Carbon Analysis in Steels by FE-EPMA: A Challenge or Contradiction?

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In the past few years significant advancements in the properties of multiphase steels have been achieved by producing complex microstructures with smaller and smaller phases. In order to understand the mechanical properties as well as the production processes of these new alloys, a detailed characterization of their microstructure is necessary, with a resolution that only electron microscopy can obtain. The capital importance of carbon in steel research is nowadays well known, as its accurate content and distribution in the microstructure have a significant influence on the mechanical properties of an alloy. Qualitative and quantitative information about the distribution of carbon can also help to understand phase transformation processes during heat treatment and quenching procedures [1]. Fig. 1 presents the carbon distribution of a bainitic steel structure containing retained austenite (highest carbon level), martensite and bainitic ferrite (with no detectable carbon).

In this work the methodology will be presented for an accurate quantification of carbon steel samples on the sub-micrometer scale by a field emission electron microprobe (FE-EPMA). The problem with carbon quantification in any electron microscopes is that the electron beam cracks ubiquitous hydrocarbons causing local carbon contamination around the measuring point. When high resolution line scans or mappings are performed, the small distance between the measuring points enhances this problem, especially at higher measuring times needed for high analytical precision. The measurement gets unstable in the first micrometers (see Fig. 2). The challenge is therefore to control and assess the carbon contamination. The developed procedure relies on the use of effective anti-contamination devices (plasma cleaner, oxygen jet, nitrogen cooling plate), optimize analytical conditions, and special acquisition and quantification method to minimize the influence of the contamination on the results. A carbon-free reference material is chosen to control the contribution of contamination. As a result, quantitative carbon profiles can be measured with concentrations lower than 1 wt%. Fig. 3b shows a quantitative carbon profile across a bainitic structure (Fig. 3a). In the first 10 μm a region of bainitic ferrite and retained austenite is crossed whereas the last part describes the carbon distribution and values of a martensite phase. The strong absorption of light elements in a heavy matrix confines the X-ray emission volume. The depth resolution is only 150 nm, but the high beam currents (~100 nA) increases the analytical resolution to about 300 – 400 nm [2].

To improve the spatial resolution a method is chosen which combines non-linear optimization with Monte-Carlo simulations to solve for the composition of a small structure inside a matrix using experimental k-ratios and predicted k-ratios [3]. From an initial guess, an iterative method uses search directions, retrieved from the Jacobian matrix approximated by finite differences, to find a local minimum. An example of a reconstruction is shown in Fig. 4 for a 100 nm thin Fe_3C layer inside a Fe matrix where the carbon concentration was varied. The simulations were performed using Wincasino 2.5.1.0 [4] and pyMonteCarlo [5]. The simulations were stopped when the Euclidian norm of calculated and reference k-ratios was below 1 %. The reference k-ratios represent the experimental data. As a result, convergence was achieved for this simple case although different starting values were taken. To apply the algorithm to a real scenario, experimental k-ratios taken from the measurement (10 keV, 100 nA) of thin retained austenite (RA) phase (see Fig. 5) were converted into concentrations for different thicknesses of the RA. The plot shows the

corrected concentration of carbon if the lateral resolution is larger than the thickness of RA. Thus, it helps the material scientist to determine the critical carbon concentration at martensitic start temperature.

References:
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[4] D Drouin et al., Scanning **29** (2007), p. 92.
[5] PT Pinard et.al., Microsc. Microanal. **19** S2 (2013), p. 822.
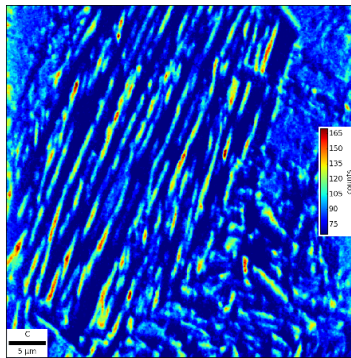
Figure 1: Carbon Kα distribution in a bainitic steel (JEOL JXA8530F, 10 kV, 100 nA, 100 ms, LDE2H crystal).
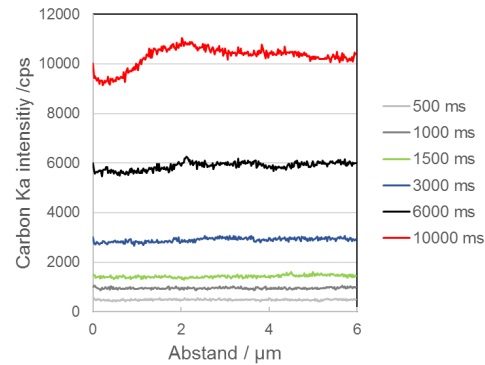

Figure 2: Beam line scans on pure Fe (15 kV, 100 nA, LDE2H crystal) with different measuring times. The step size was 20 nm.
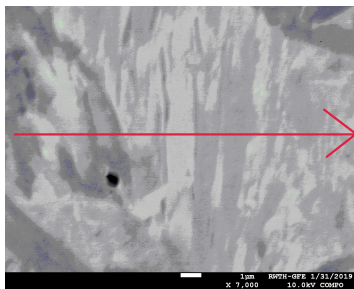

Figure 3a: Backscattered electron image of a bainitic structure. Position of the acquired line scan (see 3b) is marked.
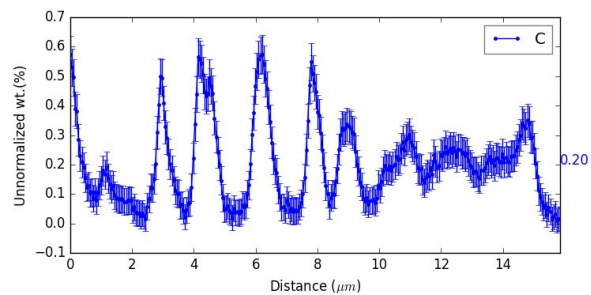

Figure 3b: Beam line scan across a bainitic structure (see 3a) at 10 kV, 100 nA, 5 s, LDE2H crystal).
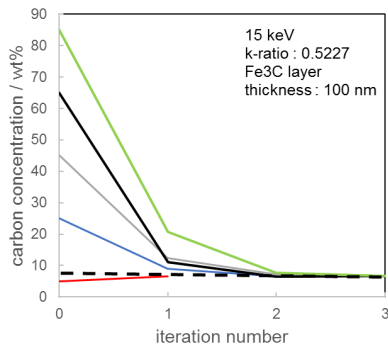

Figure 4: Iterative calculated carbon values for a 100 nm thin Fe_3C layer inside a Fe matrix for different starting values.
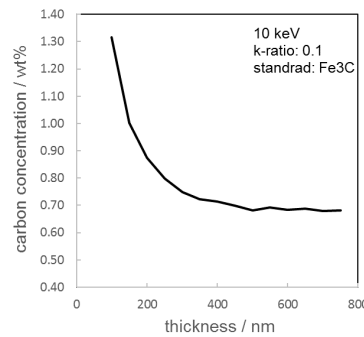

Figure 5: Corrected concentrations for different thicknesses of the carbon containing phase RA. (100 nm beam diameter, pure Fe density)