



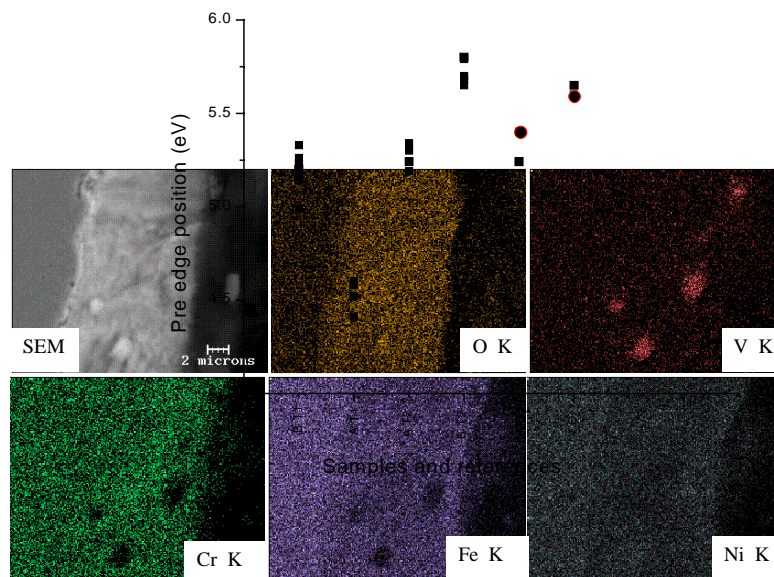
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|  | <b>Experiment title:</b><br>MicroXANES on vanadium K edge in oxide scales on alloyed steels corroded in coal gasification atmospheres | <b>Experiment number:</b><br>MI-350 |
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## Report:

The aim of the experiment was to complete the characterisation study of oxide scales formed on Fe-Ni-Cr austenitic steels in an environment simulating the build Integrated Gasification Combined Cycle (IGCC) power plant. In these environments, materials are in contact with gas streams containing CO, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub> and H<sub>2</sub>O. Moreover the gas contains fly ashes known to be responsible for accelerated corrosion. In this study, two different alloys were treated for 72 h at 400°C in a gas containing 40%<sub>vol</sub>CO-38%H<sub>2</sub>-13%H<sub>2</sub>O-8%CO<sub>2</sub>-1%H<sub>2</sub>S (gas rate 6l/h) in association with synthetic vanadium containing ashes (FeS 2.7%, Na<sub>2</sub>S-8 H<sub>2</sub>O 29.1%, Ni 7.0%, V<sub>2</sub>O<sub>5</sub> 27.5% and VSO<sub>4</sub> 33.6%). For several samples, following this treatment, an airflow was introduced in the furnace for 24h to study the influence of air. Thus, four different samples were obtained. Scanning electron microscopy coupled with energy dispersive X-ray spectrometry reveals that, as a function of the treatment and of the alloy substrate composition, the vanadium had different effects. In some case, high quantities of the element were incorporated into the scale in the form of V-O islets. In other cases, low quantities of vanadium were uniformly distributed in the scale (see for example figure 1).

The aim of the absorption study was to determine the vanadium valence in the different cases. Transverse sections were made of the sample to be examined. A micro beam is necessary to analyse particular points in the oxide scale that have an average thickness of 20 µm. Moreover, the microbeam allows us to scan the vanadium valence throughout the entire thickness of the scale.

On ID 21, the undulator beam is monochromatised by a double (Si 111) crystal fixed-exit monochromator giving a bandpass of about 0.8eV at the V K absorption edge (~5465eV). The beam was focused to 0.9 x 0.3 µm<sup>2</sup> using a Fresnel Zone Plate (FZP) lens. Due to the difficulty in preparing thin films from this kind of sample, we performed absorption spectroscopy measurements using the vanadium fluorescence signal instead of working in transmission mode. To resolve the problem related to the high X-ray penetration, the surface of the transverse section of the oxide scales was placed approximately perpendicular to the incident focused beam. The HPGe fluorescence detector was positioned at 90 degrees to the incident beam and in the



horizontal plane and accepted fluorescent X-rays with trajectories which were grazing with respect to the surface of the sample in order to collect preferentially the signal emitted by the first microns in depth

Figure 1: example of the V repartition in an oxide scale (SEM coupled to EDS)

Vanadium rich zones were localised by mapping the scale with the K alpha vanadium X-ray emission peak. For each interesting zone, the region near the vanadium absorption edge (5.65 keV) was scanned in energy from  $-100$  to  $100$  eV with a  $0.5$  eV step. All the collected spectra were normalised considering the flux variations caused by the energy scan which were primarily due to the undulator emission spectrum. For comparison with the literature data, for all the spectra, the region before the pre edge was linearly fitted, extrapolated over the entire energy scan range and subtracted from the raw data

In view of the system studied here and its possibility to develop complex oxide compositions, we focused our study upon the energy position of the pre-edge peaks that is related to the valence of the absorbing atom. In the first instance, some reference spectra collected from simple vanadium oxides ( $\text{VO}_2$  and  $\text{V}_2\text{O}_5$ ) were made. The positions of the pre-edge peak centroids in the obtained experimental spectrums were compared to the reference materials and to those given in the literature. Figure 2 shows the spectrum obtained by focusing the microbeam on the rich-vanadium islets observed in one of the oxide scales. The measured pre-edge position is in very good agreement with that of the  $\text{VO}_2$  reference and with those given by the literature data for this oxide. Thus, the  $\text{V}^{4+}$  valence can be deduced.

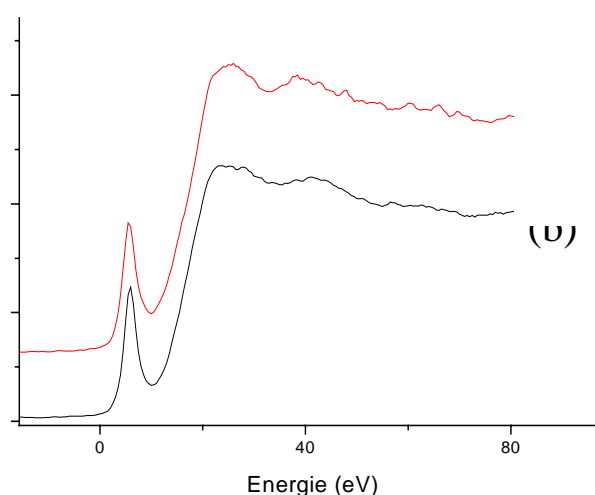


Figure 2: Figure 5 : Micro XANES spectra obtained by focusing the ID21 microbeam on (a) a vanadium rich islet in the oxide scale, (b) a  $\text{VO}_2$  reference

Figure 3 shows the different pre-edge positions measured from the analysed sample and compared to reference data. The vanadium valence in each sample seems to be very homogeneous. But, oxygen partial pressure of the atmosphere and compositions of the different substrate seems to influence the vanadium incorporation and its valence in the oxide scale.

Figure 3 : Pre-edge position (origin : 5.465 keV) measured on spectra of experimental sample (vanadium-rich islets) and references (black circle : literature data)

Complementary Rutherford Back Scattering measurements were made using the nuclear microprobe of the Pierre Süe laboratory. This kind of analysis, in favourable cases, gives the stoichiometry of constitutive phases. The obtained results are in very good agreement with the micro-XANES ones coming from ESRF. Thus, in such cases, with a combination of the two techniques it was possible to identify a particular vanadium oxide. For example, the islets showed in the figure 1 are relatively pure VO<sub>2</sub> oxides. These observations are in good agreement with thermodynamic observations.

Nevertheless, some XANES experimental spectra correspond to more complex oxides and the data analysis is very difficult; it seems also that sometimes, different valences are mixed, and the analysis becomes impossible without supplementary data. For the separation of the XANES contributions from different phases an improved energy resolution would be extremely helpful. Moreover, for this kind of complex sample, the scanning over the EXAFS energy domain could bring a lot of useful structural information. In future studies, it would be better to use Si (311) or (220) crystals. Moreover, at these energies, it should be possible to scan the EXAFS domain with a correction of the FZP focus length. Last but not least, simultaneous measurement of the incident beam intensity (I<sub>0</sub>), which will soon be implemented, should greatly improve the data quality.

### **Publications:**

DILLMANN P., WEULERSSE K., REGAD B., MOULIN G., BARRETT R., SUSINI J., BONNIN MOSBAH M., BERGER P., LEQUIEN S., Journal of Materials Science letters, submitted

K. WEULERSSE, B. REGAD, P. DILLMANN, G. MOULIN, S. DEPROT, P. BILLARD, L. LELAIT, Proceedings of the 5<sup>th</sup> international symposium "Corrosion et protection des Matériaux à Haute Température, 22 to 26 may 1999, submitted