Secondary fluorescence near phase boundaries – Typical cases in steel

M R Rijnders and C J G van Hoek
TATA Steel Research and Development, Postbus 1000, NL-1970 CA IJmuiden, The Netherlands
E-mail: marco.rijnders@tatasteel.com

Abstract. Secondary fluorescence (SF) from across a phase boundary can cause spurious analytical results. Two cases of SF in steel research are presented: Zn in Zn-coated steel across the interface, and Fe in alumina particles embedded in a steel matrix. Wavelength-dispersive X-ray spectrometry (WDS) and energy-dispersive X-ray spectrometry (EDS) measurements were performed both on couples of juxtaposed Fe/Zn as well as equivalent samples that were production-derived (i.e., high-T exposed). Subsequently the SF effect was modelled using CALCZAF to compare the measured profiles with the theoretical ones. For Zn in Fe it is shown that the calculations are in close agreement with the measurements, although some discrepancies need a more detailed research. This work shows the importance of the use of models to support the interpretation of experimental WDS and EDS results on coated steel samples where phase boundaries are involved.

1. Introduction
Secondary fluorescence (SF) near phase boundaries is a well-known but sometimes overlooked phenomenon that causes observed element concentrations to be higher than they actually are. X-rays of energy higher than the absorption edge ($E_c$) of the measured line, whether they are derived from characteristic lines or from the background continuum, are the cause of such SF. Spurious element concentrations may for example have serious consequences for phase equilibrium models and thermodynamic database development.

We frequently need to measure concentration profiles across or close to a phase boundary, e.g., particle in a steel matrix, coating on a steel substrate or phase boundaries within the bulk. As X-rays can travel tens to hundreds of micrometres through the material, secondary fluorescence will originate from across the boundary, resulting in an apparent concentration that is higher than the actual (as well as resulting in higher than 100 % analytical totals). Due to the fact that any X-ray with energy $> E_c$ may cause fluorescence, bremsstrahlung will contribute to SF. Therefore, near phase boundaries, apparent concentrations of elements heavier than the matrix (e.g., Fe in Al adjacent to Fe or Zn in Fe adjacent to Zn) can be detected.

The effect of SF across boundaries is well-known (in alloys [1], in geochronology [2], in thermobarometry [3, 4], and in metal/metal couples [5-7]), and methods that correct for the effect are available [8-12]. It is especially relevant to the analysis of trace elements if the neighbouring phase also contains a major concentration of the element of interest.

We have analysed fluorescence of iron and zinc near the coating/interface substrate of galvanised material and an undiffused Fe-Zn couple (case 1), and fluorescence of Fe in Al$_2$O$_3$ embedded in a steel matrix (case 2).
2. Method
Analyses were performed on a CAMECA SX-100 EPMA (tungsten cathode), or a JEOL 7001F FEG SEM equipped with two silicon drift detectors. Different accelerating voltages (AV) and beam currents (b.c.) were applied depending on the analysis at hand. A focussed beam was used in all measurements. Acquisition times were kept at 60 seconds. The freeware CALCZAF [13], which implements the numerical model described in [10], was subsequently used to model the secondary fluorescence effects and help explain the experimental results.

3. Results and discussion

3.1. Case 1. Fe/Zn: apparent Zn concentration in steel substrate
Steel is hot-dip galvanised for corrosion-protection. The zinc coating thickness usually is a few tens of micrometres (figure 1a). An important characteristic of galvanised iron (GI) material is that the zinc coating consists of almost pure Zn. During analysis of a Zn/steel (DP800) interface in a galvanised sample, we were faced with Zn concentration profiles that extended considerably (tens of µm) into the steel matrix. However when a de-zinced sample from the same material was analysed the effect was not observed (figure 1b). The question then arose to which extent secondary continuum fluorescence could contribute to the measured Zn profile. Because the room temperature solubility of Zn in Fe is low but not zero, the presence of a Zn diffusion profile after galvanising cannot be ruled out. To experimentally test the fluorescence, a non-diffused Fe/Zn couple (“model couple”) was produced by juxtaposing flat-polished steel (0.7Mn-0.06Al) and zinc samples in a single mount. A WDS linescan was performed on the model couple under the same instrumental conditions as the GI sample and the results were compared (figure 1c). Significant (a few wt%) concentrations of Zn in Fe and Fe in Zn were measured in the model couple despite it not having reacted. The measured profile from the undiffused couple is for zinc very similar to that of the galvanised sample, with an even higher apparent concentration of zinc (figure 1c). This shows that bremsstrahlung that was excited in the steel many micrometres away from the steel/Zn interface is causing the Zn to fluoresce, and that there was no diffusion of zinc into the steel (galvanised sample). Note that the detection limit [14] for Zn under the current conditions was about 0.034 wt%. At distances over 40 µm away from the interface, the measured Zn-concentration starts to fall below this limit. The Fe concentration profile in Zn was also measured in the model couple. The detection limit for Fe under the current conditions is about 0.019 wt%. At a distance of 50 µm away from the interface the Fe-concentration (0.08 wt%) was still higher than the detection limit.

Both Zn and Fe profiles were consequently modelled with CALCZAF. Figures 1d and 1e show the results of the calculation compared to the analysis results for the undiffused couple. Overall, the agreement between the model and the measured values is satisfactory. It shows that spurious Fe can be detected up to 75 µm into Zn, and spurious Zn up to 37 µm into Fe, respectively. These numbers will depend on course of the analytical conditions.

The apparently lower concentration of Zn in steel in the galvanised samples as compared to the undiffused couple and the calculation (figures 1c and 1d) may be due to the fact that the adjacent phase is only 20 µm thick instead of semi-infinite, so that some X-rays will pass through the coating without causing SF. The semi-infinite couple with a straight boundary is the only geometry available for SF calculation in CALCZAF. For modelling more complex geometries, other software [10, 12] is available.

3.2. Case 2. Fe/Al2O3: apparent iron concentration in aluminium oxide inclusions
Alumina (Al2O3) particles (d ≤ 10 µm) in a steel matrix were studied in relation to clogging. Earlier EDS measurements [15] had shown presence of small amounts of iron that could not be thermodynamically explained, since iron solubility in alumina is negligible. Alumina powder retrieved from the same clogging deposit showed no presence of iron, contradicting the EDS results.
**Figure 1.** a) SEM BSE image of GI coating, polished cross-section. b) Comparison of zinc concentration profiles of a GI (galvanised, blue) and a de-zinced (red) sample; WDS, 20 kV, 50 nA, peak time 60 s; x = 0 corresponds to the sample surface in the case of the dezinced sample. c) Comparison of measured zinc concentration profiles of a GI sample (blue) and of an undiffused Fe–Zn couple (grey); conditions as in figure 1b. d) Apparent concentration of zinc in iron adjacent to zinc at 20 kV, measurement in undiffused couple (blue) and calculated values (orange). e) Apparent concentration of iron in zinc adjacent to iron at 20 kV, measurement in undiffused couple (green) and calculated values (orange).
EDS linescans were performed at 10 kV and 60 s analysis time per point; both on a bulk steel/alumina couple and on alumina particles embedded in a steel matrix. Results on the Fe/Al₂O₃ interface in a clogging sample (figure 2a) are shown in figure 2b. The same figure also shows the calculated values. Both the Al and the Fe profile depart significantly from the calculated ones. The measured apparent concentration of Fe close to the interface is about 2 wt% and shows a decrease to 0.4 wt% at a position 50 µm away from the interface. However, as may be appreciated from figure 2a, the interface shape is not ideal, and moreover it is not known below the sample surface. The calculation assumes a perpendicular and flat interface between the two materials. The effect of interface orientation is discussed in two recent papers [11, 12].

![Figure 2. a) Path of the linescan performed on an Fe/Al₂O₃ sample from a steel clog. b) Apparent concentration of Al in steel (blue) and Fe in Al₂O₃ (green) (production sample) and calculated values (orange, yellow); EDS 10 kV, 60 s. c) SE image of undiffused Fe/Al₂O₃ couple; note gap of 5 µm. d) Apparent concentration of Al in steel (blue) and Fe in Al₂O₃ (green) in undiffused couple, and calculated values (orange, yellow).]
A model Fe/Al₂O₃ couple (figure 2c) was then constructed and analysed. The results are shown in figure 2d. In this case the apparent Al-profile shows a good fit with the calculation. At distances > 2 µm away from the interface, the secondary Al fluorescence caused by Al₂O₃ is negligible. The apparent Fe-profile still shows a discrepancy with the calculation, albeit less than with the clogging sample. The interfacial measured Fe-concentration lies around 1 wt%, where the model predicts 0.7 wt%, and decreasing to 0.2 wt% at 50 µm away from the interface, where the model predicts 0.08 wt%. Possible causes for discrepancy may be: 1) X-ray intensity reaching the detector is somewhat dependent on the orientation of the interface with respect to the detector [16], 2) inaccuracies in the ZAF correction. Because of the 5 µm gap between the end members (gap filled with epoxy resin), the actual measured interfacial Fe-concentration would be somewhat higher should the gap have been zero.

Note that the spurious Fe concentration is solely due to bremsstrahlung generated in the Al₂O₃.

Linescan profiles across alumina particles (figures 3a-d) show that the apparent Fe concentration is almost constant (~ 2 wt%, comparable to the interfacial concentration measured in the bulk case) throughout the particle, and does only decrease slightly when the beam moves away from the interface, as opposed to the bulk case, where the decrease continues for tens of micrometres. Similar results for spurious Fe in 15 - 20 µm copper particles embedded in Fe-rich slag have been reported by Llovet et al. [17]. The size and shape of the particle, which are de facto unknown, will certainly influence the amount of SF that is generated. Qualitatively, the particle results can be understood as follows: compared to the case of a flat interface, SF will be higher, since the particle is surrounded by the fluorescing iron matrix. As the beam moves away from one interface, it will approach the other one, i.e., decreasing SF from one side of the particle is balanced by increasing SF from the other side. The subtle difference between the two measured curves might be due to the difference in shape and volume of the particles. It would take more modelling effort to clarify this observation.

4. Conclusions
Steel research often involves the measurement of element concentration profiles across interfaces, where secondary fluorescence effects can affect the calculated element concentrations. Even though the lighter element Kα cannot directly excite Kα of a heavier element, SF can still occur due to the high-energy components of the bremsstrahlung, resulting in overestimation of the element concentration close to the interface. The effect can extend tens of µm away from the interface.

As shown by the analysis of undiffused metal/metal couples, secondary fluorescence across an interface is accurately predicted by CALCZAF for the Fe-Zn couple. The apparent concentration of Fe in Al₂O₃ could not be exactly matched with a CALCZAF calculation.

If accurate analyses near interfaces are needed, the analyst must be wary. Where possible, analytical results should be supported by model results.

Acknowledgement
The authors owe thanks to Bing Doeve and Frank van der Does for sample preparation.
Figure 3. a) Alumina particle 1. b) Alumina particle 2; apparent diameter 16 µm. c) Fe concentration profile of particle 1 shown in figure 3a; essentially a flat profile. d) Fe concentration profile of particle 2 shown in figure 3b; slight decrease towards centre of particle.

References
[1] Fournelle J H, Kim S and Perepezko J H 2005 Monte Carlo simulation of Nb Ka secondary fluorescence in EPMA: comparison of PENELOPE simulations with experimental results. Surf. Interface Anal. 37 1012-1016
[2] Jercinovic M J, Williams M L and Lane E D 2008 In-situ trace element analysis of monazite and other fine-grained accessory minerals by EPMA. Chem. Geol. 254 197-215
[3] Dalton J A and Lane S J 1996 Electron microprobe analysis of Ca in olivine close to grain boundaries: the problem of secondary X-ray fluorescence. Am. Mineral. 81 194-201
[4] Llovet X and Galán G 2003 Correction of secondary X-ray fluorescence near grain boundaries in electron microprobe analysis: Application to thermobarometry of spinel herzolites. Am. Mineral. 88 121-130
[5] Bastin G F, van Loo F J J, Vosters P J C and Vrolijk J W G A 1984 An iterative procedure for the correction of secondary fluorescence effects in electron-probe microanalysis near phase boundaries. Spectrochim. Acta B 39 1517-1522
[6] Arnould O and Hild F 2002 EPMA measurements of diffusion profiles at the submicrometre scale. Mikrochim. Acta 139 3-10
[7] Zoukel A and Khouchaf L 2014 The secondary X-ray fluorescence and absorption near the interface of multi-material: Case of EDS analysis. *Micron* 67 81-89
[8] Escuder J A, Salvat F, Llovet X and Donovan J J 2010 Numerical correction for secondary fluorescence across phase boundaries in EPMA. *IOP Conf. Ser. Mater. Sci. Engng.* 7 1-7
[9] Llovet X, Pinard P T, Donovan J J and Salvat F 2012 Secondary fluorescence in electron probe microanalysis of material couples. *J. Phys. D: Appl. Phys.* 45 225301
[10] Llovet X and Salvat F 2016 PENEPMA, a Monte Carlo programme for the simulation of X-ray emission in EPMA. *IOP Conf. Ser. Mater. Sci. Engng.* 109 1-13
[11] Ritchie N W M 2017 Efficient simulation of secondary fluorescence via NIST DTSA-II Monte Carlo. *Microsc. Microanal.* 23 618-633
[12] Llovet X and Salvat F 2017 PENEPMA: a Monte Carlo program for the simulation of X-ray emission in electron probe microanalysis. *Microsc. Microanal.* 23 634-646
[13] [http://probesoftware.com/Technical.html](http://probesoftware.com/Technical.html)
[14] Ancey M, Bastenaire F and Tixier R 1977 Statistical control and optimization of X-ray intensity measurements. *J. Phys. D: Appl. Phys.* 10 817-830
[15] Tata Steel unpublished results
[16] Llovet X 2017 personal communication
[17] Llovet X, Valovirta E and Heikinheimo E 2000 Monte Carlo simulation of secondary fluorescence in small particles at phase boundaries. *Mikrochim. Acta* 132 205-212