Depth profile analysis of nanoscale oxide layers by Glow Discharge Optical Emission Spectrometry

Michael Köster[1], Thomas Asam[1], Josef Baiker[2]

[1] TAZ GmbH, Hauptstrasse 31A, D-86495 Eurasburg, Germany;
[2] Baiker Analytik, Gampenhof 3, D-88636 Illmensee, Germany;

Introduction

Glow discharge optical emission spectrometry is the fastest depth profiling technique but is still believed to be unsuitable for the analysis of thin layers. When thin layer analysis is needed, other, more complex and costly methods, like AES, ESCA or SIMS, are usually preferred. In today´s development of new technological products, the properties and quality of the product depend more and more on their immediate surface. Beside surface analysis in advanced research, the development of a rapid testing method will become necessary. To provide the industry with fast and reliable methods and devices for production control, the sophistication of glow discharge depth profiling methods is of great importance. With the disclosed presentation of in-depth elemental composition of some of the most common metal oxide layers, we like to show the present capabilities of this surface testing method.

Experimental

GDOES-depth profile analysis has been carried out using a modern, fully equipped spectrometer (Fig. 1) with supply of 2 kHz data acquisition for all PMT channels. An dc argon-hydrogen plasma (2% H_2 v/v) running with an 2.5 mm anode-diameter and 600 V, 10 mA , was used. The current was controlled by a preset plasma pressure. The hydrogen content and a flushing interval of 100 s allows best desorption of some of the molecular substances used to be found on metal surfaces. The caracteristics of the above given settings are approved for thin film analyses during a period of more than 3 years.

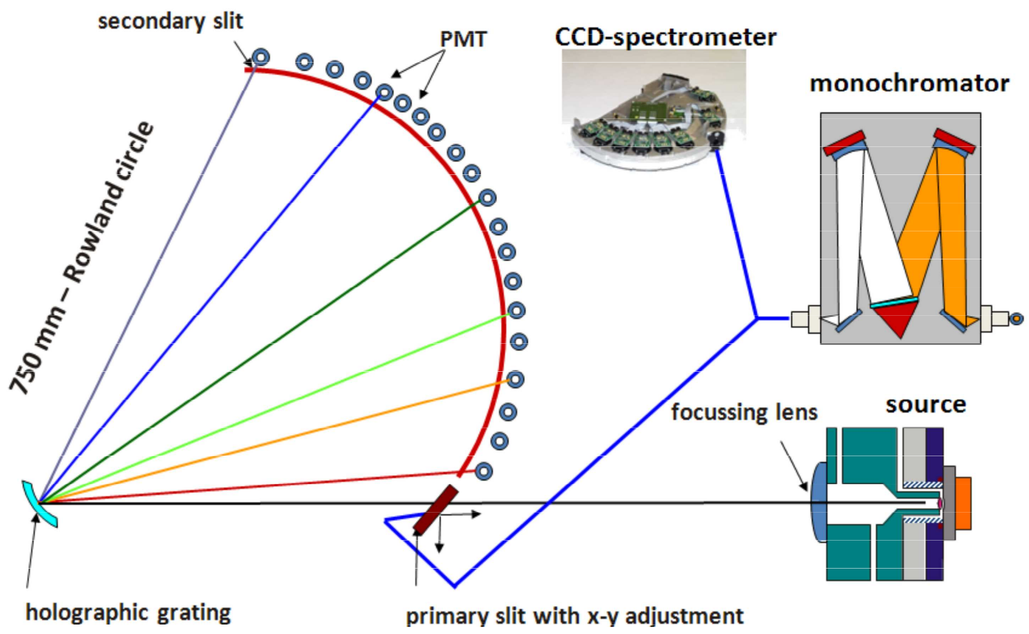

Fig. 1: Schema of the glow discharge spectrometer used in this study.

A nickel foil, a galvanic pure chromium layer and a pickled high alloyed steel sheet have been analysed using the same calibrated routine. For an estimation of practical detection limits and accuracy of results for the immediate surface, restarts were carried out after reaching the homogeneous ground material (Tab. 1). Depth profiles were created for a set of 13 elements (Fig. 2). From this selection only Nitrogen and Oxygen needed correction for interference lines (iron and water). The steel and the chromium sample were also analysed by auger-electron depth profiling with the focus on oxide layer thickness and concentration of the major elements. The comparison of both methods results are given in the discussion below.

Results (continued)

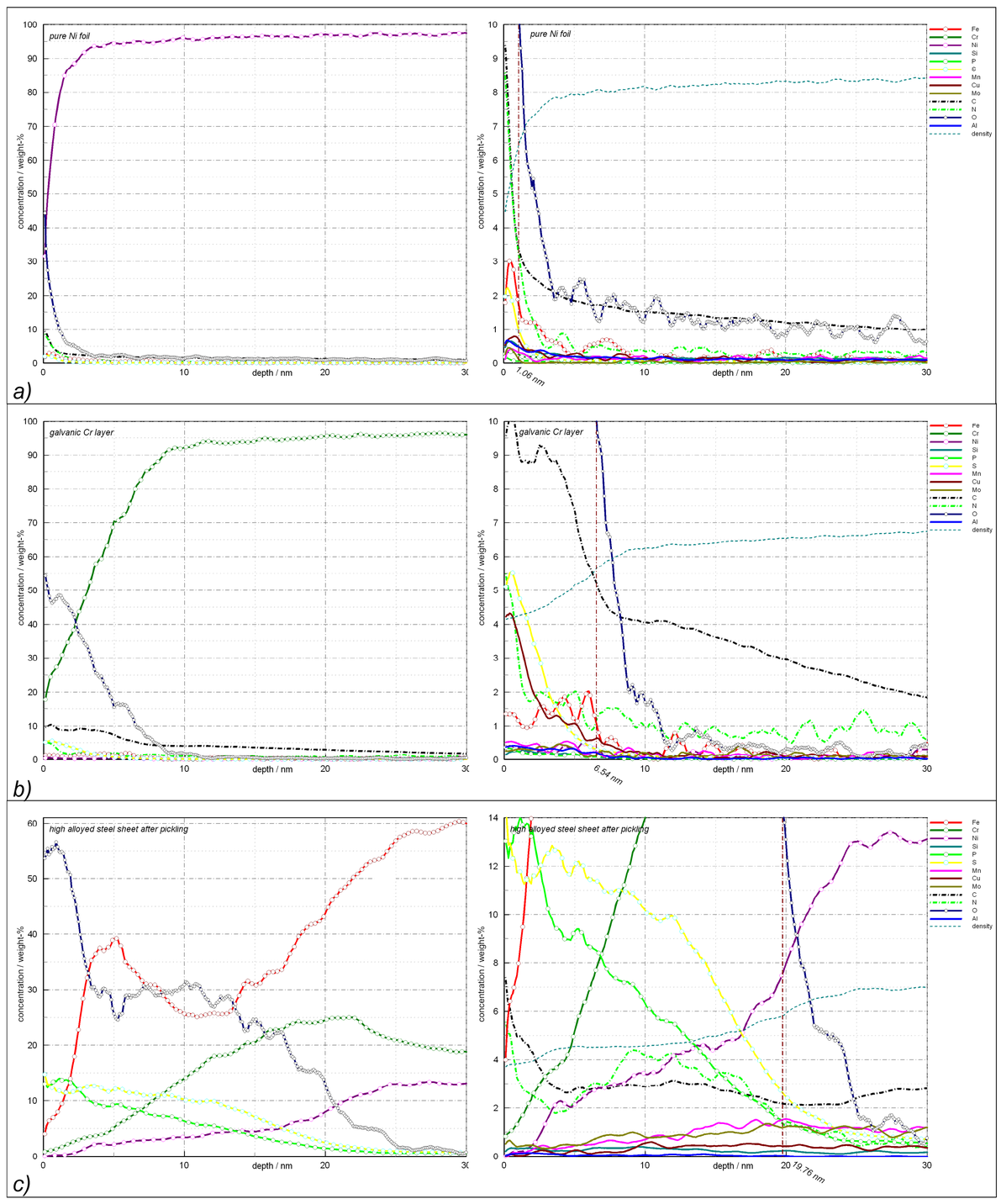

Fig. 2: glow discharge depth profiles of a) pure nickel, b) galvanic chromium and c) pickled steel sheet.

Results

Table 1: Accuracy of the first nanometer of the profiles according to the restart-experiments. %-nom equals the results at the end of a single depth profile while the restart-values represented the average concentration in the first nanometer layer of a second measurement on the same spot. The results for nonmetals C, N and O remain uncertain due to debris and moisture on technical surfaces and residuals in the plasma gas.

Element	Line	Chromium		Nickel		Steel		Typical
	nm	%-nom.	Restart	%-nom.	Restart	%-nom.	Restart	Shift %
Al	396,152	0,005	0,041	0,039	0,047	0,004	0,045	< 0,04
C	165,639	0,003	0,799	0,068	0,329	0,127	4,980	0,3 – 6
Cr	425,433	> 99,5	86,16	0,012	0,010	18,24	22,26	< 0,01
Cu	327,396	≤ 0,007	0,254	0,032	0,013	0,151	0,347	0 – 0,25
Fe	371,994	≤ 0,026	≤ 0,026	≤ 0,026	≤ 0,026	65,91	47,86	< 0,10
Mn	403,449	≤ 0,005	0,136	0,066	0,299	1,033	1,447	0,1 – 0,2
Mo	386,411	≤ 0,010	0,155	≤ 0,010	≤ 0,010	2,078	3,760	0 – 0,2
N	174,272	0,360	5,823	0,034	0,023	≤ 0,023	0,318	0 – 6
Ni	341,476	≤ 0,008	0,189	99,61	98,34	12,23	3,57	~ 0,2
O	130,217	≤ 0,019	6,240	0,024	0,823	≤ 0,019	14,75	1 – 15
P	177,433	≤ 0,002	0,033	≤ 0,002	≤ 0,002	0,034	0,051	0 – 0,02
S	180,731	≤ 0,001	0,129	≤ 0,001	0,014	≤ 0,001	0,272	0 – 0,3
Si	288,157	≤ 0,003	0,038	0,110	0,103	0,181	0,352	0 – 0,04

Contact: Mkoester@tazgmbh.de

Discussion

Glow discharge depth profile analysis were carried out on three different metallic surfaces. Oxide and reaction layers are found with thicknesses between 1 and 20 nm. The results were confirmed by auger-electron depth profiling, in which a nm layer of chromiumoxide and a nm thick reaction layer, rich in sulfur and phosphor, has been found too.

Beside the solid components of a surface, residuals of molecular substances contribute to the results for the first few nanometer of a measurement. This obviously effects the depth profiles especially for carbon, nitrogen and oxygen. With high concentration of these elements, an analytical bias seems to occur, leading to discrepancies of some 0,1% for most of the other elements. The ignition phase itself seems to have no effect on the accuracy of the depth profiling, since surfaces without adsorbed substances, like nickel in our experiment, gave results for the surface, which are in good consistence with the bulk composition. However, the repassivation processes of highly reactive metals impeded a simple proof, whether new adsorption or solely chemical reactions taken part in the surface changes during a “two-step experiment”.

According to this, if no residuals are gathered on the surface, the results for the upper atomic layers of a sample could be as good as with a glow-discharge bulk analysis. With data acquisition rates of 2 kHz, a glow discharge analysis spectrometer gives some 10 intensity values per atomic layer, far enough for good nanoscale analysis.