

CHEMICAL DEPTH PROFILING OF TOOL MATERIALS USING GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY (GD-OES)

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Abstract

Surface treatments and surface coatings on tool materials are routinely used to improve mechanical properties of the tool. In the development of existing and new surface treatments characterisation of both mechanical and chemical surface properties of the tool material composite are required.

The present investigation describes a very useful method of chemical characterisation through elemental depth profiling using glow discharge optical emission spectroscopy (GD-OES). The method is based on a simultaneous sputtering and elemental quantification of the analysed surface. Elemental depth profiles up to 100 µm deep and with a relative depth resolution of 10% can be recorded in about 30 minutes. Primarily conducting materials and compounds can be analysed; e.g. physical vapour deposited (PVD) coatings, nitrided and boronised steel, etc.

Investigated material was nitrided AISI H13 tool steel using four treatment settings. Also tested was an experimental PVD coating TaC with three settings of bias voltage during deposition. In addition to elemental depth profiling, the test materials were investigated by hardness indentation, scratch test, surface layer morphology and tribological testing.

The best wear resistance of the nitrided materials was obtained with a dense compound layer containing 5–10 wt% nitrogen, whereas porosity found in the layer containing above 10 wt% nitrogen deteriorated the wear resistance. All TaC coatings displayed good wear resistance, though a significant amount of oxygen was found in two of them. The investigation showed that GD-OES can provide new and very useful chemical information in addition to

mechanical and tribological testing and a more extensive use of the technique is believed to be beneficial for future tool material developments.

INTRODUCTION

Tools for machining and forming are today to a large extent composed of a surface coating or a surface modified layer on top of a tool steel substrate. Frequently, the surface treatments increase the service life of the tools up to orders of magnitude, which may increase the manufacturing productivity just as much.

A tremendous number of surface treatments are commercially available for tooling applications. However, PVD-coating probably dominates in machining and in cold forming tools. In hot forming nitriding is frequent, as well as the use of uncoated tools. Further information about these methods can be found in [1] and [2].

Characterisation methods for surface treated tool materials . Development of new surface treatments and improvement of existing techniques, incorporate several characterisation methods, both mechanical and chemical. Also laboratory tests are essential, which imitates the actual application and, if possible, field tests.

Typical methods of mechanical evaluation incorporate hardness and scratch testing. Thickness and morphology of a surface layer can be studied in a cross-section, which can be either fractured or polished. Residual stresses in surface coatings are typically assessed by either X-ray diffraction (XRD) or a beam deflection technique [3]. XRD also provides chemical phase information. A very informative, though time consuming, method of surface evaluation is of course transmission electron microscopy (TEM), which enables information about both morphology and chemical information.

Elemental depth profile information can be obtained with e.g. X-ray photo electron spectroscopy (XPS), auger electron spectroscopy (AES) and the method used in this study, GD-OES. All these techniques are based on material removal by argon sputtering and elemental analysis, either simultaneously or in steps.

The GD-OES-technique and its typical features. The advantages of GD-OES are its rapid, multi-elemental acquisition, the high sensitivity of

light elements, e.g. C, N and O and a very good quantification accuracy. The depth resolution is about 10 % of the depth analysed and the minimum information depth is approximately 1 nm. The method is based on a Grimm type glow discharge lamp [4], see Fig. 1. An electrical current in the lamp ionises the atoms sputtered from the specimen, and forms a plasma with wavelengths characteristic for the elements of the removed material. An example of sputtering rate is the one in iron of about $30 \times 10^{-9} \text{ ms}^{-1}$. The spot analysed is typically 4 mm in diameter but can be reduced to 2 mm. Conductive materials are analysed using a lamp with a DC current and non-conductive materials, e.g. insulating ceramic coatings and polymers, can be analysed with an RF-lamp using an AC current.

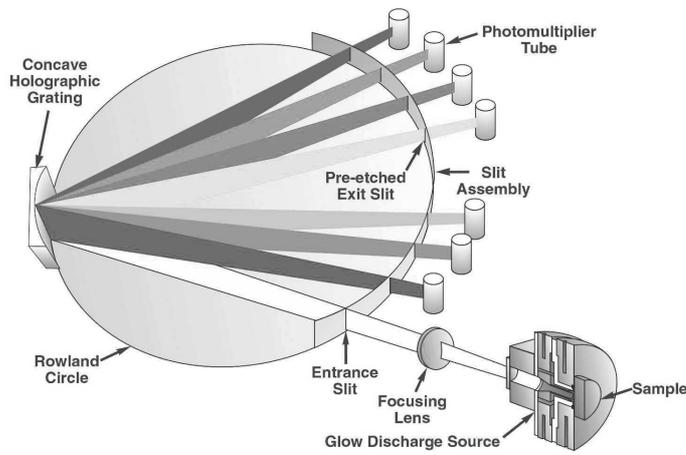


Figure 1. Schematic of the GD-OES principle.

Aim and motivation of the investigation. The aim of this investigation was to show the potential of the GD-OES technique as a mean of chemical characterisation of tool material composites. The chemical depth profile information together with mechanical evaluation is used in the development of new surface coatings and in the optimisation of existing surface treatments for tool materials.

In the present study, materials representing two major types of surface treatments for tool materials were studied. An experimental PVD-coating for low friction applications, TaC, was developed by varying the bias voltage during coating deposition. The surface modification method studied was nitriding of AISI H13 hot work tool steel to be used in dies for aluminium extrusion. Gas nitriding with three various depths was compared with the reference treatment salt-bath nitriding. An untreated H13 steel was also included for comparison.

The test specimens were subjected to mechanical evaluation, morphology studies and tribological testing methods neighbouring to the actual tooling applications. The results were compared with chemical information by GD-OES.

EXPERIMENTAL

MATERIALS

As substrate material for the nitriding evaluation was used test blocks $5 \times 10 \times 30 \text{ mm}^3$ of a premium AISI H13 hot work tool steel (Orvar Supreme, Uddeholm Tooling designation). Its nominal chemical composition is (wt%) 0.38 C, 5.3 Cr, 0.9 V, 1.3 Mo, 0.4 Mn and 1.0 Si. The specimens were hardened and tempered to 47 HRC and polished with $3 \mu\text{m}$ diamond grits in the final step prior to nitriding.

Commercial nitriding units for aluminium extrusion dies were used for surface treatment. A salt-bath nitriding designated SN was used as a reference treatment and compared with gas nitriding of three depths: GS (Gas-Shallow), GN (Gas-Normal) and GD (Gas-Deep), respectively. The untreated steel specimen was denoted as H13.

The TaC coatings were deposited on single crystal silicon wafers in a commercial PVD unit. A tantalum foil and a graphite target were magnetron sputtered simultaneously with a reference bias voltage of -50 V and two experimental voltages of 0 V and $+50 \text{ V}$. The purpose of the experimental coatings was to reduce the inherent residual stress and thereby enable an increased coating thickness.

SURFACE CHARACTERISATION

The nitrided steel specimens were evaluated by hardness indentation using a Vickers diamond stylus. The top surface hardness was evaluated using

both 10 gf and 100 gf. Hardness profiles were recorded on polished cross-sectioned specimens with 25 gf. A hardness value for the TaC coatings was assessed using nano-indentation with a Berkovich geometry.

The TaC coatings were evaluated by scratch testing with a continuously increased load from 0–100 N. The critical load was determined to be the load of coating break-through, exposing the substrate. Thickness and morphology of the surface layers were evaluated by scanning electron microscopy (SEM) on cross-sectioned specimens. The nitrided cross-sections were polished and etched and the TaC coatings were fractured prior to microscopy.

Chemical phase information was obtained with XRD. The elemental depth profiles were recorded with a Leco 750 A spectrometer, calibrated with certified reference materials. A spot 4 mm in diameter on the specimen surface was analysed with a plasma determined by an argon pressure. The pressure was controlled by a DC voltage of 700 V and a 20 mA current. Data recording continued until the surface coating was penetrated, observed as a significant intensity decrease of the element analysed.

WEAR TESTS

A block-on-ring configuration, experimentally simulating the wear of dies for aluminium extrusion was used for wear testing of the nitrided steel specimens. The surface treated specimen, corresponding to the tool surface, was pressed against a rotating Al-cylinder, representing the extrudate, at 550°C and inert atmosphere. A detailed description of this test can be found in [5].

The TaC coatings was developed for machine element applications, e.g. bearings, and were consequently wear tested with a method similar to such applications, a ball-on-disk test. An uncoated ball of bearing steel was pressed with a normal force of 5 N onto a rotating TaC coated steel disk rotating at 0.07 ms⁻¹.

The volume of removed material from the specimens in the two tests was assessed by white light optical interference profilometry with a resolution of about 2 nm in depth and about 1 µm laterally.

RESULTS

SURFACE CHARACTERISATION

The hardness, surface layer thickness and phase composition of the investigated nitrided specimens are presented in Table 1. The nitriding case depth varied from about 80 μm to 150 μm , see Fig.2. Cross-sections re-

Table 1. Surface properties of the nitrided steel specimens

	H13	GS	GN	GD	SN
Top surface hardness ¹ [GPa]	5.6 ± 0.4	13.5 ± 2	14.3 ± 1	6.6 ± 1	6.3 ± 0.6
Top surface hardness ² [GPa]	5.5 ± 0.1	12.8 ± 0.5	11.3 ± 0.5	9.6 ± 1	8.0 ± 1
Compound layer thickness [μm]	—	0.8 ± 0.2	4.5 ± 0.9	10.6 ± 1.3	4.6 ± 0.4
Compound layer phase	—	α and ϵ	ϵ	ϵ	ϵ and Fe_3O_4

1. Measured with 10 gf

2. Measured with 100 gf

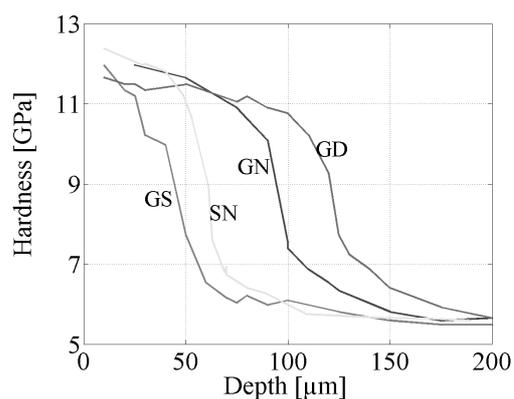


Figure 2. Hardness profiles of nitrided steel specimens.

vealed that the compound layers of the GN and GS specimens were dense,

as exemplified in Fig. 3 (a). However, about half of the GD compound layer and almost the entire layer of the SN contained porosity, see Fig. 3 (b).

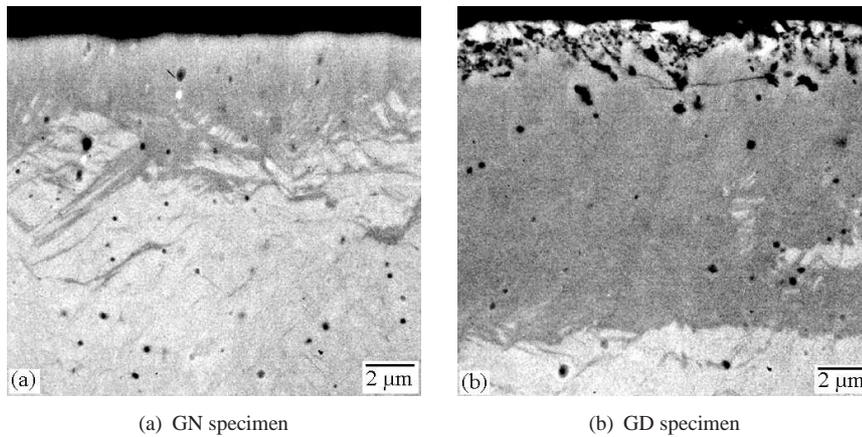


Figure 3. Cross-section of the GN and the GD specimen, representing a dense and a porous compound layer, respectively. The compound layers are observed as dark-grey in compo-mode. (SEM).

The TaC coatings displayed a dense structure when studied in cross-sections by SEM. Other evaluated surface properties of these coatings are summarised in Table 3.

Table 2. Surface properties of TaC coatings

	-50 V	0 V	+50 V
Top surface hardness [GPa]	15.4	14.5	13.4
Coating thickness [µm]	1.3	1.3	0.9
Phase composition	bcc TaC	bcc TaC	bcc TaC
Critical load [N]	24	24	25

GD-OES elemental depth profiles. Depth profiles recorded on the nitrated specimens showed that the GD (Gas-Deep) material had a nitrogen concentration exceeding 5 wt% to a depth of about 12 µm, see Fig. 4. The

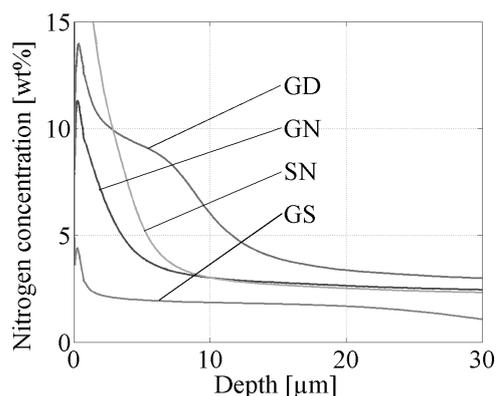


Figure 4. Elemental depth profiles of the nitrided steel specimens.

corresponding depth of the GN and SN materials was about 4 μm and 5 μm , respectively. The GS material had no layer exceeding 5 wt% nitrogen and its maximum content was only 4.5 wt%.

The thickness of the TaC coatings measured with GD-OES was about 1.04, 1.14 and 1.15 μm and the Ta concentration was about 73, 70 and 70 wt% in the -50 , 0 V and $+50$ V coatings, mainly balanced with carbon, see Fig. 5. Oxygen was present in all coatings up to 1 wt% in the -50 V, up to 7 wt% in the 0 V and about 3 wt% in the $+50$ V coating. The level of oxygen was relatively constant in the -50 V coating while it had a significant peak at a depth of about 0.3 μm in the two latter coatings. The very small levels of hydrogen found in the coatings were located to the oxygen content peak.

WEAR TESTS

The GN (Gas-Normal) specimen displayed the highest wear resistance of the nitrided materials at about $3.5 \times 10^{-3} \text{ Nm} \times \mu\text{m}^{-3}$. Relatively low wear resistance was obtained with the SN (Salt-bath Normal) and GS (Gas-Shallow) materials, about 0.6 and $1.1 \times 10^{-3} \text{ Nm} \times \mu\text{m}^{-3}$, respectively, see Fig. 6(a). The TaC coatings manufactured with -50 V and 0 V displayed similar wear resistance while that of the $+50$ V specimen was about half the level of the former ones, see Fig. 6(b).

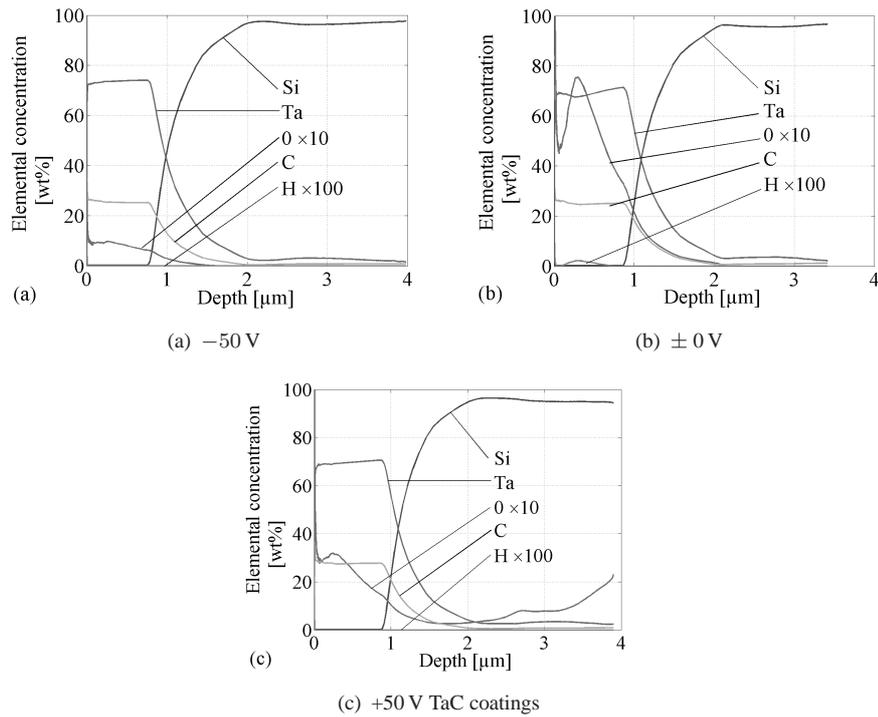


Figure 5. Elemental depth profiles of the coatings.

DISCUSSION

The most important finding of this study is the significant difference in wear resistance of the nitrided steel specimens in the extrusion simulation test. The wear resistance of these materials was not proportional to the thickness of the compound layer. Instead, porosity found in the compound layers probably affected the wear resistance of the GD (Gas-Deep) and the SN (Salt-bath Normal). It is believed that they would have been significantly better in the wear test with an entirely dense compound layer, instead of the porous ones found.

The porosity of these materials was detected prior to wear tests with both a relatively low micro-hardness and excessive nitrogen levels recorded by GD-OES. However, the latter method also provided information about the

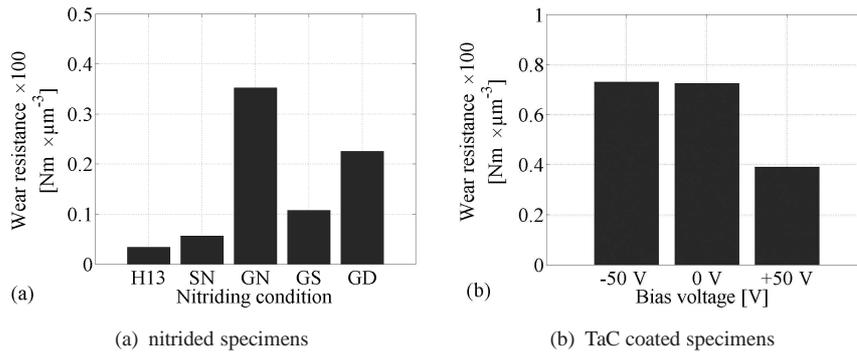


Figure 6. Wear resistance.

residual compound layer thickness. Consequently, GD-OES could be very useful in predicting the wear resistance of a nitrided tool steel and would be a powerful tool during development of nitriding processes, e.g. for new tool steel grades.

All TaC coatings displayed relatively good wear resistance in the ball-on-disk test. The low level of the +50 V-coating is probably a result of its lower coating thickness. Furthermore, the wear resistance was not affected by the significant amount of oxygen found by GD-OES in the 0 V and the +50 V coatings.

When utilising a conventional negative potential during coating deposition, coating material is sputtered and deposited simultaneously on the tool material. Generally, the more negative bias voltage the more sputtering, which eventually reduces the deposition rate to zero. The impurities found with GD-OES in these coatings probably reflects the reduced sputtering when utilising zero or positive bias voltage, as compared to the conventional negative potential. Also in development of PVD-coatings, GD-OES is a powerful method for the detection of impurity elements, which may affect the mechanical properties of the coating. Fortunately, this was not the case with these coatings.

CONCLUSIONS

The following conclusions can be drawn from this work:

- The best wear resistance of nitrided hot work tool steel in a wear simulation test of aluminium extrusion was obtained with a dense compound layer of about 5 µm thickness.
- Porosity in the compound layer of nitrided steel probably decreases the wear resistance significantly.
- The GD-OES technique has been proven to be very promising in predicting the wear resistance of nitrided steel. It can provide two of the most important parameters, excessive nitrogen levels indicating porosity and the total thickness of the compound layer.
- PVD TaC coatings of good quality for machine component applications were manufactured with bias voltages of -50 V, 0 V and +50 V.
- Relatively high levels of oxygen in the TaC coatings, detected by GD-OES, did not affect the mechanical performance of the materials.

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