APPLICATION NOTE

Standardless Measurements of Titanium and Zirconium Based Conversion Coatings

Using the Thermo Scientific Niton XL5 Plus XRF Analyzer

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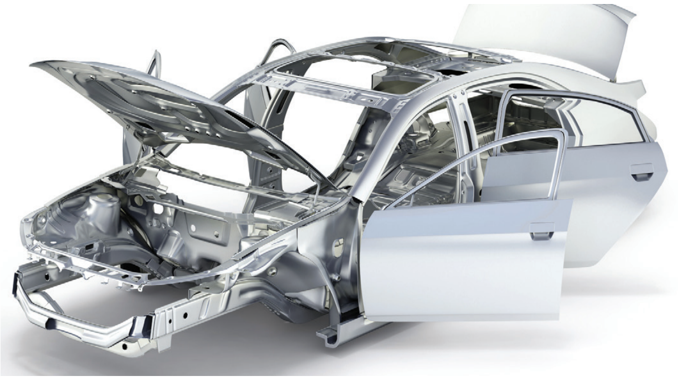
Application

Conversion coatings are coating layers created over the surface of a metal substrate either by a chemical or electro-chemical process to provide a decorative color and to improve physical and chemical properties such as corrosion resistance and paint adhesion. Common examples are anodization, chromate or phosphate conversion coatings. Zinc phosphate and related compound conversion coatings have long been the state-of-the-art in pre-treatment of car bodies and automotive components made of steel and galvanized steel. Over the past decade, new coatings based on zirconium (Zr) and titanium (Ti) have been increasingly used with the goal of replacing phosphate-based coatings as a pre-treatment layer.[1,2] The Zr based and Zr/Ti based coatings have numerous advantages over zinc- and zinc-manganese-nickel-phosphates such as[1,2]

- increased corrosion resistance (better salt spray resistance)
- thinner coatings
- reduced environmental impact and wastewater treatment (phosphate-free, no regulated heavy metals)
- Improved maintenance (less sludge, less scale, low foaming)
- reduced operating cost (lower temperature, less waste and chemical consumption)

The Thermo Scientific™ Niton™ XL3 handheld XRF analyzer has been used globally by producers of coating chemicals as well as by numerous factories in the automotive and general industry. The Niton XL3 analyzer



Zr- and Ti-based conversion coatings improve paint adhesion and enhance corrosion protection of automotive bodies made of aluminum

The Niton XL5 Plus Handheld XRF Analyzer

has provided quality control of Zr- and Ti-based coatings on substrates such as aluminum alloys, cold rolled steel (CRS), electro galvanized steel (EG) and hot dip galvanized steel (HDG). For such applications, the new Thermo Scientific™ Niton™ XL5 Plus handheld XRF analyzer will be more powerful and the workflow for application

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development and analysis will also be greatly simplified and flexible thanks to a fundamental parameter algorithm.

Niton XL5 Plus Analyzer

Of all the high-performance X-ray fluorescence (XRF) metal analyzers on the market, the Niton XL5 Plus analyzer is the smallest and most lightweight. The compact measurement geometry, large area detector with graphene detector and powerful 5W X-ray tube provide best-in-class sensitivity for the most demanding applications such as measurement of thin coating layers.

The fundamental parameter-based, standardless Coatings Mode of the Niton XL5 Plus analyzer accurately determines coating thickness of up to 4 layers of pure element or alloy coatings over various substrates made of pure elements, alloys, plastics or wood.[3] As a result, the Niton XL5 Plus analyzer can easily measure the coat weight of Ti- and Zr-based conversion coatings over alloys such as steel or aluminum or coated materials such as galvanized steel. Users can operate the instrument “out of the box” with no need for multiple calibration samples or advanced training. An easy-to-use type standardization feature is still available for users who want to fine tune their analyzer with their own reference materials.

Test Method and Results

Multiple previously characterized samples of Zr- and Ti-based conversion coatings over HDG, CRS and aluminum alloys were analyzed with the Niton XL5 Plus analyzer with no previous adjustment. Only the nature of the substrate (such as steel or aluminum grades and coating elements such as Zinc (Zn) for galvanized steel, Zr or Ti) as well as the unit of measurement and measurement time were entered in the measurement profiles (analytical methods).

Figures 1a-d show the correlation plots between laboratory-obtained reference values and measurements carried out with Niton XL5 Plus analyzer for Zr and Ti on different substrates. Zr and Ti are generally present in the coatings at levels equivalent to a few atomic layers. The correlation coefficient R^2, the slope and the intercept of the linear regression are provided in Figures 2a-d. The R^2 value is a measure of how closely the data sets correlate with each other, where a perfect correlation would have an R^2 of 1. Assuming a good correlation, the slope is then an indicator of the accuracy of the analyzer response. Ideally, the slope is equal or close to.[1] High values of intercepts of the calibration curve can be an indicator of the presence of the coating element in the substrate.

With R^2 higher than 0.98, all the values measured with the Niton XL5 Plus Coatings Mode “out of the box” showed a strong a correlation with lab reference values for Zr and Ti over different substrates. With values around 0.93, the slopes were also close to 1 for Zr on HDG (Fig. 2b) as well as for Zr and Ti over aluminum (Figures 2c and 2d). A slope of 0.804 was obtained for Zr over CRS (Figure 2a). This departure from the ideal response of 1 can be related to compounds and elements other than Zr being present in the coatings and having an impact on the density and mass absorption coefficient of the matrix, and thus on the Zr signal. In this case, for a given formulation, a simple post calibration adjustment can be made to improve the accuracy using the type standardization feature.

With a value of 9.03 mg/m², it has also been noticed in the

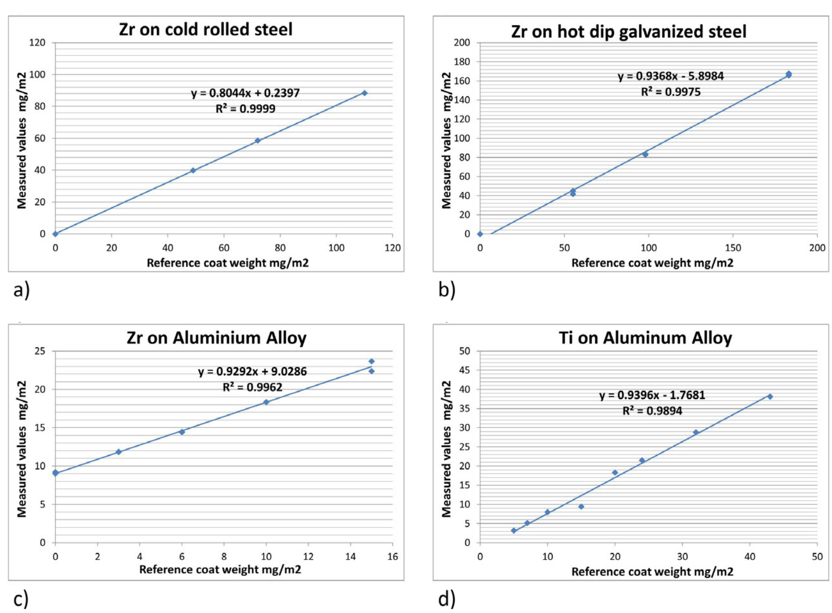
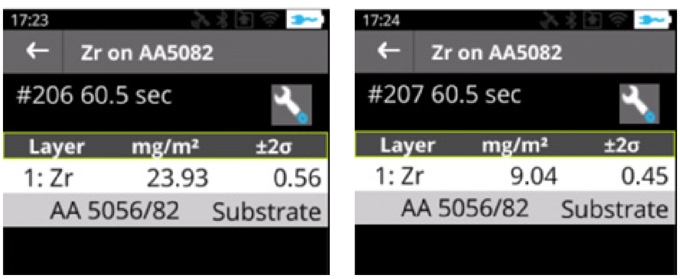


Figure 1: correlation curves measured versus reference values obtained without any calibration adjustment for a) Zr over cold rolled steel, b) Zr over hot dip galvanized steel, c) Zr over aluminum (coating # 1), d) Ti over electro galvanized steel, Ti over aluminum

case of Zr over aluminum that the intercept of the linear regression differs significantly from 0. This is related to the presence of Zr in the substrate. Indeed, Zr and also Ti are often present in aluminum alloys at trace levels that are not necessarily specified by the alloy grade standard. Therefore, for a given batch and formulation of Zr-based conversion coatings, it is adequate to measure one coated sample and a non-coated sample, and then calculate the difference of the results. Figure 3a shows an example where measured coat weight for a Zr-coated aluminum was 23.9 mg/m^2 versus an expected value of 15 mg/m^2. The non-coated substrate of the same batch yielded a value of 9.0 mg/m^2 Zr (Figure 3b), which should be subtracted from the result of the coated sample. The resulting Zr (Zr net) value of 14.9 mg/m^2 is very close to the expected value of 15 mg/m^2. Such a subtraction can be done only when the layer is thin, as is the case for Ti- and Zr-based conversion coatings.



a) b)

Figure 3 a) Analytical results for an aluminum alloy grade AA5082 sample coated with 15 mg/m^2 Zr, b) Non-coated sample of the same batch of alloy AA5082

Conclusion

The Niton XL5 Plus analyzer is perfectly suited for modern conversion coating applications. Good correlations and agreements were obtained between expected and measured values of Zr and Ti over various substrates such as steel, galvanized steel or aluminum alloys. As compared to empirical calibrations available on the Niton XL3 analyzer, the fundamental parameter-based Coatings Mode of the Niton XL5 Plus analyzer is easier to use, more flexible and does not require many reference samples. The accuracy of the standardless calibration can be evaluated using few samples per coating type and, if needed, the analytical response of the analyzer can be easily fine-tuned by the user to achieve optimum accuracy.

The Niton XL5 Plus analyzer has been demonstrated to be ideal for controlling the coat weight of Zr- and Ti-based coatings in automotive and metal finishing industries. Fast return on investment is provided by:

- Improved productivity. The Niton XL5 Plus analyzer displays measured coat weight in real time within seconds allowing immediate control of the coating process and fast decision-making in quality control of finished or semi-finished products.
- The analytical performance matching lab instrumentation with lower initial investment and low operational costs.
- Ease of use. Method development and operation of the Niton XL5 Plus analyzer do not require skilled lab personnel.
- Non-destructive analysis. The analyzer moves to the sample: measurements can be done directly on finished products without the need to cut a sample and bring it to the lab.
- Versatility. The Niton XL5 Plus analyzer can be used to determine the alloy grade versus specification of non-coated material such as aluminum alloys.

References

1. Gardobond® X 4707 Product Info, www.chemetall.com, Chemetall GmbH, Frankfurt am Main, Germany 2012.

2. I. Milosev, G. S. Frankel, Review—Conversion Coatings Based on Zirconium and/or Titanium, *Journal of The Electrochemical Society*, 165 (3) C127-C144 (2018).

3. M. Bauer, Application Note: *Measuring Metal Coating Thickness at Line using the Thermo Scientific Niton XL5 Plus*, Thermo Fisher Scientific, Tewksbury, MA, USA.

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