Survey on the Suitability of Coatings Containing Hydrogen as Layered CRM for GDS

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1. Introduction

The development of certified reference materials (CRM) for hydrogen is essential for a reliable GD-OES quantification, not only for the *bulk* analysis, but especially for depth profiling of *layers*, which is affected by contamination or contain frequently themselves hydrogen.

Despite of the very large offer of analytical methods existing nowadays, there still are severe limitations as far as the quantitative analysis of hydrogen in (layered) solid samples is concerned.

Analytical method	Detection of H	Quantification of H	Limitations
Hot Extraction			no local information (i.e., no depth profiles)
NRA			analysed depth of up to only 1-2 µm
ERDA			”
SIMS		–	lack of H-CRM, thin layers
GD-OES		–	lack of H-CRM

2. Demand and availability of H-CRM for GD-OES

The combination of quick *qualitative* analysis (m/min) of layered materials up to a depth of 100 m and low detection limit of H (1 g/g) makes GD-OES a powerful technique for the analysis of H.

Nevertheless, the reliable *quantification* of H by GD-OES is not possible yet due to the lack of certified reference materials (CRM) necessary for calibration. At present there is no CRM suitable for the GD-OES calibration of H (www.comar.bam.de).

Trials of production of *bulk* materials (charged with H) or hydride pellets, where the H concentration was not stable over longer periods of time (even at room temperature), have failed. The reliable alternative has been proven to be some thick *coatings* containing H in *bound* form and hence unable to diffuse easily even at higher temperatures. Different matrices are needed to perform a matrix independent calibration.

Some examples from the survey carried out are given below.

3. Coatings proved as unstable

Various coatings containing H have been proved as *unstable* with respect to its concentration in the coating over longer periods of time.

Fig. 1 shows a Ti plate charged with H (5 m), which has suffered a strong depletion of H during several months at room temperature.

Other thick electroplated coatings such as hard Cr (60 m), see Fig. 2, and CoPt(W), see Fig. 3, show a relative homogeneous in-depth distribution of H; however, after heat treatments which are usual in industrial applications, almost all H diffuse out from the coating - so that such materials are *not suitable* as reference coatings for H.

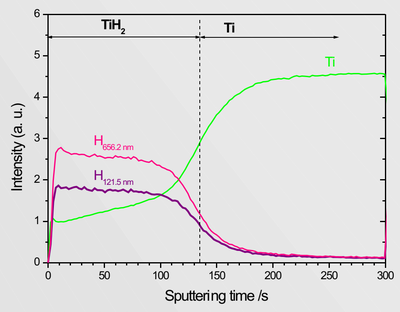

Fig. 1 GD-OES depth profiles of TiH_2 / Ti; Ti I 365.3 nm, H I 121.5 nm, H I 656.2 nm.

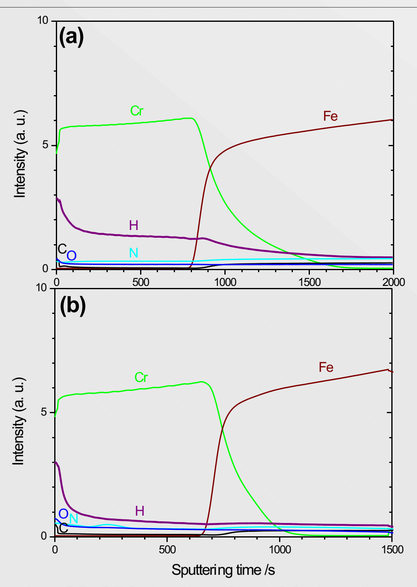

Fig. 2 GD-OES depth profiles of Cr / steel; (a) as plated, (b) after heat treatment: Cr I 425.4 nm, H I 121.5 nm, C I 156.1 nm, O I 130.2 nm, N I 149.2 nm, Fe I 371.9 nm.

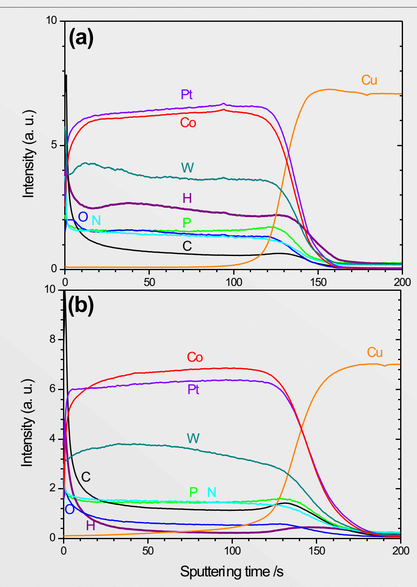

Fig. 3 GD-OES depth profiles of CoPt(W) / Cu: (a) as plated, (b) after heat treatment; Co I 345.3 nm, Pt I 265.9 nm, W I 400.8 nm, H I 121.5 nm, P I 177.4 nm, C I 156.1 nm, O I 130.2 nm, N I 149.2 nm.

4. Potential candidates for H-CRM

Electrolytically coated thick layers like **Zn(H)** have provided a homogeneous and stable H concentration at various conditions, see Fig. 4a (Zn(H) thickness: 12 m; H concentration: 10 at.-%) Comparatively to Fig. 4b (Zn thickness: 20 m), where no H is present in a hot dip Zn coating.

WC(H) hard coatings, see Fig. 5 (WC(H) thickness: 2 m; H concentration: 22 at.-%), has been established a second class of coatings where the homogeneous H concentration keeps stable.

Another suitable candidate of H-CRM might be Si(H), Fig. 6 (185 nm thickness; H concentration: 10 at.-%), unfortunately the existent coatings were destined for NRA, so that the coating thickness is rather low for GD-OES.

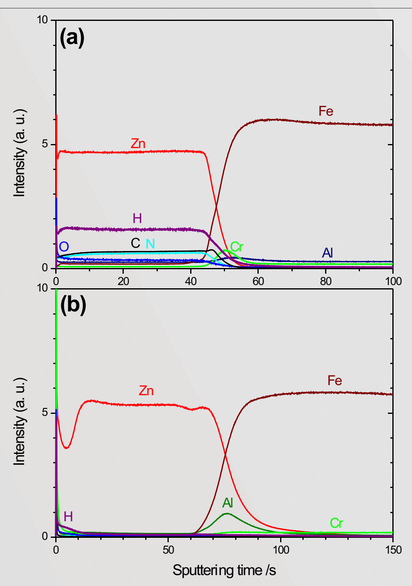

Fig. 4 GD-OES depth profiles of Zn / steel; (a) electroplated Zn, (b) hot dip Zn: Zn I 330.2 nm, H I 121.5 nm, C I 156.1 nm, O I 130.2 nm, N I 149.2 nm, Fe I 371.9 nm, Cr I 425.4 nm, Al I 396.1 nm.

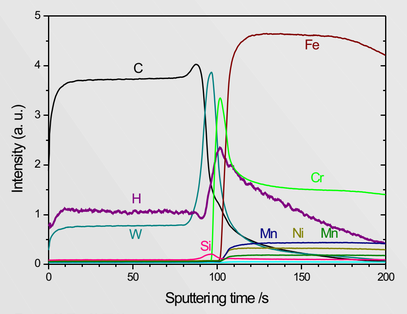

Fig. 5 GD-OES depth profiles of WC(H) / steel; C I 156.1 nm, W I 400.8 nm, H I 121.5 nm, Fe I 371.9 nm, Cr I 425.4 nm, Mn I 403.4 nm, Ni I 349.2 nm, Mo I 386.4 nm, Si I 288.1 nm.

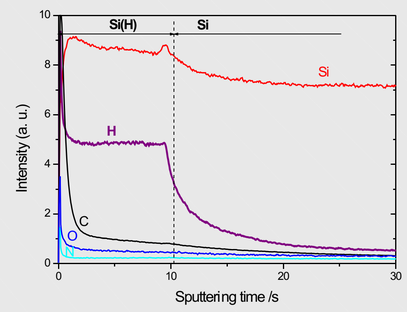

Fig. 6 GD-OES depth profiles of Si(H) / Si; Si I 288.1 nm, H I 121.5 nm, C I 156.1 nm, N I 149.2 nm, O I 130.2 nm.

5. Certification of the H concentration

A further characterisation/*certification* of the coatings found having *stable and homogeneous* H concentrations (Sec. 4) is planned by using a *combination* of the analytical methods presented in the Introduction, i.e.:

in-depth and lateral homogeneity checked by *qualitative* GD-OES depth profiling, and

the topmost 1-2 m analysed quantitatively by ERDA and NRA.

Additionally, the integral concentration of H in the coating will be measured by HE, too.

Different concentrations of H will be also precisely defined for each selected type of coating.

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6. Potential hot applications

Prediction of *hydrogen embrittlement* by GD-OES depth profiling as a fast and low priced alternative to the costly heat treatment procedures.

7. Conclusions

Two types of coatings have been proven in a survey as well-suited candidates for CRM for H: Zn(H) and W-DLC(H)

Different concentrations of H (at least three) must be further defined (for each type of coating) and reproducibly produced

Further homogeneity & stability measurements by combining more analytical methods are necessary

H emission yields will be evaluated and expected matrix effects investigated.