Depth Analysis of Chemical Environments using Resonant Raman Spectroscopy in Total Reflection Geometry

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INTRODUCTION

Total Reflection of X-rays is a largely proved spectroscopic technique that allows the study of material surfaces. As the refractive index is less than unity, X-rays incident on a material are, theoretically, totally reflected if the glancing angle is less than a critical angle derived from the Snell´s law [1]. Making use of this phenomenon, different depths of a sample surface could be studied by means of the correct election of the incident radiation angle. In this way, analysis of the reflected intensity could provide a method for studying surface properties, as variations of electron density with depth (e.g., corrosion, porosity, aging, etc.) with a resolution from Amstrongs to hundred nanometers deep [2]. X-ray resonant Raman scattering (RRS) is an inelastic scattering process which presents fundamental differences compared to other scattering interactions between X-rays and atoms; when the energy of the incident photon approaches from below to an absorption edge of the target element, a strong resonant behavior takes place. Both total reflection and resonant Raman scattering techniques are used combined with the aim of discriminate oxidation states in nano-layers of materials. Samples of pure Cu and Fe oxidized in water and salty water, respectively, were studied in the Brazilian synchrotron using monochromatic radiation and an energy dispersive setup. The measurement were carried out in total reflection geometry scanning the incident radiation angle around the critical angle with incident energy lower and close to the K absorption edge of both elements in order to study the RRS emissions. The results not only allowed to observe the presence of very thin oxides, invisible with the use of conventional irradiation geometries, but besides they permit the identification of the oxidation state present in a particular depth of the sample with nanometric resolution, or even Åmstrongs, using a low-resolution system.

EXPERIMENT

The measurements were carried out in XRF station of the D09BXRF beamline [3] at the Brazilian synchrotron facility (LNLS, Campinas). The XRF beamline is equipped with a double crystal channel-cut monochromator, the energy resolution of the monochromator is 3 eV at 10 keV using a Si(111) crystal. For the measurements performed in this work, the incident beam was collimated with orthogonal slits to 1 X 1 mm and monitored with ionization chambers, resulting in a flux intensity on the sample of 100000000ph/s a 10 keV. The

detection systems are energy-dispersive setups composed by several solid-state detectors with different windows and different electronic chains. The detector used in this work was an KETEK AXAS-A solid-state detector with a Be windows of 8 mm and an energy resolution of 139 eV for the Mn-Ka line. Pulse processing was accomplished by a fast amplifier with triangular shaping and spectra were processed and collected with a 8K MCA. The samples consisted of pure Fe and Cu foils (>99.99A scanning of the incident radiation angle around the critical angle was performed. The measuring livetime for each incident radiation angle were 3000s and 2000s for Fe and Cu foils respectively. The spectra were analyzed with specific programs ([4],[5]) using non-conventional functions for data fitting and a FFT smoothing procedure was applied. After smoothing, the RRS residuals are studied in order to detect variation with respect to the theoretical curve. These variations are closely related with the chemical environments of the absorbing element and can provide relevant structural information of the sample ([6],[7]).

RESULTS AND DISCUSSION

The residuals show an oscillation pattern that change smoothly with the incident angle, i.e. with the observed depth, allowing a depth study of the oxidation state. In summary, by
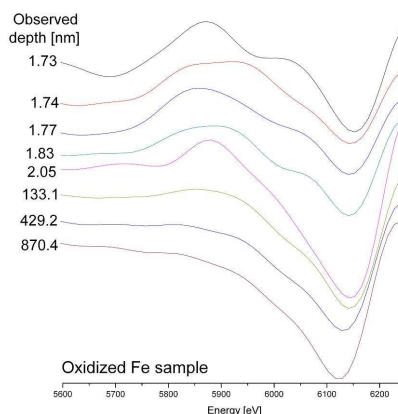

FIG. 1: Fe residuals between experimental spectra and data fitting

the direct comparison with previous pure-compounds residuals ([8],[9]) the results say that the pure Cu foil submerged in water seems to be oxidized as a Cu(II) (cupric oxide), de-
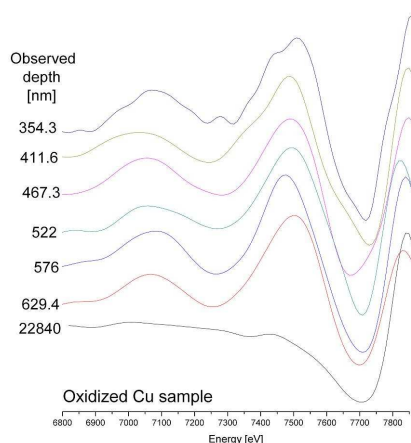
FIG. 2: Cu residuals between experimental spectra and data fitting

creasing gradually the intensity of the oxidation as the studied depth increase. In the case of the Fe foil submerged in salty water, the sample seems to be oxidized mainly as Fe(III) (ferric oxide) decreasing smoothly the intensity of the oxidation as the observed depth increase, presenting also a thin contribution of Fe(II,III) (ferric ferrous oxide) in the most external layers of the sample. These results have a consistent behavior with the expected ones. Although these results still represent only qualitative results and they can be smeared for no-controlled processes; the application of this new RRS technique in total reflection geometry not only allowed to observe the presence of very thin oxides, invisible with the use of conventional geometries, but besides it permits the identification of the oxidation state present in a particular depth of the sample with nanometric resolution, or even Åmstrongs.

CONCLUSION

For the first time, both resonant Raman scattering and total reflection techniques are used combined as a hybrid tool allowing discrimination of oxidation states in nano-layers of materials using a low resolution spectrometer. The main con-

tribution of this article relies on the possibility of obtaining structural information with nanometric resolution, or even Åmstrongs, by using a typical energy dispersive setup. In this way, a lot of possibilities appear from the combination of RRS spectroscopy with other X-ray techniques, even three-dimensional analysis by RRS combined with confocal setups. In these cases, it will be able to obtain detailed spatially resolved information, which would be impossible to achieve by conventional absorption techniques. This new RRS chemical environment technique will offer an opportunity to study the oxidation state of different kind of samples (such as mineral, environmental and/or biological ones) in the nano and micro regime, reaching a complete characterization impossible to achieve by other methods. Currently, further investigations are carried out in order to reach a complete understanding of the processes involved with the aim of turn this practical method into a true and complete analytical tool.

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