



MICRO-XRF

Analysis of steel corrosion using micro-XRF

Application Note # XRF 451

Introduction

Low-alloy steel is highly sensitive to corrosion. This is the reason why parts and structures made of such a steel are often protected by a Zn coating. The coating inhibits corrosion but as soon as it is damaged – even in a small area only – corrosion is even worse, compared to an unprotected part. This effect can be avoided by substituting the Zn coating by a ZnAl coating.

This lab report describes the examination of differently treated and corroded low-alloy steels using micro-XRF. The distribution analysis of the involved elements contributes to an improved understanding of corrosion processes and the influence of Al on the reduction of corrosion.

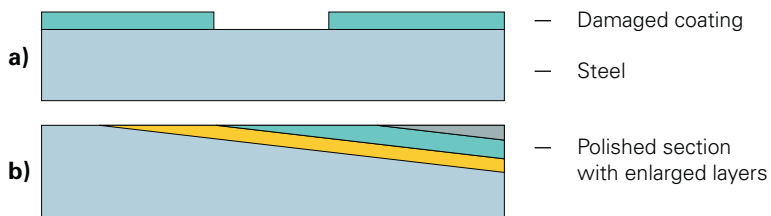
Instrumentation

The analysis was performed with the Bruker M4 TORNADO. This instrument is equipped with the following features:

- Large vacuum chamber for sample sizes of up to 200 x 300 x 125 mm³
- Fast X-Y-Z TurboSpeed stage for distribution analysis on-the-fly
- Effective excitation of fluorescence by a high brilliance X-ray tube combined with X-ray optics for concentration of tube radiation to spot sizes down to < 25 μm
- Detection of fluorescence radiation with silicon drift detectors (SDD) providing highest count rates
- Measurement in vacuum to detect light elements

Figure 1

a): Layer structure of a steel sample with coating and damaged area,
b): structure of a prepared sample (polished section)



The samples

The samples were pieces of low-alloy steel which were treated differently. Parts were either coated with galvanic Zn layers or dip-coated in a ZnAl alloy melt at approx. 600 °C. The coating was removed at a small area of the sample. Its structure is shown in Figure 1a. Then these structures were treated with seawater, respectively with a 5 % NaCl solution at 50° C for 64 hours. For distribution analysis the samples were embedded in epoxy. Because coatings and corrosion layers are relatively thin, the samples were polished at an angle of 5.7 deg. This led to an enlargement of the layers by a factor of 10. The according structure is shown in Figure 1b. A sample prepared in this manner is shown in Figure 2. Here the corrosion is very strong due to a treatment in NaCl solution. In the center the Zn coating was removed which leads to even more noticeable corrosion. The corrosion penetrates into the steel and the corroded area seems to be very thick. Nevertheless, it has to be considered that the upper layer can be seen through the epoxy.

Analyses

The analyses of differently treated samples were performed by element mapping with the following parameters:

- Mapped area: approx. 20 x 5 mm²
- Step size: 20 µm
- Measurement time: 10 ms/per pixel, less than 1 h total

The multi-element distributions of Zn and ZnAl coated samples treated with seawater are depicted in Figure 3 and Figure 4. Both figures show Zn-coated areas (green) on the left and right side and an area with removed Zn coating in the middle. The red areas in the upper section of both figures display the polished steel (Fe). Cl (blue) and S (purple) in the lower section result from the epoxy as it contains Cl and S, which are here on top of the polished sample. It will be thicker with larger distance from pure steel and can be found also within the cracks in the corrosion layer. The remnants in the cracks are residue

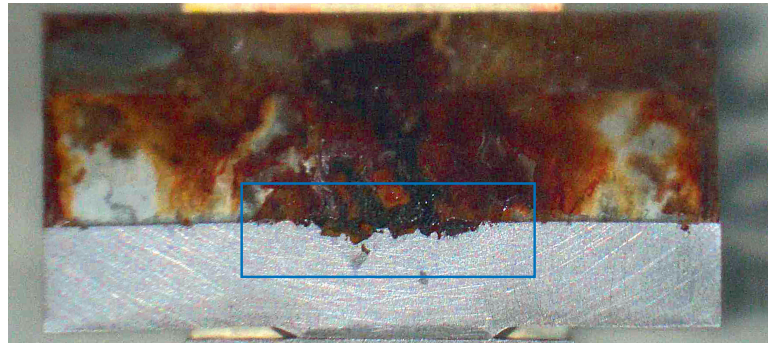


Figure 2

A sample embedded in epoxy with area marked for analysis

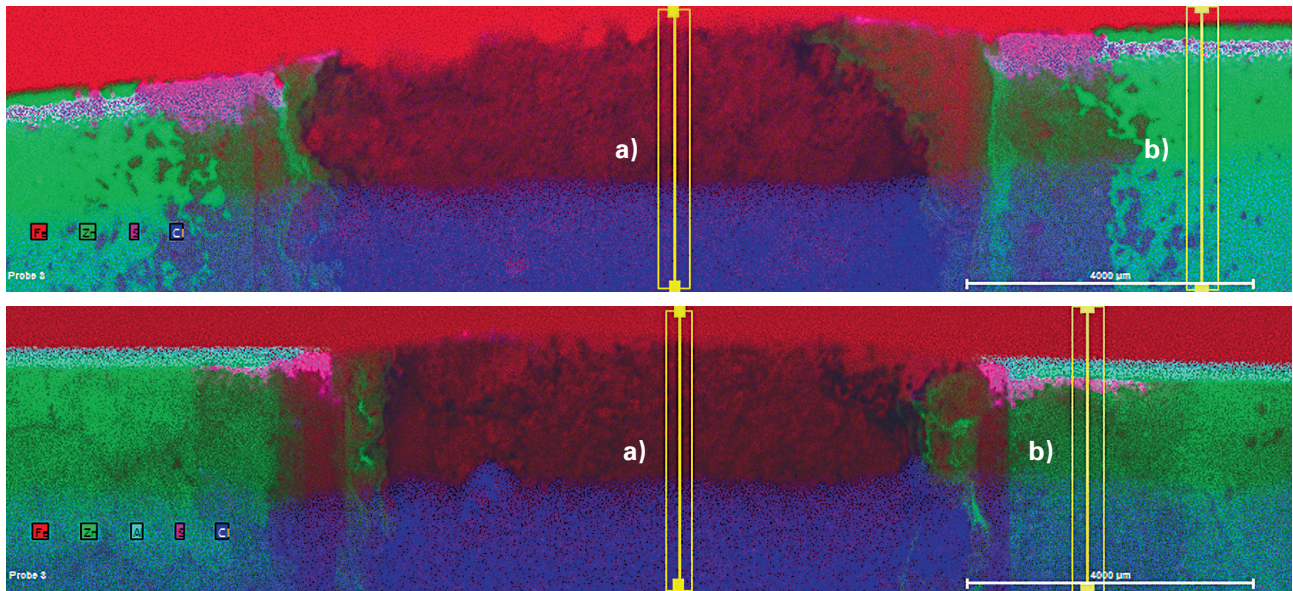


Figure 4

Multi-element distribution of ZnAl-coated steel after seawater treatment, with areas of line scans

from the seawater treatment. The distribution of Al in Figure 4 is bluish green. It is concentrated within the coated area between steel (Fe) and Zn coating.

Comparing the boundaries of the element distributions in Figure 3 and Figure 4 it can be concluded that conventional Zn coating is more sensitive to corrosion than ZnAl coating. It seems that Al is concentrated at the interface between steel and Zn coating.

More detailed information can be deduced from the single element distribution of line scans perpendicular to the layer system (broad yellow lines in Figures 3 and 4). These distributions can be calculated from map data because for all pixels the complete spectra are saved. In that line scans the intensities are normalized to the highest intensity of every element. Therefore they do not represent the real intensities. For a better understanding of the differences in corrosion protection the line scans were calculated for two different areas of each sample – for one with protective coating (line scans a) and for one with removed coating (line scans b). The resulting lines for the distributions of both coating types are shown in Figure 5 top to 6 bottom.

Figure 5 top shows the linear element distribution of the line scan a in Figure 3 perpendicular through the layer system in the Zn-coated area. At the top of the sample, respectively on the left side of the line scan, the Fe intensity (red) is high and represents the steel. It decreases significantly while the Zn intensity of the coating (green) increases. In between there are higher intensities of S (purple) and Cl (blue) which are affected by corrosion penetration. Cl increases slightly on the right side due to its content in the epoxy. The sharp boundary between Fe and Zn shows that the corrosion protection works well.

Figure 5 bottom shows the element distribution of the line scan b in Figure 3 in the area of the same sample, where Zn was removed. Here the distribution of Fe decreases slowly because it is diffused into the corroded region by the corrosion process. Zn increases slowly due to the same process. Both Cl and S increase again on the right side of the line scan – a result of their content in the epoxy. In general it can be seen that the corrosion protection is less effective because Fe is diffused in the corrosion area.

The element distributions in Figure 6 top and Figure 6 bottom show the distributions of



Figure 5

Top: Line scan (a in Figure 3) of Zn-coated material, bottom: Line scan (b in Figure 3), in the region where Zn was removed

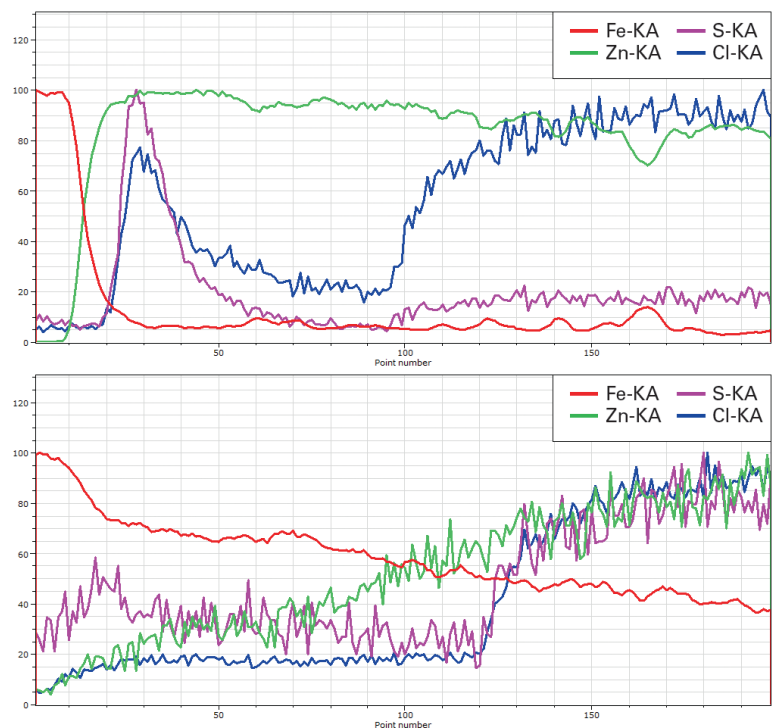


Figure 6

Top: Line scan (a in Figure 4) of ZnAl-coated material, bottom: Line scan (b in Figure 4), in the region where ZnAl was removed

a sample with ZnAl coating after the same seawater treatment. The decrease of Fe in the coated area (Figure 6 top, line scan a in Figure 4) is very strong. Al is mainly concentrated on top of the steel and the Zn coating is almost free of Al. S again penetrates between steel and protective coating but does not reach the steel due to the Al layer. On the right side both S and Cl increase as a result of the epoxy embedding. Also in the area free from Zn (Figure 6 bottom, line scan b in Figure 4) the Fe intensity decreases significantly but the Al intensity is very low. The strong fluctuations are caused by statistics. The concentrations of Cl and Zn are also low in that area. They increase as well as S in the epoxy.

Interpretation of analytical results

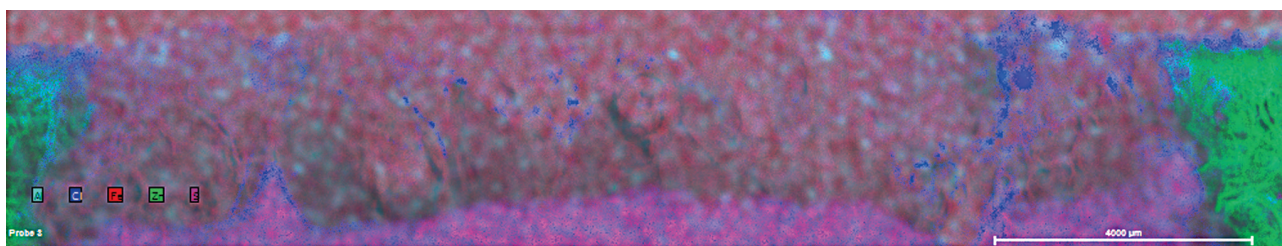
From these examinations it can be concluded that even in case of an intact protec-

tion layer corrosion protection with a ZnAl alloy is more efficient than a Zn only coating. Because Al is concentrated on top of the steel it provides additional protection. Al reduces the corrosion process even in case of a damaged protection layer.

These conclusions are also valid in case of a treatment with the more aggressive NaCl solution. This can be seen in the distribution shown in Figure 7 of the Zn-coated sample depicted in Figure 2. There is a high Fe content in the corroded area which is diffused there by the corrosion process. Cl can be detected between Fe and the Zn coating, i.e. it is diffused in that area during the corrosion process, too. It seems that Fe has damaged the Zn coating at the edges of the damaged region because it diffuses into that area. This means the corrosion layer is very strong and the protection is not very effective.

Figure 7

Image of an IC and the elemental distribution of Ni, Ag and Au that shows the lead frame together with Au-bonding



Conclusion

Micro-XRF allows to analyze the elemental distribution of coated areas. If coatings are very thin it is possible to enlarge the areas of these different coatings by polishing at a small angle.

This preparation technique was used for the analysis of the corrosion processes of differently treated samples. The distribution of all elements – base material (steel), coating material (Zn and ZnAl alloy) and the elements

used for treatment – could be distinguished. Their distribution

provides information for a better understanding of the corrosion process. It shows that the susceptibility to corrosion is reduced by adding Al in a coating.

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