Spectroscopy Application Note

Adjustment, Improvement, and Control of a Physical Vapor Deposition (PVD) Process Using Quantitative Depth Profile (QDP) Analysis

Investigations on New Coatings—
Information Delivered by the GD-OES Technique

Thickness, Composition, and Homogeneity of

- **CrN Coating**
- **NiP Coating**
- **Combination CrN/NiP Coatings**

The purpose of this application note is to show how Glow Discharge Optical Emission Spectrometry (GD-OES) has been used in research to improve a PVD process. Since all information is provided in a very short period of time, this technique can be used for routine control of the PVD process and as a quality check of the finished product.

It is known that conventional PVD coatings like TiN or CrN offer limited corrosion resistance (due to their intrinsic porosity) that locally expose the substrate. The CrN coating is well known for its anti-wearing property, but it has poor resistance to corrosion. In the manufacturing of cutting tools, this may restrict the types of steels that present a high hardness after heat treatment, but have a low corrosion resistance. Cold work tool steels and high speed steels are good examples. This research project, "*Enhancing Corrosion Resistance of PVD Coated Tools*", examines a way to overcome this problem using an electroless NiP interlayer with a PVD CrN top layer. This improved the corrosion resistance when compared to single PVD CrN coatings and presented a satisfactory adhesion. In this application note, the purpose is not to discuss the technical issue and concerns of the PVD process and the investigations to improve it, but to discuss the role of the GD-OES technique as a supporting tool.

Although electroless nickel is a corrosion resistant coating, there are many factors that affect its ability to protect a substrate. These factors are composition, surface finish of the substrate, pretreatment and deposition thickness. The Quantitative Depth Profile (QDP) analysis will reveal significant information regarding these important factors.

GDS-Series

CrN coatings directly applied on the steel substrate, NiP coatings directly applied on the steel substrate, and the complete process of CrN/NiP/Steel substrate were successively investigated.

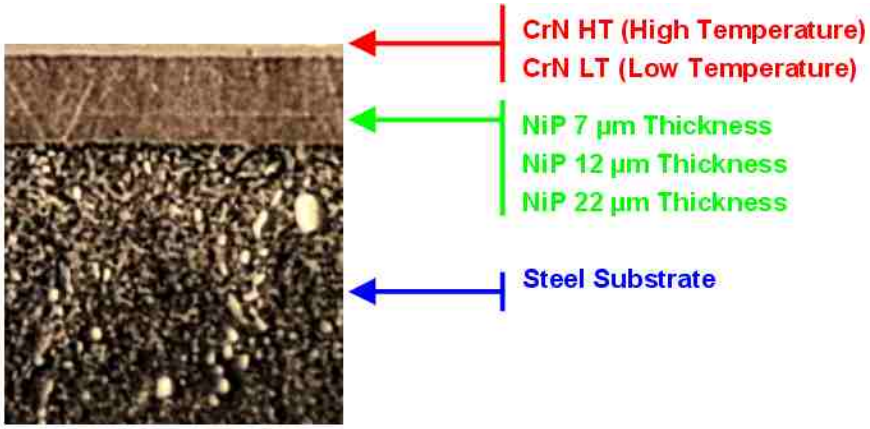


Figure 1: Cross section of the sample showing the different layers CrN, NiP and Steel substrate

As described in Figure 1 (above), two different CrN coatings have been evaluated:

- a CrN coating made at Low Temperature (CrN LT)
- a CrN coating made at High Temperature (CrN HT)

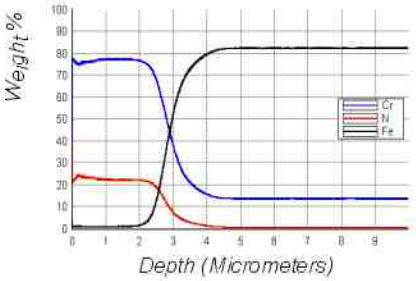
Several NiP coatings were also tested:

- a 7 µm thickness NiP coating
- a 12 µm thickness NiP coating
- a 22 µm thickness NiP coating

The same steel substrate was used during all these investigations.

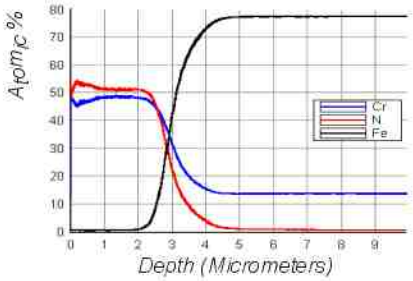
Single CrN Coatings on Steel

The depth profiles in Figures 2 and 3 (below) show two overlapped replicates of a steel sample coated with a single CrN LT (Low Temperature) made on two different pieces:



Cr-N Micron	Cr %	N %
2.92	77.0	21.9
2.91	76.9	21.9

Figure 2: Single CrN LT (Low Temperature) Two overlapped replicates (on two different pieces) Weight %



Cr%Atom	N%Atom
48.4	51.0
48.3	51.1

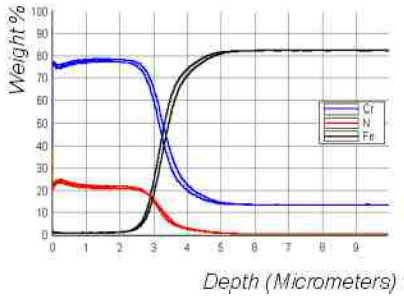
Figure 3: Single CrN LT (Low Temperature) Two overlapped replicates (on two different pieces) Atomic %

The profiles in Figure 2 (above) show the Weight % versus the Depth; the profiles in Figure 3 (above) show the Atomic % versus the Depth for the same sample. The respective tables show the Weight % and Atomic % composition for Cr and N in the CrN coating, and the CrN coating thickness.

The weight % display reports 77% Cr and 21.9 % N. The Atomic % display is useful for the stoichiometry check; in this case, it shows that the stoichiometry is not exactly 1:1. The calculation of the CrN depth shows a thickness of 2.92 micrometers.

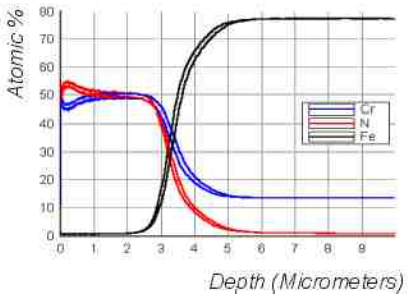
Figures 2 and 3 (see page 2) show a perfect overlapping of the two replicates, demonstrating the excellent reproducibility of the process. The results in the tables confirm that both samples have exactly the same thickness and composition. The flatness of the Cr and N profiles indicate a homogeneous CrN coating. The width of the interface CrN/Steel (i.e. the diffusion of the Cr and N in the Steel and vice versa) gives information regarding the preparation of the substrate in terms of polishing and cleanliness. These quantitative depth profiles were obtained in 300 seconds. As soon as the data is acquired, the display of the quantitative depth profiles and the associated calculation is immediately available.

The depth profiles in Figure 4 (below) show two overlapped replicates of a steel sample coated with a single CrN HT (High Temperature) made on two different pieces:



Cr-N Micron	Cr %	N %
3.25	77.2	21.6
3.38	78.2	20.7

Figure 4: Single CrN HT (High Temperature)
Two overlapped replicates
(on two different pieces)
Weight %

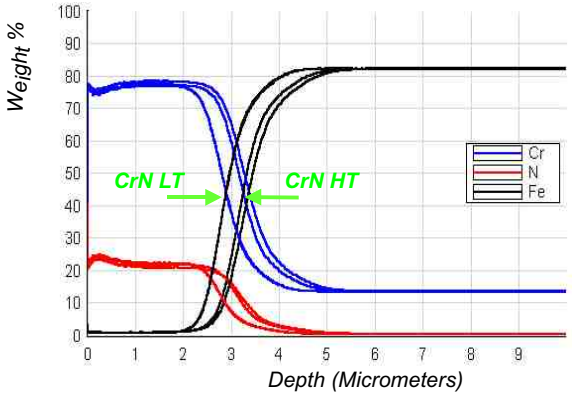


Cr%Atom	N%Atom
48.7	50.6
50.1	49.3

Figure 5: Single CrN HT (High Temperature)
Two overlapped replicates
(on two different pieces)
Atomic %

Figure 4 (plot and table, above) reports an average Cr content of 77.8% and N content of 21.2%.
Figure 5 (above) shows that the stoichiometry is near 1:1, except at the surface. The CrN thickness obtained with this HT process is 3.31 micrometers. The reproducibility between the two pieces obtained with HT process is good, but not as good as the reproducibility obtained with the previous LT process. These quantitative depth profiles and all the associated calculations were obtained in less than 300 seconds.

It is interesting to compare the results obtained with the LT and HT process. Because of the flexibility of the software, the plot and table in Figure 6 (below) can be obtained easily.



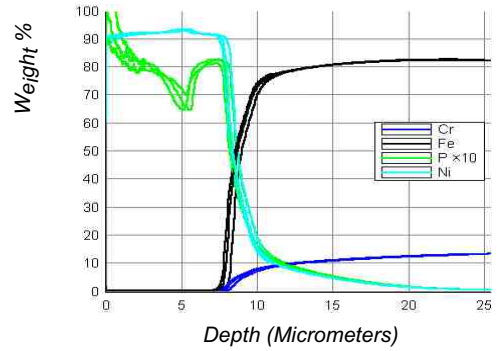
Sample Name	Cr-N Micron	Cr %	N %
CrN HT 1	3.25	77.2	21.6
CrN HT 2	3.38	78.2	20.7
CrN LT 1	2.92	77.0	21.9
CrN LT 2	2.91	76.9	21.9

Figure 6: Comparison HT/LT process; Two pieces CrN HT overlapped; Two pieces CrN LT overlapped

We can see that both the high and low temperature processes produce homogeneous CrN coatings with similar compositions. The reproducibility is also excellent for both processes. The only difference which can be reported is the CrN thickness. The CrN coating obtained with the High Temperature process is thicker than the Low Temperature process.

Single NiP Coatings on Steel

Three different NiP coatings have been evaluated: 7, 12, and 22 micrometers thickness. Several pieces of each type have been analyzed. Below are the depth profiles obtained.

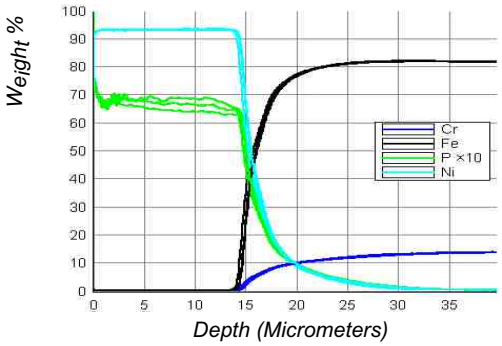


Ni-P Micron	Ni%	P%
8.88	92.4	7.4
8.41	92.6	7.2
8.58	92.2	7.6

Figure 7: NiP 7 microns on steel Three overlapped replicates (made on three different pieces)

The NiP coating is thicker than expected; a 7 micrometers thickness was expected, but the depth profile in Figure 7 (above) shows a thickness of 8.6 microns. Regarding the homogeneity, we see a constant Ni content in the coating (92.4%), but a fluctuating P content. The diffusion of Ni and P in the substrate reveals information about the preparation of the substrate in terms of polishing. The three pieces analyzed show exactly the same profiles, confirming the P fluctuation. The quantitative depth profiles and all the associated calculations were obtained in less than 400 seconds.

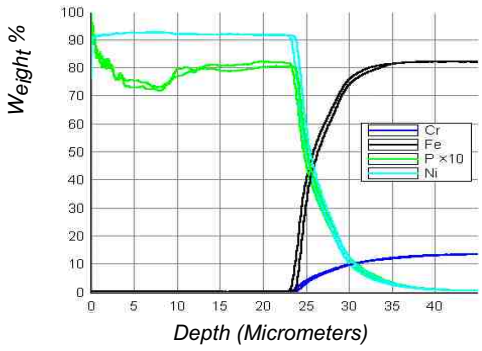
The expected NiP thickness was 12 microns, but the depth profile analysis in Figure 8 (below) shows a thickness of 15.7 microns. We can see a very homogeneous NiP coating and a very reproducible process. This quantitative depth profile analysis was completed in approximately 800 seconds.



Ni-P Micron	Ni%	P%
15.8	92.9	6.9
15.5	93.1	6.7
15.7	93.3	6.4

Figure 8: NiP 12 microns on steel
Three overlapped replicates
(made on three different pieces)

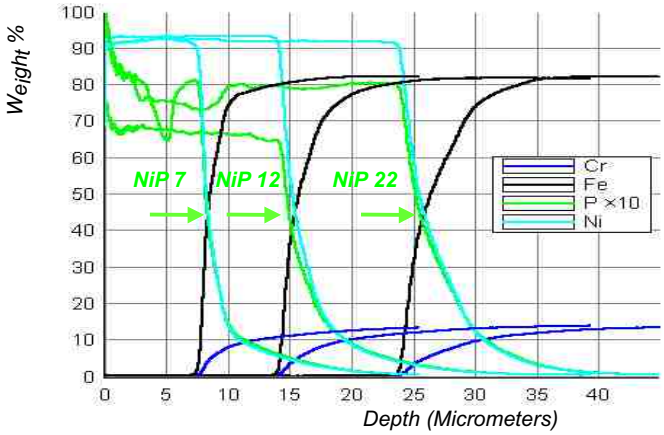
The expected NiP thickness was 22 microns, but the real thickness given by the depth profile analysis in Figure 9 (below) is 25.7 microns. The Ni is very homogeneous, but the P in the NiP shows some fluctuations. This process is very reproducible, and the two pieces show the same P fluctuations. This quantitative depth profile analysis was completed in approximately 1000 seconds.



Ni-P Micron	Ni%	P%
25.4	91.8	8.0
26.0	91.8	8.0

Figure 9: NiP 22 microns on steel
Two overlapped replicates
(made on two different pieces)

The overlap of the profiles obtained with the three different NiP processes allows an easier comparison--see Figure 10 (below):



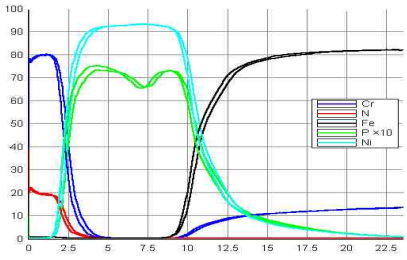
Sample Name	Ni-P Micron	Ni%	P%
NiP 22 / Sub.	26.0	91.8	8.0
NiP 12 / Sub.	15.5	93.1	6.7
NiP 7 / Sub.	8.41	92.6	7.2

Figure 10: Overlap of the 7, 12, and 22 microns NiP coatings on steel

From this overlap, we see that the three processes provide a NiP coating with similar Ni and P contents. The average P contents observed on the profiles seem different due to the scale factor x10 applied to the P profile, so it is easier to look at the table. The profiles clearly reveal that the P is not homogeneous. The worse P profile has been obtained with the 7 micron process; the best one with the 12 micron process. Generally, the thickness of the NiP coatings obtained has always been thicker than expected. Regarding the interface, we can note that a thicker NiP coating may have an important effect on the diffusion of the coating into the substrate. Notice that all the samples have the same substrate composition; this point will be developed later in this application note.

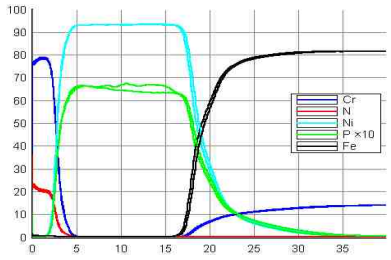
Complete Process: CrN LT Coating on Steel with Intermediate NiP Layer

Each CrN process (Low and High temperature) was applied on each NiP layer (7, 12, and 22 microns). The first series of results shown in Figures 11, 12, and 13 (below) are the CrN LT applied on each NiP layer. 600, 800 and 1000 seconds were necessary to get the respective quantitative depth profile analysis of these three complete processes.



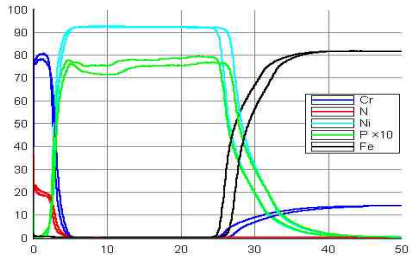
Cr-N Micron	Cr %	N %	Ni-P Micron	Ni %	P %
2.87	79.7	18.9	8.45	92.8	6.9
2.62	79.7	19.1	8.37	92.9	6.8

Figure 11: CrN LT/NiP 7
Two overlapped replicates
(made on two different pieces)



Cr-N Micron	Cr %	N %	Ni-P Micron	Ni %	P %
2.82	78.6	19.8	16.0	93.1	6.7
2.85	78.1	20.5	16.3	93.3	6.4

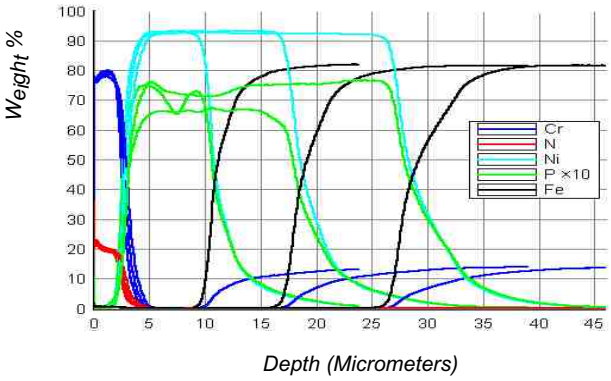
Figure 12: CrN LT/NiP 12
Two overlapped replicates
(made on two different pieces)



Cr-N Micron	Cr %	N %	Ni-P Micron	Ni %	P %
2.77	80.3	18.4	24.2	92.0	7.8
3.06	77.4	19.7	25.6	92.3	7.5

Figure 13: CrN LT/NiP 22
Two overlapped replicates
(made on two different pieces)

Software permits an overlap of the three complete processes to make the comparison of results easier. See Figure 14 (below):



Sample Name	Cr-N Micron	Cr %	N %	Ni-P Micron	Ni %	P %
CrN LT / NiP 7 / Sub.	2.62	79.7	19.1	8.38	92.9	6.8
CrN LT / NiP 12 / Sub.	2.82	78.6	19.8	16.0	93.1	6.7
CrN LT / NiP 22 / Sub.	3.06	77.4	19.7	25.6	92.3	7.5

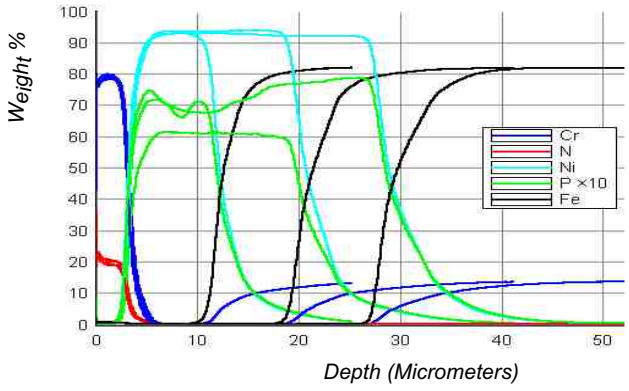
Figure 14: Overlap of the three complete processes with CrN LT

Conclusions

- The CrN LT coating is very homogeneous and the thickness is approximately 2.9 microns for all the samples, confirming the excellent reproducibility of this process.
- The NiP 7 and NiP 22 show the same P fluctuations that were previously observed in Figures 7, 9, and 10, proving that this process does not provide homogeneous layers.
- In Figure 13, we can note that the NiP 22 layer is not very reproducible in terms of thickness.
- The respective NiP 7, 12, and 22 thicknesses are similar to those obtained previously (Figure 10), but do not correspond to the expected thicknesses.
- The diffusion of the Ni and P in the substrate increases when the NiP thickness increases. Note the excellent resolution at the interface CrN/NiP.

Complete Process: CrN HT Coating on Steel with Intermediate NiP Layer

The set of profiles below is the CrN HT applied on each NiP layer. The overlap of the three complete processes is displayed in Figure 15 (below).



Sample Name	Cr-N Micron	Cr %	N %	Ni-P Micron	Ni %	P %
CrN HT / NiP 7 / Sub.	3.25	79.5	19.0	9.16	92.9	6.8
CrN HT / NiP 12 / Sub.	3.37	78.7	20.1	17.7	93.7	6.1
CrN HT / NiP 22 / Sub.	3.14	78.4	20.4	26.2	92.4	7.4

Figure 15: Overlap of the three complete processes with CrN HT

Conclusions

- The CrN HT coating is very reproducible in terms of thickness and composition, confirming the results obtained in Figures 4, 5, and 6.
- The thickness of the CrN HT is approximately 3.2 microns. This is similar to the thickness obtained in Figure 6.
- We confirm that the CrN HT process provides a CrN layer slightly thicker than the CrN LT process.
- All the comments previously made regarding the NiP layers in Figure 14 are valid for Figure 15.

Composition of the Substrate

Depth profile analysis can also provide the complete composition of the substrate.
See Figure 16 (below).

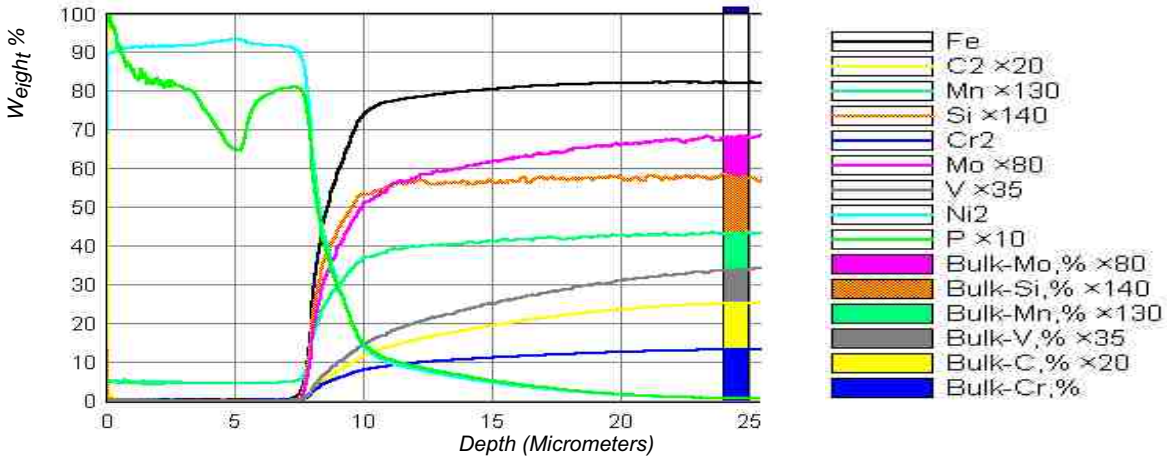


Figure 16: Bulk analysis of the substrate made from the Depth Profile Analysis

By integration of the signals in the substrate when the profiles are flat, the software will calculate an accurate composition of the substrate and will display the results in a table as shown in Table 1 (below).

Name	Cr% Sub	C% Sub	V% Sub	Mo% Sub	Si% Sub	Mn% Sub
PVD 3	13.7	1.31	0.98	0.83	0.43	0.33

Table 1: Composition of the substrate

Report Generator

The report generator, part of the QDP software, helps the operator to easily produce a polished report. Documents like the one below (Figure 17) can be generated automatically. Reports can be customized to include a variety of information including coating weight, text, logos, notes relative to each sample, file references, date/time of the analysis, and more.

NOTE: All the thicknesses shown in this document are in metric units, but the software can also perform the US equivalents of the metric units.

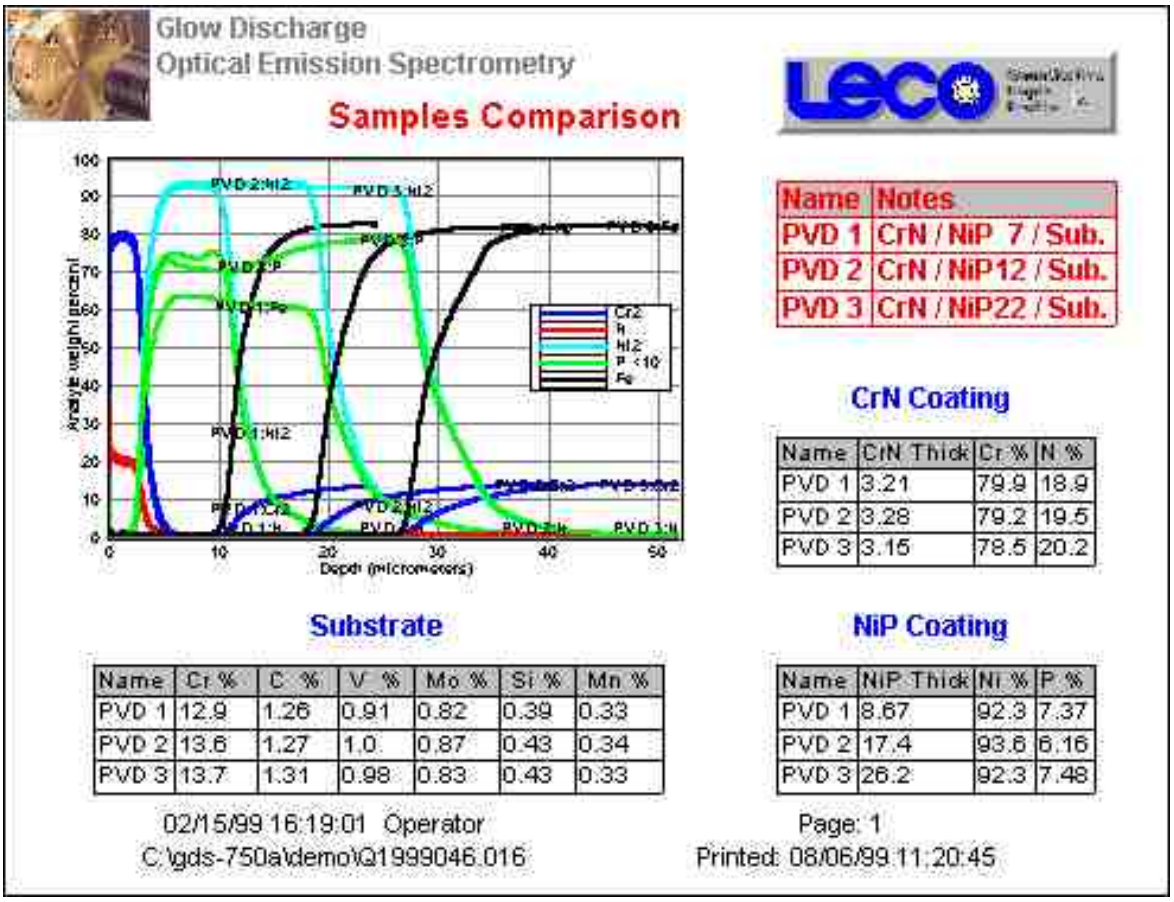


Figure 17: Example of Customized Report

Report highlights

- The overlap of the depth profile for several samples and all the calculation made from these profiles.
- Thickness and composition of each layer for each sample.
- Substrate composition.

Summary

This application note confirms that the GD-OES technique is an ideal tool for quickly checking the composition, thickness, and homogeneity of single or multilayer coatings (including the substrate). Other benefits of GD-OES:

- Observation of the migration and diffusion phenomena at the interface.
- Control of the processes and display of deviation.
- Quality control of the finished products and anticipation of problems.
- Investigation in R&D to explain the origin of unexpected phenomena.

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