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## **Recalibration-free measurement of the compound layer thickness of nitrocarburized samples by glow discharge optical emission spectrometry (GD-OES)**

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### **Introduction**

Nitriding and nitrocarburizing are commonly used surface treatment processes for the improvement of material properties, such as wear resistance, fatigue endurance and corrosion resistance. Such nitride layers are formed thermochemically in a nitrogen and carbon rich atmosphere or salt bath and normally consist of  $\epsilon$ -,  $\gamma'$ -nitride and  $\epsilon$ -carbonitride. These phases affect the mechanical properties and, to a certain extent, can be controlled by the nitriding parameters. The wide use of nitrided parts is caused by the low size alternation and deformation as well as the lower energy input in comparison to other surface treatments.

In glow discharge optical emission spectrometry, sputtering and atomic emission in an argon glow discharge are combined to provide an extremely rapid technique for depth profil analysis up to 200  $\mu\text{m}$ . During the measurement, positive argon ions are accelerated towards the cathode causing a continuous material loss in the sample surface. The sputtered sample atoms are excited by the plasma and de-excited by photon emission with characteristic wavelength, enabling element determination. High sputtering rates of more than 1  $\mu\text{m}/\text{min}$ , high element sensitivity, good depth resolution, low matrix effects and no ultra-high vacuum requirements are some advantages of the method [1]. GD-OES has been broadly used for quantitative depth profile analysis not only in the field of research but also in the area of quality assurance and the process accompanying analysis. Because of the extremely short measurement times, the high reproducibility, the low operating and analysis costs and the possibility to measure curved surfaces with an adapter, GD-OES becomes a method in the routine analysis of nitrided and nitrocarburized samples [2-5].

The decreasing transparency as a result of contaminations on the lens between the glow discharge source and the optical spectrometer demands a periodical recalibration of the instrument. At a high sample throughput during shift operation this represents an additional workload which can not be neglected. Furthermore in the standard quantification algorithms the density is calculated as a weighted average of the density of the pure elements, according to their concentration in atomic percent. This rather crude assumption gives very accurate results for all types of metal alloy but the electronic and lattice structures in nitrides and oxides causes deviations which can exceed 10% [1]. This deviations cause relevant errors in the calculated depth.

The purpose of this work is to present a method for an accurate recalibration-free measurement of the compound layer thickness by analysing characteristic points in the depth profile of the elements Fe, C and N.

## Experimental

The measurements were carried out using an GDA 750 spectrometer (Spectrums Hof/Saale, Germany) equipped with a Grimm-type glow discharge source of 2,5 mm in diameter. The depth profiles were measured in the DC excitation mode with optimised parameters 1200V, 13mA for good depth resolution. The wavelengths of interest are Fe<sub>2</sub> (238,204 nm), N (149,262 nm) and C (156,143 nm). For comparative studies a standard calibration was carried out by using the reference materials NIST 1262, NIST 1271, NIST 1661-1167, MBH 13XNSC4, JK-8F, JK 41-1N, JK-49. It is worth mentioning that there exist a lack of suitable reference materials for high N-concentrations. There is only one special cutting material Coronite (JK 41-1N) with a high nitrogen concentration of 6,9 wt% but with a very different matrix as that to be analysed.

The nitrocarburized samples were manufactured by the Lohnhärtereier Faulhaber, Zella-Mehlis, by using the typical nitriding steel 31CrMoV9. The sample surface was grinded before nitriding to ensure a smooth surface with  $R_z < 5\mu\text{m}$ , so that no penetration of atmosphere gasses during measurement could occur. 6 nitrocarburized samples with compound layer thickness in the range of 1-24  $\mu\text{m}$  were prepared to set up calibration graphs by using several characteristic points in the depth profile of the elements Fe, C and N. Also 4 control samples under similar conditions as well as 2 gas nitrided and 2 salt bath nitrided samples were prepared. The compound layer thickness was measured metallographically with a light optical microscope as well as an electron microscope.

## Results and Discussion

Quantitative depth profiles with excellent results in terms of composition and depth can be obtained with the standard software models based on emission yield. This holds true for all kinds of metallic alloys, but as mentioned above for nitrides and oxides the lattice structure of these compounds leads to derivation in the calculated depth. In the present work a conventional way of calibration is applied, by plotting the sputter time of characteristic points (Fig. 1) versus the known layer thickness of calibration samples. The best linear correlations were found for the inflection and turning points of the Fe- and N-profiles and for the inflection, turning and maximum points of the C-profiles. By doing so, it is not necessary to define one point of the profile which represents the thickness of the compound layer but it is possible to use all points which change continuously with the increasing layer thickness. This also improves accuracy of the method. Fig. 2 shows the good linear correlation for the N - turning and inflection points. The divergence of the two regression lines with increasing depth arises from the fall of depth resolution with sputter time. The zero point offset includes failures during calibration, plasma stabilisation times, adsorption layers and the influence of surface near porosity. Furthermore the slope of the regression line includes the observed drop in the sputter rate with increasing depth.

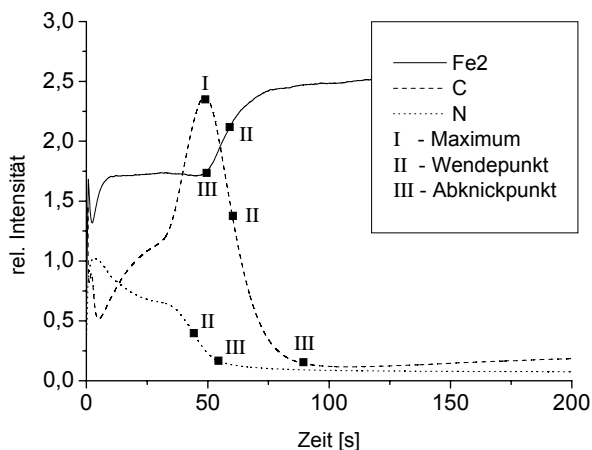


Fig. 1: clarification of characteristic points

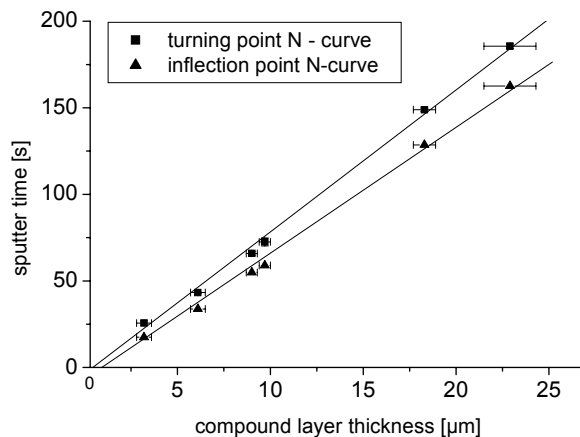


Fig. 2: N linear calibration graph for the nitrogen-turning and inflection points

The results suggest that under regular operating conditions the determination of the sputter time of the selected points is independent of the decreasing transparency of the lens and the changing background. Fig. 3 shows the transparency loss over one month after cleaning of the lens, when the drop of transparency is most pronounced. The remaining differences in sputter time are results of normal thickness fluctuations.

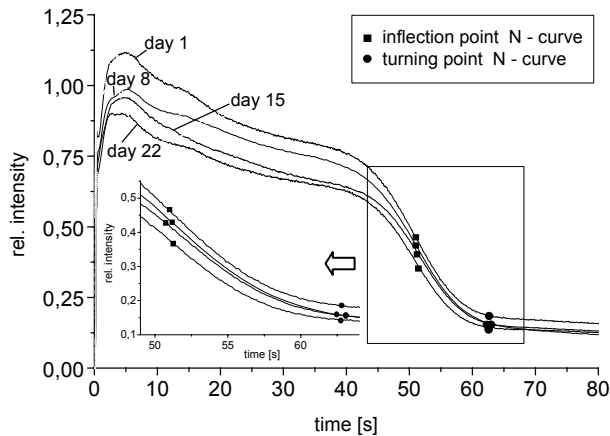


Fig 3: N-signal and position of characteristic points depending on transparency loss

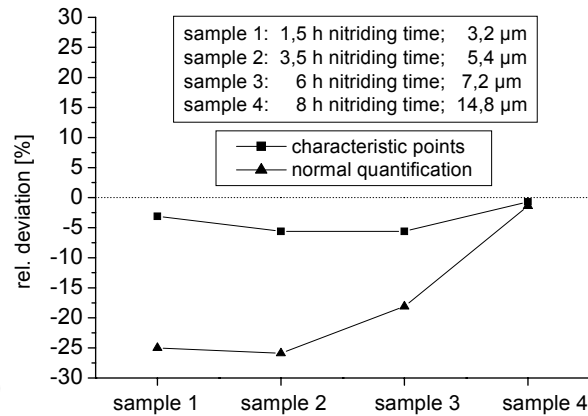


Fig 4: results of the control samples with standard quantification and characteristic points (average)

The results of the 4 nitrocarburized control samples suggest that recalibration free measurements with an accuracy better than 6% can be performed (Fig. 4). The relative high deviations for the standard quantification algorithm result from the above mentioned density problem and the changing porosity in the nitride layers. For the gas nitrided and salt bath nitrided samples changes in the depth profiles and changes in the porosity respectively lead to deviations less than 10%.

Further investigations are necessary to determine the effect for different bulk materials. But the short time span to record such calibration graphs and the low workload also allow to prepare several graphs for different materials. Furthermore tests on other surface coatings especially of thicknesses notably below 1 µm are planned.

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