Lab Report XRF 137

S8 TIGER Series 2 with ML*plus*

- Determination of Layer Thickness and Composition by WDXRF

Introduction

Many of the advanced materials today need to be coated in order to improve either the properties or the appearance of the material. This coating could be a passivation coating to prevent corrosion, a protective coating to disable degradation of an engine component or glass that has been coated to give it additional properties (e.g. self cleaning glass).

The determination of layer thickness for materials is of vital importance to many industries for a variety of reasons. For applications where the coating material adds an additional property the coating must be thick enough to work but not so thick that it alters the basic property of the material itself. In other cases coating is expensive, e.g. jewellery manufacturers who plate materials with precious metals need to ensure that the plating is done as economically as possible, but must be able to determine the amount of precious metal that has been used in the plating in order to price it correctly.

Many different methods exist for determining the thickness and composition of layers on substrates, however many of these are destructive methods, for example cutting cross sections and analyzing by SEM or TEM, or wet chemical / gravimetric techniques.

Fig. 1: WDXRF spectrometer S8 TIGER Series 2

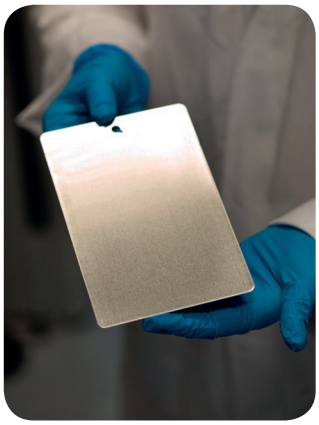


Fig. 2: Test sample for coating thickness

Fig. 3: Production of zink-coated steel

X-Ray Fluorescence Spectroscopy (XRF) offers a simple, non-destructive method for determining the thickness of a layer on a particular substrate. This technique uses the principle that as a beam of X-Rays passes through a material, the material will have an absorbing or enhancing effect on that beam. Knowing what the intermediate material is made of, allows us to calculate and compute the effect this will have on the beam of X-Ray radiation. These computations and calculations are based on a complex mathematical procedure, known as Fundamental Parameters.

Software ML*plus*

ML*plus* is the easy-to-use software for analyzing thin layers or multilayer samples with the S8 TIGER Series 2. In all different applications, e.g. surface engineering, coating, painting, silicon wafers, oxidation, study of corrosion products, ML*plus* can be used to control layer thickness and composition of single and multilayer systems – in research or production control.

The crucial part of the multiplayer analysis is the choice of the calculation model. Three models are available:

- Emission model
  The intensity of a strong fluorescence line from one element representing the layer is used for calculating the layer thickness.
- Absorption model
  A fluorescence line from an element representing the material below the analyzed layer is measured and its absorption is determined.
- Optimize the sum
  This model can be used for layers containing more than one element.

In all cases ML*plus* is based on full fundamental parameter calculations and the integrated standardless software QUANT-EXPRESS of the S8 TIGER can be used for all evaluations. This enables layer thickness and composition determination without prior calibrations and search for expensive standards.

ML*plus* is an optional software module extending the possibilities of SPECTRA*plus* V4 for the analysis of single layer and multilayer samples. ML*plus* can determine thickness and composition of layers in multilayer samples down to several atomic layers (less than 1nm) and up to the µm or even mm-range. The number of layers which can be determined and the actual thickness range is determined by the elements present in bulk and layers and not by software features.

ML*plus* is using a full fundamental parameter (FP) approach for all calculations. The determination of thickness and composition in ML*plus* can be based on the standardless calibration of SPECTRA*plus*, therefore no specific multilayer standards are required.

The software's 'Interactive mode' enables the user to define the sample structure (which element in which layer, typical values for thickness and composition) and helps them to find the optimum element lines for the measurement. Once an interactive evaluation has been set up successfully, the parameters can be stored for automatic evaluation of similar samples.

ML*plus*: Excellent analytical tool for simulation and evaluation of multilayer analysis

Let's say your sample is represented by the sample on Fig. 4. When the sample is excited by the x-ray tube, the intensity of the signal emitted by one element (e.g. Zn Kα_1) depends on the number of atoms in the sample.

If the layer is thicker, the number of excited atoms increases, and the intensity is higher. This is only true as long as the sample thickness does not exceed a given value: the layer is then considered as an "intermediate " sample (or a sample with an "infinite" thickness). The curve is an asymptotic curve; in case of the usual measurements (bulk and homogeneous sample), the limit thickness, the transition between finite and infinite thickness, is estimated by the d90% thickness that gives 90 % of the maximum intensity. The d90% thickness is also called the "saturation thickness" or the "90% absorption path".

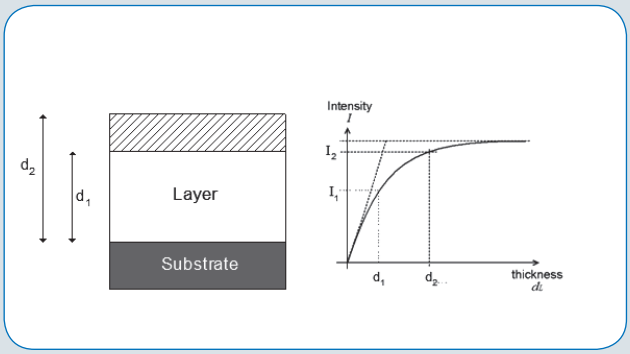


Fig. 4: Layer thickness as function of the intensity

Let's say your sample is represented by the sample on Fig. 5. When the substrate is excited by the xray tube, the intensity of Fe Kα_1 depends on the thickness of the Zn layer. This effect is influenced by:

- The absorption of the incoming radiation
- The absorption of the emitted radiation from the substrate
- Let's say that one of your layers consists of Cr and Ni and the lines Cr Kα_1 and Ni Kα_1 are measured.

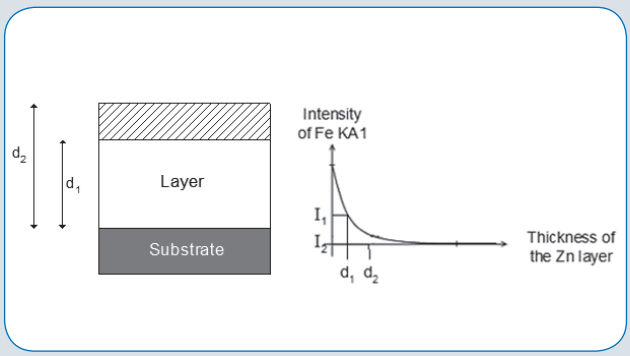


Fig. 5: Absorption

You can then determine the thickness of the Cr+Ni layer using the assumption that:

Concentration(Cr) + Concentration(Ni) = 100%

In that case the software:

Uses the Cr Kα_1 and Ni Kα_1 to calculate the concentrations of Cr and Ni in the layer, and then calculates

Searches the thickness for which the measured intensities of Cr Kα_1 and Ni Kα_1 fulfil the assumption Concentration(Cr) + Concentration(Ni) = 100%.

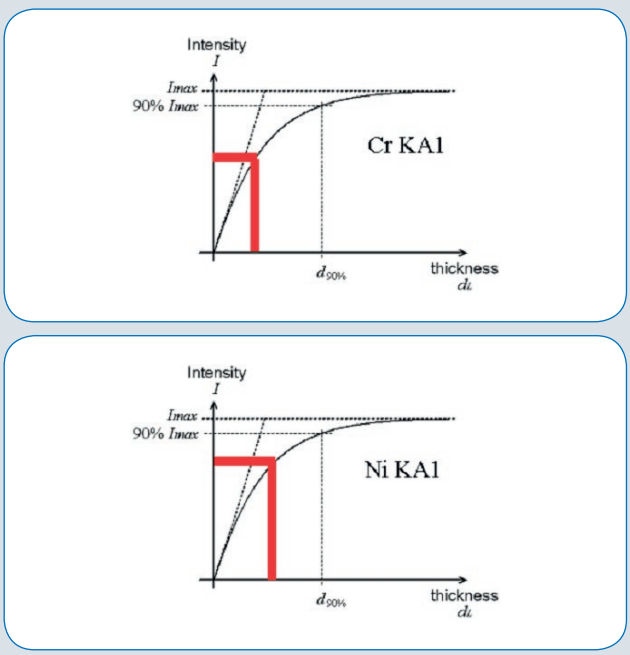
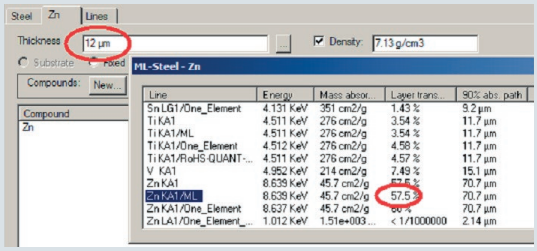


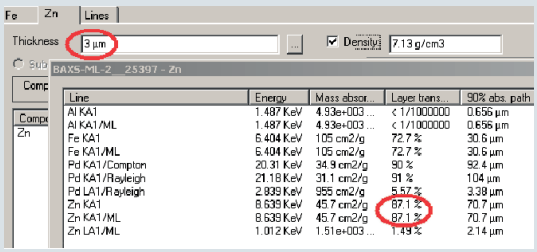
Fig. 6: Optimize Sum

Validating the Choice of the Model

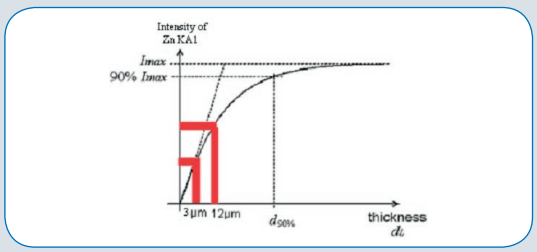
Click on any Layer tab, then on the **Absorption bar** button. This displays the Absorption window, which contains the mass absorption coefficients μ, the amount of energy that is absorbed by the layer for each line, and the $d_{90\%}$ limit thickness (90 % absorption path) of each line for this layer. You can then compare this with the thickness of the layer, and see if you are in the accuracy limit (below $d_{90\%}$ for the determination by emission, below $3.d_{90\%}$ for the determination by absorption).



For a value of 12 µm, the software calculates a transmission value of around 57% for the Zn Kα1/ML line.



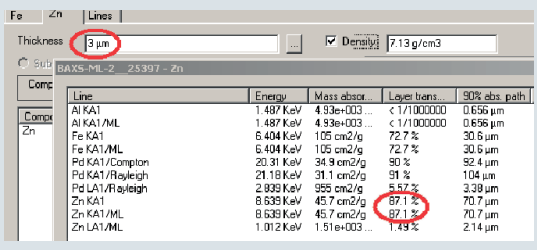
Change the value to 3 µm, the transmission value changes to 87%.



The emission of Zn Kα1/ML can be used for calculating the thickness of the layer

The intensity of Zn Kα1/ML depends on the layer thickness: The software calculates a d90 of about 70.7 µm.

Fig. 7: Layer thickness as function of the intensity

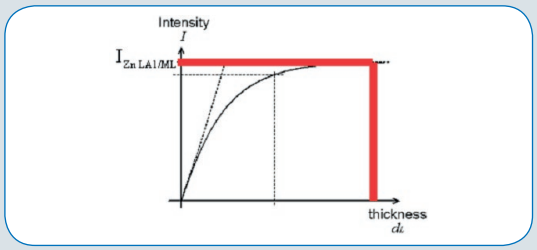


Look at the Zn Lα1/ML line.

The energy of Zn La1 is much lower than the energy of Zn Ka1:

- E(Zn Lα1) = 1.0 keV
- E(Zn Kα1) = 8.6 keV

The software calculates a transmission value of 1% for a layer thickness of 3 µm. That means that the Zn Lα1 signal is absorbed in the layer.



The software provides a value of d90 of about 2.14 µm. For layers which thickness is higher than 2 µm, the line Zn La1/ML cannot be used for calculating the layer thickness.

Fig. 8: Layer thickness as function of the intensity

Application Details

Some model samples were used to test the accuracy of the ML*plus* software.

- Titanium substrate with aluminum layers
- Copper substrate with aluminum layers
- Aluminum substrate with organic layers

We have also tested the real world example of aluminum drinks cans, which must be coated with an organic polymer to protect the can from the drink it is to contain. Many carbonated drinks have very low pH values, which would cause the metal cans to corrode in very short spaces of time causing either the can to fail completely, or leaving traces of metals in the drinks themselves.

Titanium and Copper substrate with aluminum layers

- Substrate: Pure Ti or Pure Cu
- Layers: Aluminum foil

The thickness of the aluminum foil used was measured to be 10.6 µm by use of a Vernier guage prior to measurements.

The first sample consisted of a single sheet of aluminum foil with either the pure titanium or pure copper substrate behind it. Subsequent samples consisted of an increasing number of aluminum sheets, up to a maximum of six sheets.

Aluminum substrate with organic layers

- Substrate: Pure Al
- Layers: 2.5 µm MYLAR film

In much the same way as the metal layered samples were constructed, layers of MYLAR were added to a pure aluminum (up to a maximum of 6 layers) to simulate an organic layer on a metal substrate.

Aluminum drink cans

Three examples of cans used to hold carbonated soft drinks were analyzed to determine the thickness of the protective organic layer on the inside of the can.

The composition of this organic layer was determined by FTIR using a Bruker ALPHA.

In all cases, a second piece of each metal was cleaned with wet-and-dry paper to remove the organic layer to confirm that we could see a difference in the organic layer thickness.

Measurement Conditions

All samples were measured on an S8 TIGER Series 2 with 4 kW excitation instrument, under vacuum, using the Full Analysis measurement method included with the standardless QUANT-EXPRESS package. With the HighSense detector electronics the S8 TIGER Series 2 can handle even higher countrates up to app 2 Mio cps. For the excitation of weaker L- or M-lines or light elements in very thin layers the S8 TIGER Series 2 can be equipped with the HighSense X-ray tubes with 50 µm or 28 µm tube window in order to enhance the sensitivity with up to more than 50 % additional signal.

Results

Titanium substrate with aluminum layers

A model was constructed consisting of a titanium substrate and an aluminum layer. An absorbance model was chosen to determine the thickness of the aluminum, using the Ti-Kβ line. This is due to the very high count rates observed for the Ti-Kα. Table 1 shows the determined layer thickness values for this simulated sample. There is excellent agreement between the expected value (10.6 µm per aluminum layer) and the calculated value from ML*plus*.

Figure 9 shows the excellent correlation between number of layers and determined layer thickness, but also the gradual decrease in the intensities of the two signals observed from the substrate, as the number of foil layers are increased.

No. Layers	Calc. Thickness (um)	Ti-Kα Intensity (kcps)	Ti-Kβ Intensity (kcps)
1	10.4	1164.3	206.19
2	20.1	384.3	84.82
3	29.6	131.2	35.69
4	39.0	45.4	15.07
5	47.8	15.9	6.99
6	57.4	5.7	3.05

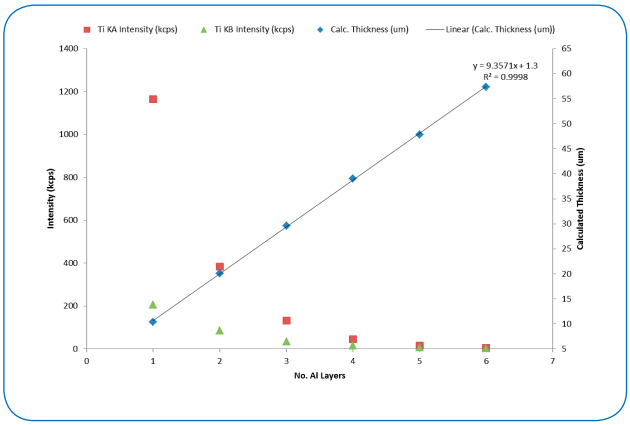


Fig 9: Results for aluminum layers on titanium and correlation between layer thickness and intensity

Copper substrate with aluminum layers

A model was setup with a copper substrate and aluminum layers, again using an absorbance model to determine the thickness of the aluminum. Absorbance of the Cu-Kβ line was used, again due to the high signal intensities observed for the Cu-Kα.

The table shows the calculated thicknesses observed, with increasing number of aluminum foil layers. The results are in excellent agreement with the expected value of 10.6 µm per aluminum foil layer. The correlation between number of layers and calculated layer thickness is shown in Figure 10.

No. Layers	Calc. Thickness (um)	Cu-Kα Intensity (kcps)	Cu-Kβ Intensity (kcps)
1	10.9	18134.15	2895.98
2	20.2	14025.61	2460.93
3	30.4	10775.20	2061.32
4	40.1	8541.27	1751.70
5	50.0	6810.24	1479.44
6	60.1	5426.13	1235.79

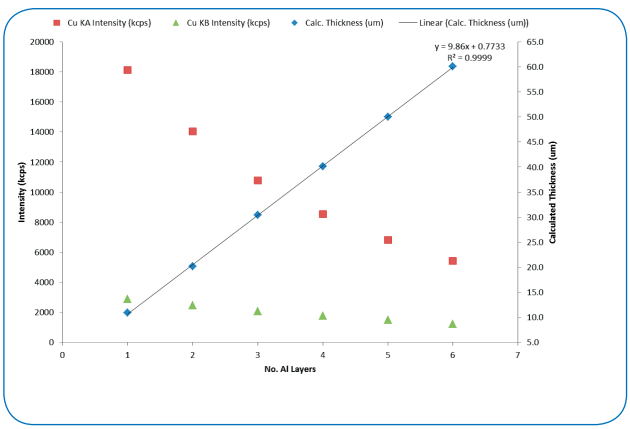


Fig 10: Results for aluminum layers on copper and correlation between layer thickness and intensity

Aluminium substrate with organic layers

A mode was setup with an aluminum substrate and organic layers ($C_{10}H_8O_4$, density 1.39g cm^{-1}). The organic layer thickness was determined by absorbance of the Al-Kα signal. The nominal layer thickness for each MYLAR layer is 2.5 µm.

Even for organic materials, an excellent agreement is observed between the expected values and the calculated values from ML*plus* as shown in Table 3. The correlation and the decrease in measured intensity is shown in Figure 11.

No. Layers	Calc. Thickness (µm)	Expected Thickness (µm)	Al-Kα Intensity (kcps)
1	2.88	2.5	1889.19
2	5.23	5.0	1130.56
3	7.63	7.5	670.56
4	10.10	10.0	371.55
5	13.00	12.5	207.97
6	15.20	15.0	129.62

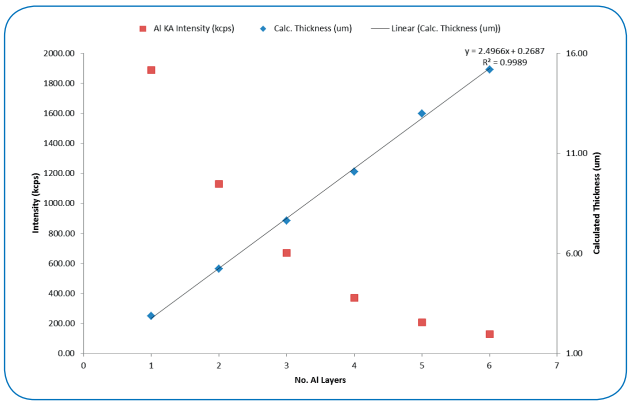


Fig 11: Results for organic layers (paint or foil) on aluminum substrates and correlation between layer thickness and intensity

Aluminum drinks cans

The three examples of aluminum drinks cans were analyzed using the same measuring method. A model was constructed for an aluminum substrate with an organic layer, the make-up of which had been determined by FTIR to be mainly of an epoxy type resin with small amounts of other polymers.

Using the interference bands from the FTIR spectrum, the organic layer was determined to be approximately 4µm (±1µm) thick in all cases.

Sample Name	Can Type	Calc. thickness (µm)
Green	Non-carbonated, juice based drink	3.86
Green_ Cleaned	Non-carbonated, juice based drink	0.75
Red	Cola type drink	2.93
Red_Cleaned	Cola type drink	0.78
Black	Carbonated, energy drink	3.69
Black_Cleaned	Carbonated, energy drink	0.77

Fig 12: Results for coated aluminum sheet metal for drink cans

Conclusions

The thickness of a layer on a substrate can be easily determined using XRF and ML*plus* in a non-destructive way. From the model samples that have been shown in this report, a very high degree of accuracy can be obtained, provided that an appropriate model is constructed for the sample types. The strength of ML*plus* is the simulation of the multilayer system without any measurement in order to evaluate the optimal evaluation path. The high accuracy of the S8 TIGER Series 2 plus its enhanced sensitivity for low energy radiation makes the usability of L-lines for evaluation and therefore the analysis of very thin layers and multiple layers possible.

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