Surface Analysis of Aluminium by Glow-Discharge Optical Emission Spectrometry

J.M. Long

School of Engineering and Technology, Deakin University, Geelong, Victoria 3217

Surface engineering in solids has become an important field in materials science. Glow-discharge optical emission spectrometry (GD-OES) has proven to be a powerful tool for the rapid analysis of elements in the surface of solids. One may employ GD-OES to determine quantitatively the bulk concentration of elements in a sample, and elemental concentrations as a function of depth. Presented here is an overview of GD-OES analysis and an application to aluminium.

1.   Introduction

Surface treatments in metals have advanced from classic treatments such as case hardening and galvanising, to advanced techniques such as polymer coating, conversion coatings and chemical vapour deposition [1,2]. In such applications, knowledge of layer compositions, thicknesses, and sharpness of transition from one layer to another is critical. All these factors influence the overall performance of the material.

Glow-discharge optical emission spectrometry (GD-OES) has proven to be a powerful tool for the rapid analysis of elements in the surface of solids [3]. With appropriate calibration GD-OES may be employed to quickly determine quantitatively the bulk concentration of elements in a sample. More recent advances allow the calibration of sputter rate. As a result, one may not only determine elemental concentrations in the bulk, but also elemental concentrations as a function of depth into the sample.

Emission spectrometry is a well-known technique for quantitatively analysing an unknown material for the elements present. There are three common means of exciting the sample to produce the optical emission. The first is to apply a high electrical voltage across the sample, which heats the sample in a spark discharge (arc/spark). The second is to dissolve the sample in acid, and "burn" the solution in an argon plasma (ICP). The third, glow discharge, sputters the sample surface with ionised argon atoms, and excites the sputtered surface atoms in the argon plasma.

Figure 1 shows a schematic of the glow-discharge lamp. The sample forms the cathode and a thin (2-8 mm diameter) metal tube forms the anode. A small O-ring separates the anode from the cathode. High-purity argon is pumped into the anode chamber. A high voltage (DC or RF) between sample and anode ionises the argon to produce a glow discharge. The excited argon ions cause uniform sputtering of the sample surface. The sputtered atoms from the sample enter the plasma, and they are excited by collisions with electrons or other argon atoms. The resulting optical emission forms the atomic spectrum from the sample.
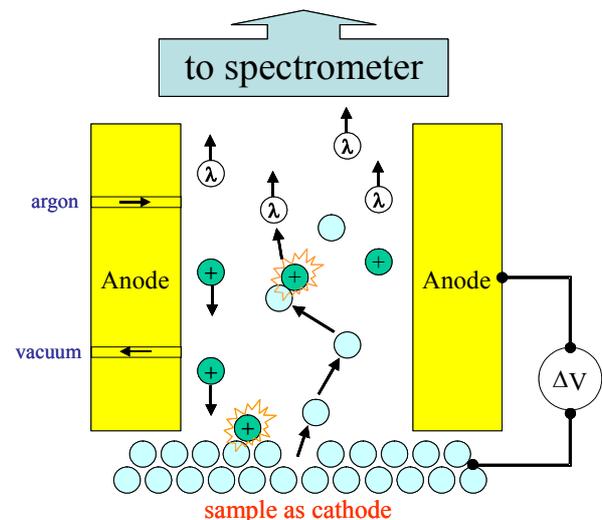

Fig. 1. The glow-discharge lamp.

The emitted light passes into a standard polychromator. A series of fixed photomultiplier tubes detect and record specific wavelengths, corresponding to selected elements. Through sputter-rate calibrations, one can transform a plot of detector intensity versus time into a profile of elemental concentration versus depth into the sample. This allows depth profiling on a host of advanced materials: diffusion-treated metals, coated metals and other materials, multi-layers, painted surfaces, hard materials coated with polymers, thin films, and many others. If an RF glow-discharge source is used, it is also possible to perform depth profiling on ceramics, polymers, and non-conductive coatings on metals.

2. Experimental

In this study, the instrument used was a Leco GDS-850A spectrometer, equipped with a Grimm-type DC lamp for conductive samples [4,5]. It is the first GD-OES instrument in Australia with the ability to perform quantitative depth profiling. The anode has a diameter of 4 mm, for a sampling area of 12.5 mm^2. The spectrometer is equipped with dual Rowland circles, having curved, holographic diffraction gratings of 1800 lines/mm and 3600 lines/mm, respectively, for a spectral range of 120–800 nm. There are 32 detectors, having the ability to detect 29 elements, including most standard metals, nitrogen, oxygen, carbon, hydrogen, boron, chlorine, some rare earths, and others. The instrument was calibrated by Leco against a large number of certified and non-certified reference materials. Sputter rates are also calibrated against a database developed and provided by Leco. The day-to-day optical drift of the spectrometer is corrected by means of a series of setting-up standards. For the present analysis of aluminium, the glow-discharge lamp was held at a constant DC voltage of 700 volts with respect to the sample. The plasma current was held at 20 mA. As sputtering progressed, a variable argon pressure, nominally held around 5 torr, controlled the current. The test sample is an aluminium casting, coated with an oxide layer.

3. Results

The calibration for major elements employs the multi-matrix method [3]. Figure 2 shows the calibration curve for aluminium. Each *y*-data point is the product of the weight fraction of aluminium, and the standard's sputter rate in micro-grams per second. Plotted along the *x*-axis is the intensity of the spectral line in volts. The standards used are a mixture of aluminium alloys and other metals. The calibration curve is a second-order polynomial fit to the data.
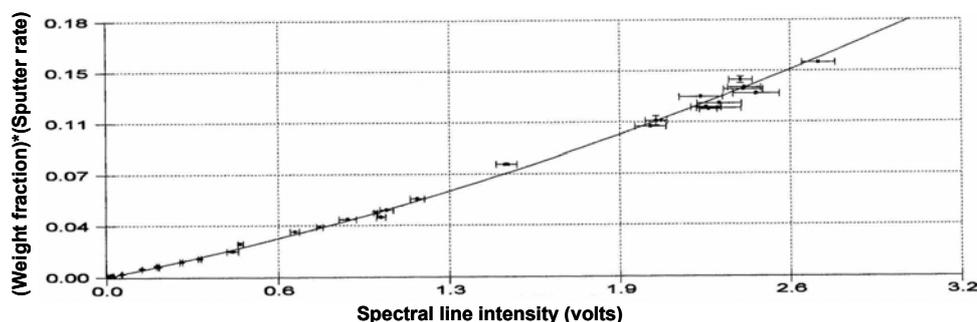

Fig. 2. Multi-matrix calibration curve for the aluminium spectral line at 396.15 nm.

Figure 3 shows quantitative depth profiling of the sample. The total analysis sputtered to a depth of 20 microns in 8 minutes. The oxide layer is about 1.5 microns deep and is accompanied by a peak in nitrogen and silicon. There is also about 1% carbon on the surface. Also detected in the bulk of the metal were other trace elements typical of aluminium alloys.
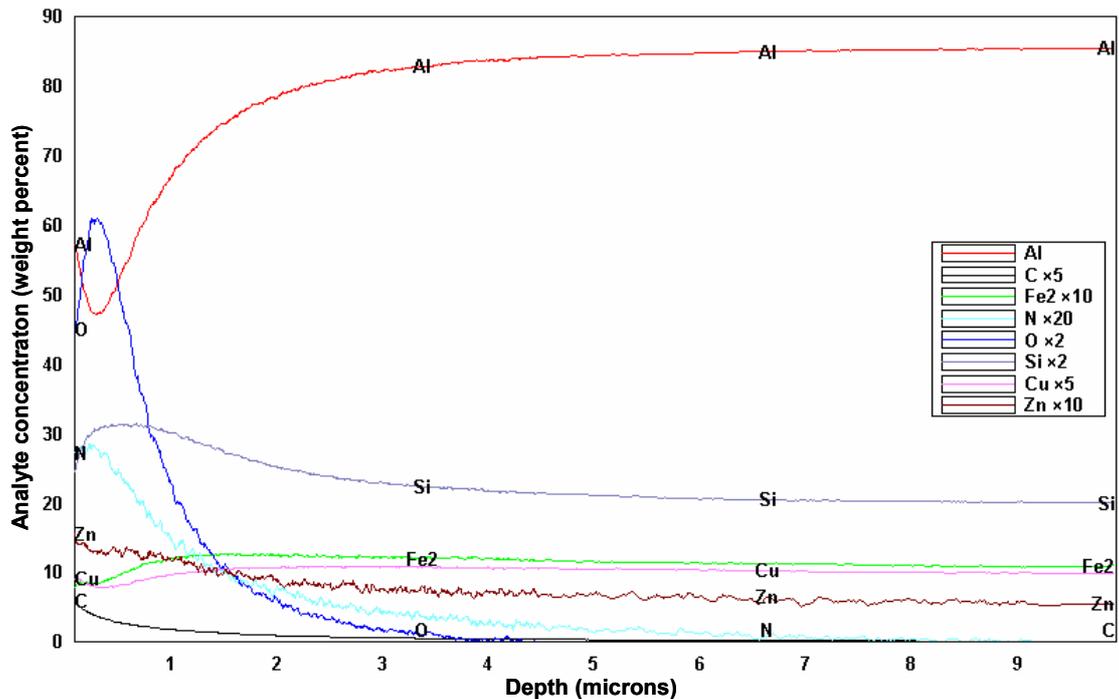
Fig. 3. Concentrations of selected elements in weight percent as a function of depth.

In a similar analysis on the same sample, sputtering occurred through some pores in the metal. This was accompanied by sharp, positive spikes in the nitrogen concentration, and similar negative spikes in the aluminium signal. There was no such effect in the oxygen signal. Thus these pores contained mostly nitrogen gas.

The analysis demonstrates the usefulness of GD-OES to the analysis of aluminium and its ability to measure thin oxide layers on aluminium. The use of a DC lamp requires the sample to be electrically conducting. For the measurement of thick oxide layers, such as in anodised aluminium, an RF glow-discharge lamp and another calibration are required.

Acknowledgments

References

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