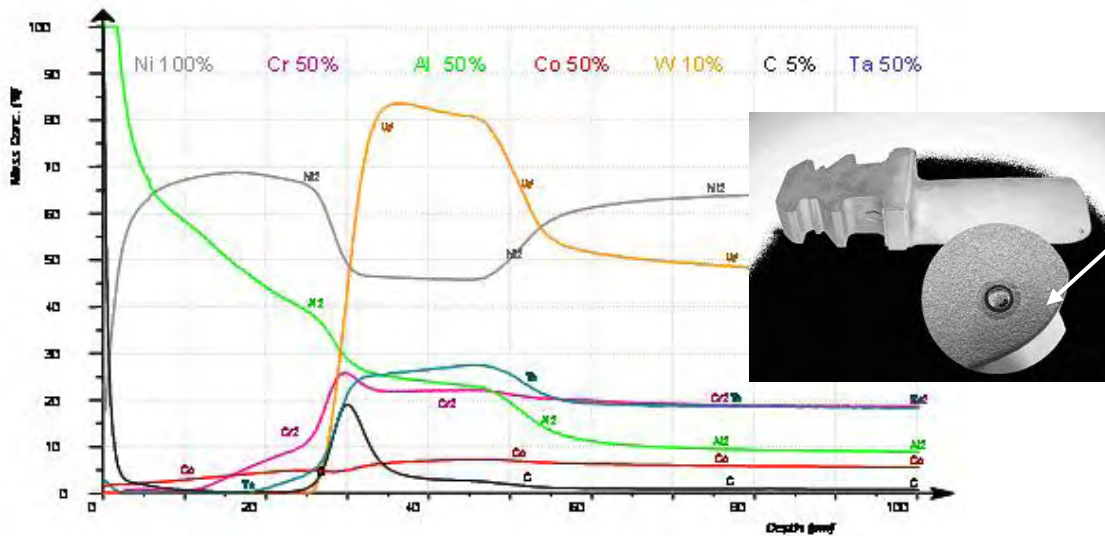


Fig. 5. CrNiAl thin-film GD-OES analysis results (substrate-turbine blade)

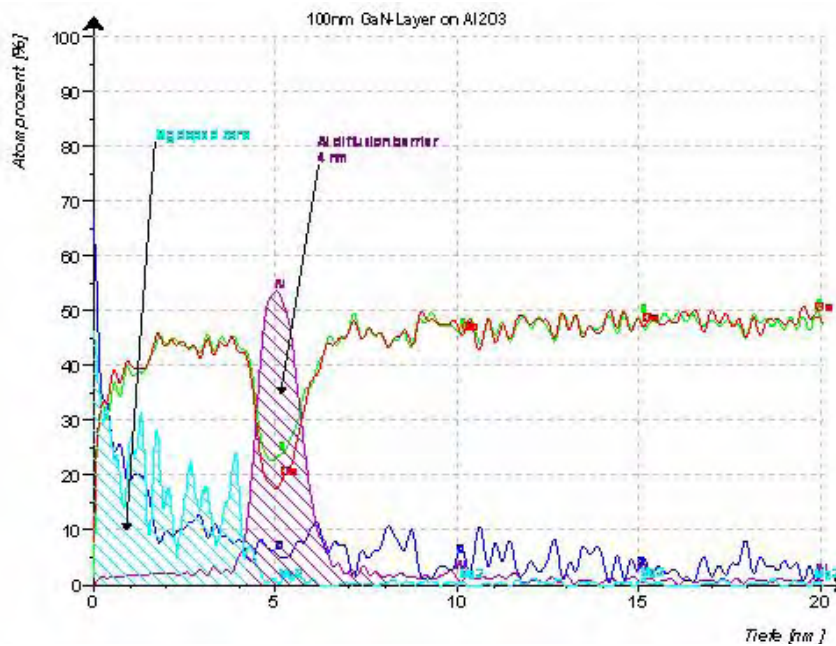
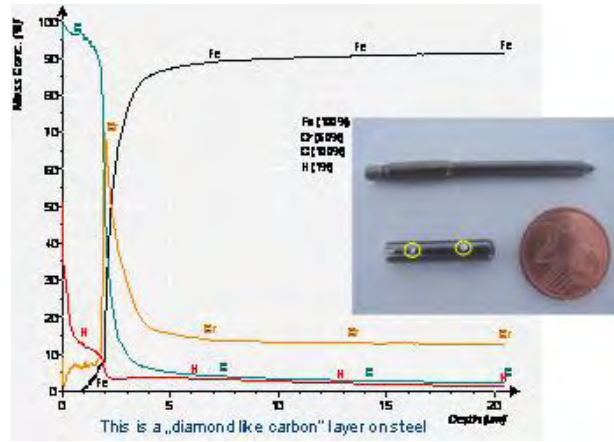
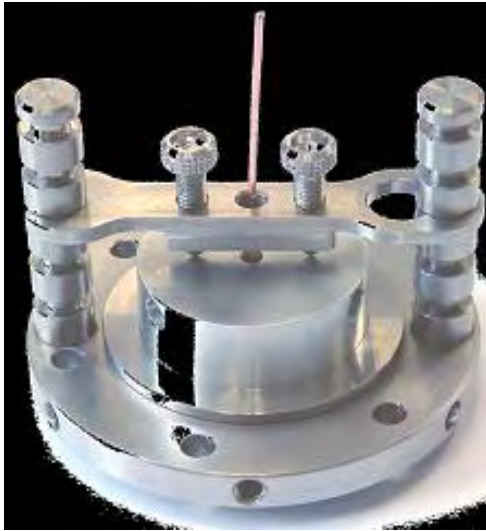


Fig. 7. GD-OES analysis of a GaN semiconductor layer

Table 1. Comparative economical analysis on different spectral techniques

Instrument	Estimative acquisition cost	Costs for consumables /month	Manpower
GDOES	130.000,-€	approx.150,-€	Laboratory assistant / engineer
REM/EDX	250.000,-€	approx.250,-€	Laboratory assistant / engineer
AUGER	500.000,-€	approx.3.000,-€	Engineer /doctor´s degree
SIMS	500.000,-€	approx.3.000,-€	Engineer /doctor´s degree
ESCA	500.000,-€	approx.3.000,-€	Engineer /doctor´s degree

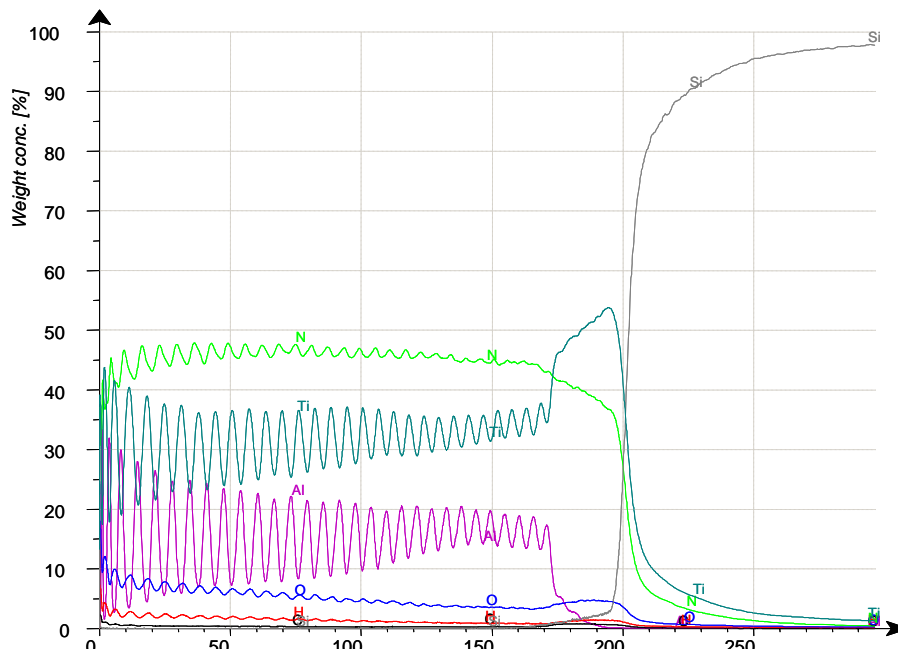


Fig. 8. The RF GD-OES TiN/TiAlN/.../TiAlN/TiN/Si thin - film

Referring on the RF-GDOES analytical possibilities, figure 8 presents the depth concentration profiles of a succession of 60 layers, TiN/TiAlN/.../TiAlN/TiN/Si types, with approx. 3nm per layer.

In terms of prices, sustenance costs, consumables and the necessary manpower, table 1 presents a comparative analysis.

## 5. Conclusions

In the field of metal analysis, the GDA is ideal for concentration profile analysis and surface analysis. All kinds of surface treatment processes as well as surface coating processes can be monitored by analyzing the surface and near-surface areas of the treated material. Coating thickness and chemical composition can be accurately measured using the technique of depth profile analysis.

Glow Discharge Spectroscopy is the preferred method of analysis for materials that were previously impossible to analyze by traditional methods. Non-conductive materials and coatings such as glass, ceramics, varnish and paint layers can be analyzed using the optional Radio Frequency source (GDA 750 spectrometer – Spectruma Analytik GmbH).

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