CROSS-SECTION ANALYSIS AND MAPPING USING RAMAN SPECTROSCOPY

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Abstract:

When dealing with corroded objects, it is necessary to identify the corrosion products to develop a proper treatment for this particular object. Using X-ray diffraction is still suitable to do the phase composition analysis of the material; however it does the analysis of the material in bulk. It is also possible to use SEM to analyze the structure of the corrosion layers on a cross-section by EBSD method; however this method is time consuming. It is more suitable to use Raman spectroscopy when studying the structure of corrosion layers. Using proper equipment, such as Raman microscope it is possible to do not only analysis of precisely given point, but it is also possible to do mapping (both 1D and 2D) of the cross-section. Taking map of surface also does need time, but is definitely less time consuming compared to EBSD method.

Keywords: Corrosion, cross-section, mapping, micro-Raman spectroscopy

1. INTRODUCTION

Phase composition of the bulk has been analyzed using XRD; however such information is insufficient when studying the corrosion layers. The XRD gives the information on bulk, but it does not give the information on distribution of these phases. Using optical microscopy it is seen there are layers of different color and texture, but optical microscopy itself does not tell if these optical differences corresponds also to the phase differences. In other words, the optical difference might be just an artefact caused by orientation of crystals and/or grains.

According to the articles [1-3] the energy dispersive spectroscopy (EDS) might be used to do the point analysis of phase composition; however the sensitivity of the method is different for light and heavy elements. The sensitivity is also dependent on the type of detector used and its configuration, the older generation windowed detectors using Beryllium windows are less sensitive to light elements.

Other works [4, 5] also suggest, it is possible to use EDS for analyzing light elements, due to usage of silicon drift detectors (SDD), but these works also note the surface preparation and homogeneity of the sample is important. It is also necessary to keep in mind the amount of light elements in such sample is partially estimated, based on the amount of heavy elements using built in algorithm [6].

There is also problem to distinguish phases of same composition but of different crystalline structure [7].

2. METHODS - ADVANTAGES AND DISADVANTAGES

To precisely determine the structure electron backscatter diffraction (EBSD) can be used. Scanning the surface under steep angle (about 70°) to primary beam is generating Kikuchi diffraction pattern. In this manner the crystallographic orientation is obtained and thus phase at analyzed point is determined. Scanning surface by EBSD, the surface map containing individual grains could be created. The EBSD is capable to map and analyze the crystallographic orientation of grains in given structure and grain boundaries as well. On the other hand it is a matter of question, if the analysis of such complexity is really needed.

Preparation of the sample and the method itself is time consuming. It is necessary to prepare sample with very fine polished surface. The EBSD technique doesn't allow studying unpolished sample, which might be studied

under optical microscopy. It is also time consuming to scan the whole surface point by point to reconstruct the map.

The phase composition is determined for corrosion product layers, but also for each grain in each layer. This is useful and necessary when the point of interest is corrosion as a process. To analyze how the corrosion occur under controlled conditions when using electrochemical impedance spectroscopy, or studying the reactions of rust converters, such as tannic acid solution, this information is mandatory. In other words, when crystal growth and corrosion processes are matter of concern, this information is useful, as works such as [1], but when the simple information on composition of corrosion layers is needed, it is a different situation.

3. RESULTING INSTRUMENTATION

If the magnification level of optical microscopy is sufficient and can be used for studying surface and/or cross section, then the resolution of optical microscopy is enough. If the SEM is needed, then resolution needed is higher than the resolution optical microscopy is capable of. Usually, for studying corrosion product layers, the resolution given by optical microscopy is enough, and there is no need for information on orientation of grains either.

The other method used instead of SEM EBSD should have following capabilities:

- Magnification of metallographic optical microscope.
- Capability to detect various oxides and hydroxides (oxy-hydroxides)
- Fast acquisition time, since either linear or planar maps should be taken
- Good signal to noise ratio, as the acquisition should be reasonable fast

Taking these into account the Raman microscopy seems to be a suitable choice, but nevertheless there are some limitations, which have to be considered. The method is not able to detect the pure metal, so whenever there is a pure metal only, nothing could be seen. As long as the points of interest are corrosion products, and as long as the composition of the metal could be obtained by other method or is not a point of interest, this is not a problem.

4. METHODOLOGY

The samples were embedded in resin and cross-sections were prepared by grinding and polishing, and the structure was observed optically.

The composition of bulk was measured on Bruker D8 Advance XRD, the experimental conditions were as follows: generator settings 40mA and 40kV, tube position line focus, axial soller 250°, slits 0.6 mm, angular range (2Ө) 5-90º, step size (2Ө) 0.01º, counting time/step 0.01s, anode material Cu.

The micro-Raman mapping was done using DXR Raman microscope (Thermo Scientific) on the cross sections of samples embedded in resin.

Raman spectra were collected using a high resolution grating (1800 lines.mm^{-1}, spectral resolution 2 cm^{-1}) in the spectral range 1800 - 50 cm^{-1}, focused with 20x lens (N.A 0.40). The spectra were excited with 532 nm laser using 0.1 mW power on the sample to avoid the sample transformation or destruction.

5. EXPERIMENT

The measurement was done on three set of samples shown in **Table 1**, samples from industrial pipeline, exposed to corrosion in soils for approximately 50 years. Materials exposed to the atmospheric corrosion environment were steel structure of railway roof, exposed for 100 years and decorated fountain exposed for 150 years.

Table 1 Phase composition of the bulk analysed on Bruker D8 Advance XRD

Sample	Phase composition
Industrial pipeline	magnetite, goethite, lepidocrocite
Decorated fountain	hematite, akageneite
Industrial roofing	hematite, maghemite, goethite, lepidocrocite, wustite

Base materials of the pipeline and the steel structure might be overlooked as similar from the point of view of chemical composition and manufactural technology; both are steels, more or less of the same kind. On the other hand there is a difference between these two steels and the wrought iron - the material of which the fountain is made. In this case the assumption of similar materials - pipeline and steel structure and their corrosion products are correct, at least to some point, but the situation is different for the fountain.
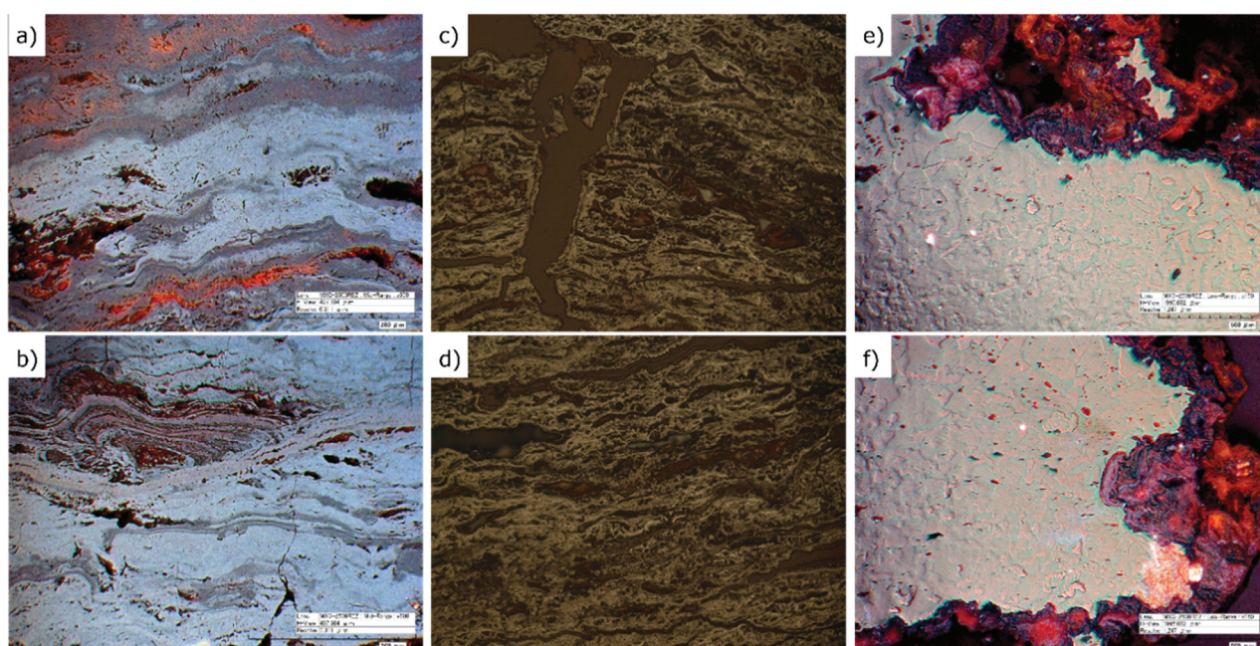

Figure 1 corrosion products on cross-sections of steel structure (a and b) and industrial pipeline (c and d) compared to the corrosion of fountain (e and f)

Metallographic observation, as shown in **Figure 1**, gives addition information on the corrosion layers and metal. On the sample taken from fountain it can be clearly seen the material is corroded on the surface. There are corrosion cracks striking deep into the material, but these are not going through the whole object and the core consist of metal, not metal oxides. On the contrary the samples of steel structure and pipeline are heavily corroded through the material; even there are some parts of the samples where the metal is still intact.

Difference in color of these layers can be seen by optical microscopy, but it is a matter of question, whether or not the difference in color is based on difference in phase composition in that layer. Thus Raman spectroscopy should be used to determine the phase composition.

If the phases are distributed in the layers, simple linear scan might be used. Best results will be obtained when done in multiple parallel scans. In such case comparison between scans show if the structure of layers obtained by Raman spectroscopy corresponds to the structure obtained by optical microscopy. Statement the layer structure corresponds could be made when layers are observed as bulk and homogeneous. Linear map in **Figure 2** shows the distribution of phases among corrosion layers. There however is still a point of uncertainty as the space between each two points is extrapolated. According to the sampling step (10 μm) and the metallography this should not be significant.
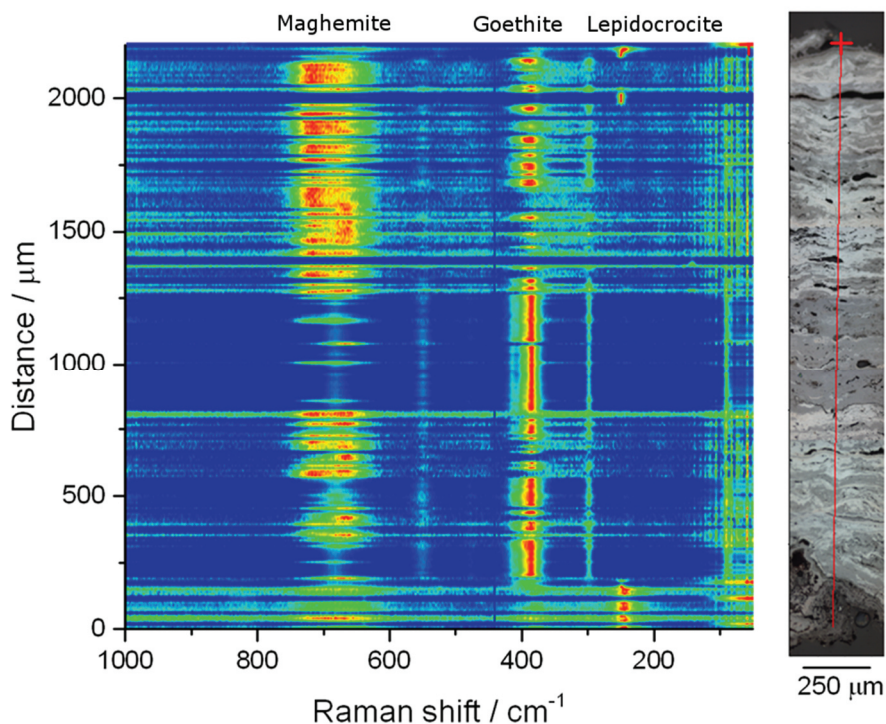
Figure 2 Raman spectra as a map of intensities for the steel structure samples (on the left) and video image of the sample with the line of measured points (on the right). Red color corresponds to the spectral ranges with the highest intensities, blue color to the ranges without presence of the peaks. The spectra are depicted in **Figure 4**.
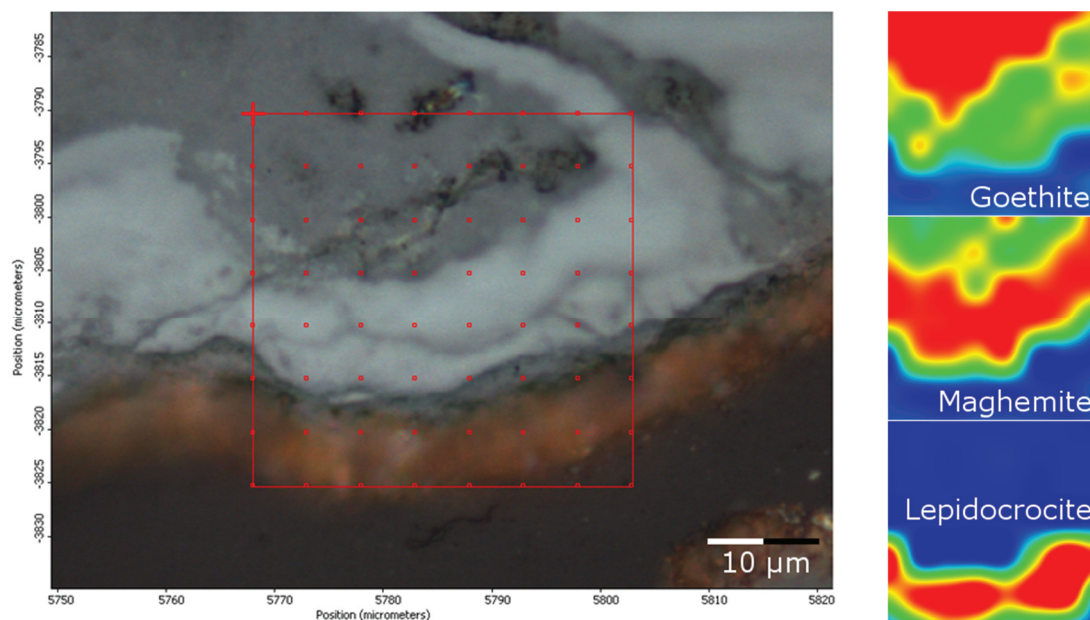

Figure 3 Industrial pipeline sample: image with the map of measured area (on the left) and Raman maps of intensities of this area for lepidocrocite, maghemite and goethite (on the right). Red colors correspond to the regions with highest intensity of selected phase; the blue regions are without this phase.

For investigation a specific location in the sample is better to use a planar 2D scanning instead, this is the situation shown in **Figure 3**. Sampling step for measurement depicted on **Figure 3** was 5 µm. As the corrosion

occurs on the metal surface, the corrosion layers shows how the surface topology has changed during the corrosion process.

As the information on each point measured is superposition of phases in given point and its vicinity, the 2D map shows the relative amount of phase in given point. This results in multiple maps for the sample, but in exchange it gives back information on the area between points and the multiphase areas in the sample.

The spectra of all identified phases are shown in **Figure 4**; these spectra were measured with same experimental setup on same sample, showing the maghemite spectrum is very low intensity that means more prone to the noise than spectra of lepidocrocite and goethite.
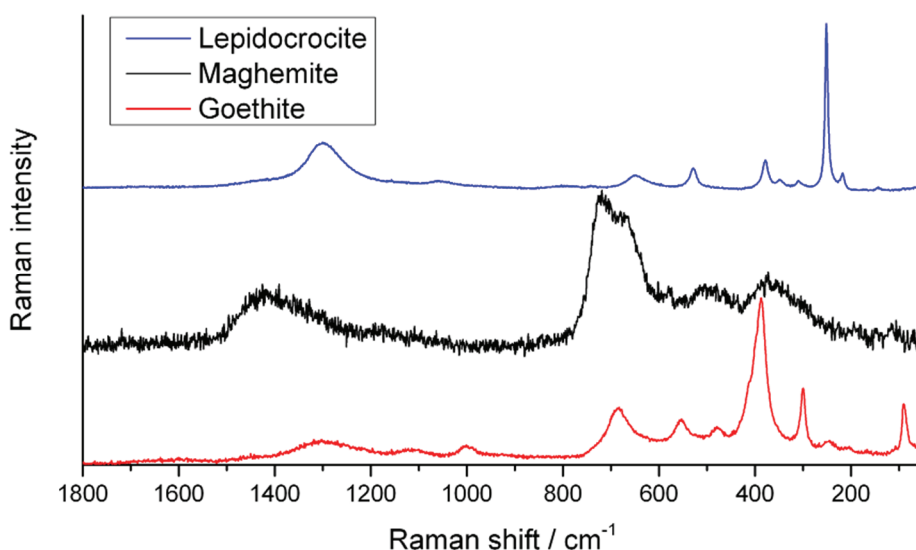

Figure 4 Raman spectra of measured phases in the samples (these particular spectra were measured on pipeline sample). Identification of spectra was done based on information from article. [8]

6.   DISCUSSION

When the structural information is needed as order of corrosion layers, the linear 1D scanning is suitable. However this scan is done on the expense of information on changes in metal surface in result of corrosion process. As the curvature of layers gives information on changes topography of the surface and corrosion-metal interface propagation. But time for mapping is saved (or could be used for decreasing the step). The result might be overviewed as a type of semi-bulk analysis.

If the area is geometrically complicated, or the information on changes in metal surface are needed the 2D scan should be preferred. Both 1D and 2D scan can be used to analyze the sample as far as the composition of layer is needed. Superposition of distribution maps for phases could be used to point out presence of two or more phases in one layer or the presence of additional layers between two measured points. When grains are the point of interest the method is insufficient and the EBDS should be used instead. However the results of Raman microscopy could be used to determine composition of layers and give the first information on what phase composition should be expected for EBSD.

On the contrary to the phase analysis previously made by XRD, phases observed by Raman spectroscopy were goethite, lepidocorcite and maghemite. No magnetite was found when mapping, this may be result of phase transformation suggested in [9]. However it is still possible magnetite is present. Raman spectroscopy was done on several parts of the sample and the magnetite may not be present in examined areas. For the results of XRD however maghemite should be found in the sample. Beside the phase transformation, it is also

possible the maghemite spectrum is noisy enough not to be detected (unless directly looked for its presence). This is however a hypothesis that should be verified.

7. CONCLUSIONS

- Using Raman spectroscopy gives results of acceptable detail for studying corrosion layers
- Compared to EBSD, the micro Raman spectroscopy is less time consuming (both the scan, but mostly the sample preparation)
- When information on grains, is not needed the usage of Raman microscopy should be favored
- Superposition of 2D maps for given phases could be used to point out location of coexisting phases

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REFERENCES

[1] S. HOERLÉ, S., MAZAUDIER, F., DILLMANN P., SANTARINI G. Advances in understanding atmospheric corrosion of iron II. Mechanistic modelling of wet-dry cycles, *Corrosion Science,* 2004, vol. 46, pp. 1431-1465.

[2] NEFF, D., DILLMANN P., BELLOT-GURLET, L., BERANGER, G. Corrosion of iron archaeological artefacts in soil: characterization of the corrosion system, *Corrosion Science*, 2004, vol. 47, pp. 515-535.

[3] VEGA, E., DILLMANN P., FLUZIN, Ph., A study on species transport in the corrosion products of ferrous archaeological analogues - a contribution to the modelling of iron long term corrosion behavior. In *Eurocorr 2004..*

[4] NEWBURY, D. E., RITCHIE, N. W. E. Performing elemental microanalysis with high accuracy and high precision by scanning electron microscopy/silicon drift detector energy-dispersive X-ray spectrometry (SEM/SDD-EDS). *Journal of Material Science*, 2015, vol. 50, no. 2, pp. 493-518.

[5] KONOPKA, J. F., Quantitative Analysis of Oxygen in Metal Oxides with SEM/EDS by Direct Measurement of all X-ray Peaks, *American Geophysical Union*, Fall Meeting 2012, abstract #V23C-2831.

[6] Using SEM/EDS for the Quantitative Analysis of Light Elements, online source http://www.azom.com/article.aspx?ArticleID=11975

[7] SCHWARTZ, A. J., KUMAR, M., ADAMS, B. L., FIELD, D. P. Electron Backscatter Diffraction. In *Material Science, 2009.* Springer Science+Business Media 2009.

[8] BELLOT-GURLET, L., NEFF, D., REGUER, S., MONNIER, J., SAHEB, M., et al. Raman studies of corrosion layers formed on archaeological irons in various media. *Journal of Nano Research*, 2009, vol. 8, pp. 147-156.

[9] Raman Microspectroscopy of Some Iron Oxides and Oxyhydroxides, *Journal of Raman Spectroscopy*, 1997, vol. 28, pp. 873-878