Correcting Errors of Secondary Fluorescence in SEM and EPMA EDS and WDS Quantitative Analysis with the PENELOPE Monte Carlo Simulation

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The scanning electron microscope (SEM) and the electron probe microanalyzer (EPMA) have been workhorses in scientific and technical laboratories for >40 years. Instrumentation and automation have improved many aspects of these tools, aided by modern cheap fast computers. One thing that hasn't changed is the physics of electron – material interaction, and related to this the problem of secondary fluorescence of phases far from the electron "spot" on the sample. Secondary fluorescence (SF) is the production of "stray" x-rays from phases at some distance – up to hundreds of microns distance in some cases – far from the primary electron impact zone and its associated electron scattering volume. Regardless of how well focused the electron beam is, both characteristic and bremstrahlung x-rays that are produced under it may have sufficient energies to excite distant atoms; x-rays are uncharged and thus can travel long distances without electrostatic interaction before they may be ultimately annihilated. A peak on an x-ray spectrum may fool the unwary! (Fig 1) Secondary fluorescence is a potential problem for several sample types, i.e. diffusion couples; small phases enclosed in a larger phase; eutectic intergrowths. In cases where lower intensities of x-rays are assumed to be present, the analyst may easily misinterpret the data. In many cases it is difficult or impossible to fabricate non-diffused samples (i.e., 2 metals squeezed together). The Monte Carlo simulation program PENELOPE (Penetration and Energy Loss of Positrons and Electrons - photons introduced later) presents the ability to simulate and evaluate the extent of SF [1,2]. It uses ionization cross sections from optical data and bremsstrahlung cross sections that reproduce radiative stopping power derived from partial wave calculations. Llovet and co-workers have demonstrated PENELOPE correctly simulating SF: small Cu particles in Fe matrix, in Fe-Cu metal non-diffused couples and in Ca in olivine due to adjacent Ca-bearing minerals [3]. I present here two other cases where SF is a problem, and demonstrate the ease and utility of the PENELOPE simulation package.

Nb in Pd_2HfAl [4]: One lab found ~10 wt% Nb in Pd_3Hf and Pd_2HfAl in a eutectic assemblage (where there was adjacent Nb), measuring Nb Ka with EDS at 30 keV (Fig 1). However, our WDS measurement of Nb La showed no Nb present, although we did see an Nb Ka peak on our EDS display (E_0=28 keV; Fig. 1). Later WDS analysis with an LIF220 crystal and a non-diffused couple of untreated Nb/Pd_2HfAl yielded an Nb Ka pseudo-diffusion profile which we then modeled with PENELOPE (Fig 2). Our initial modeling was somewhat offset from the EPMA intensities, which led to the discovery that sample-detector geometry is important, i.e. if the fluoresced material faces the detector , the counts are higher. When the experimental data was re-collected with this geometry, there was a close match to the PENELOPE simulated Nb Ka intensities. All measured Nb in the eutectic phases is explained by SF from Nb ss within 5 μm. This correction also resulted in a significant change in the eutectic phases' Pd contents due to changes in the matrix correction.

Al in Mo_3SiB coating [5]: The extent of SF of Al in Mo_3Al_8 coating on Mo_3SiB substrate was modeled (in cross-section), to correct errors in EPMA measurements. At 5 μm from the coating, there was an apparent 4.4 wt% Al, dropping to 0.9 wt% at 10 μm, 0.4 wt% at 50 μm, 0.2 wt% at 100 μm and 0.006 wt% at 200 μm. PENELOPE has a clear use in evaluating thin films in any geometry.

PENELOPE: This is available at no cost. The Fortran source code will need to be compiled on the user's computer (free g77 compilers available online). The necessary modules, sample input files, documentation, and tutorial are readily available. A 253 page manual is available at www.nea.fr/html/dbprog/peneloperef.html [6] and information about acquiring this program in your country can be found at www.nea.fr/html/dbprog/. If there appear to be any unreasonable fees being charged, the program's authors may directly provide the code. An online library of articles relating to PENELOPE can be found at www.geology.wisc.edu/~johnf/g777/777Penelope.html. A new 2005 version offers many improvements [7].

References:

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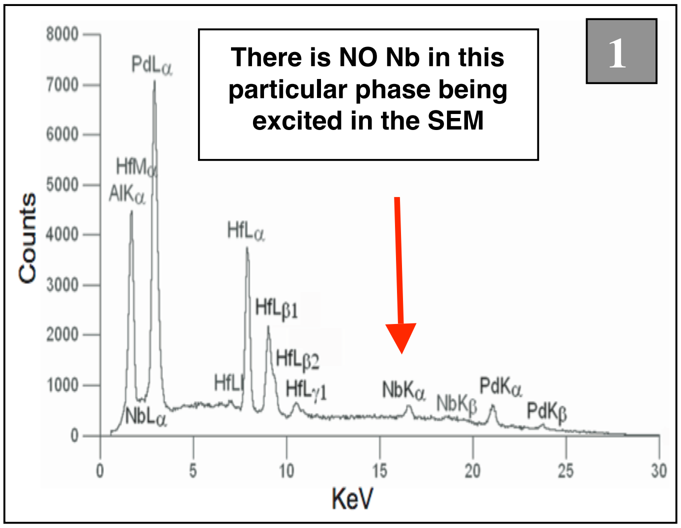
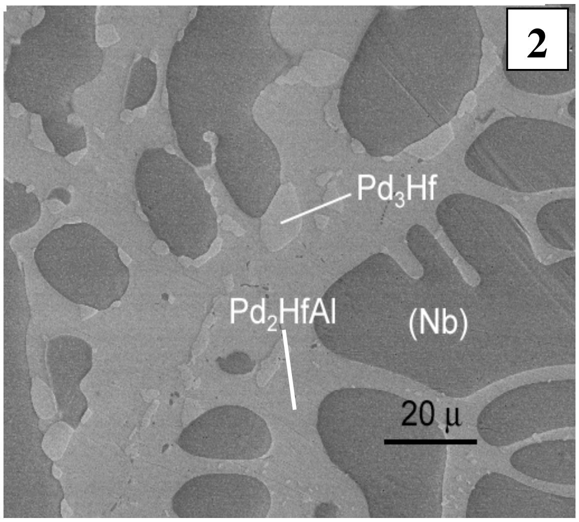
[7] I acknowledge invaluable assistance of Francesc Salvat and Xavier Llovet. (Universitat de Barcelona)





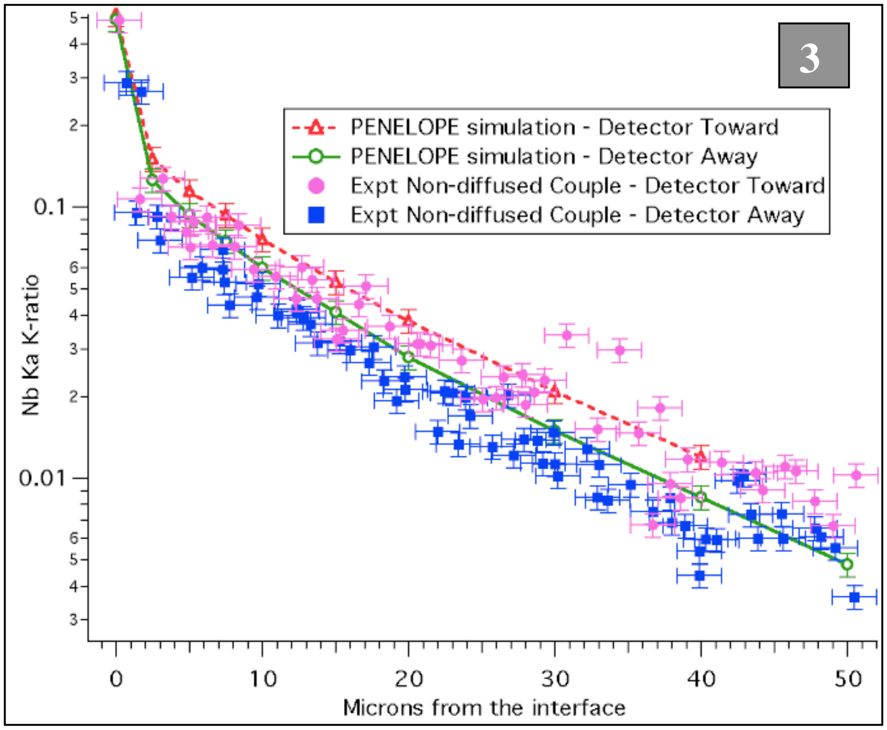


FIG. 1 EDS spectrum where the Nb Ka peak in Pd_2HfAl is totally caused by SF from adjacent Nb ss.

FIG. 2. BSE image of annealed eutectic sample. Note the close proximity of the Nb ss to the Pd_3Hf and matrix Pd_2HfAl phases. Both experiment and PENELOPE indicate SF.

FIG 3. Experimental WDS Nb Ka K-ratio data (28 keV) acquired with SX51 with LIF220 shown as solid circles or squares, oriented either away from or toward the detector. Lines connect simulated K-ratios by PENELOPE. There is very close correspondence.