

Combined SEM and Raman spectroscopy A new analytical tool for corrosion and oxidation studies - analysis of oxidised copper wire and reactor steel

Introduction

The Renishaw structural and chemical analyser (SCA) shown in Figure 1 allows corrosion and oxidation scientists to benefit from the imaging and analytical capabilities of scanning electron microscopes (SEMs) combined with the chemical and structural characterisation available from Raman spectroscopy. The SEM-Raman system is unique, allowing both rapid observation and elemental analysis at macro and micro scale. An overview and detailed classification of the sample is now available in a single instrument.

Oxidation and corrosion are related processes that refer to the conversion of metals into various compounds. The conversion process can be gradual, limited, or rapid, and an understanding of the mechanisms and kinetics involved is fundamental to determining the performance of metal components through their lifetime.



Figure 1
The SEM-SCA at Bologna University - Italy

Traditional methods of analysing oxides and corrosion products - such as x-ray analysis, x-ray diffraction, and surface analysis (e.g. Auger, XPS, SIMS) - are either limited to "bulk" samples, or are poor at determining the precise chemical composition. Raman spectroscopy, although unable to collect spectra from native metals, can provide specific chemical identification from most metal oxides and corrosion products. Raman spectroscopy has traditionally been carried out in parallel with optical

microscopy, but the limited depth of field, spatial resolution, and contrast mechanisms of the latter has meant that identification of regions of interest can be quite difficult. Combining Raman spectroscopy with an analytical SEM, however, capitalises on the imaging and elemental analysis capabilities of the SEM, and the chemical specificity of Raman spectroscopy.

SEM-Raman investigation into oxidation of copper wire

Copper wire is widely used for many electrical applications and although copper is not considered to corrode or oxidise, this is not the case. Oxide or corrosion film growth can significantly compromise copper's conduction.

The aim of this study was to understand how copper wire - from a test vehicle forming part of Renault's continuing commitment to quality - was oxidising or corroding. This information can be used to avoid in-service failure and to define service regimes.

"Control" samples of wire that had been exposed to various temperature and environmental regimes and showed varying degrees of oxidation or corrosion were provided for comparison, and the results from analysing these are presented here.

SEM images of a wire that had been exposed to hydrated corrosion conditions are shown in Figures 2 and 3. The points from which the Raman spectra (shown in Figure 4) were collected, are indicated on Figure 2.

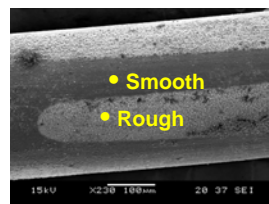


Figure 2
SEM image showing "rough" and "smooth" areas

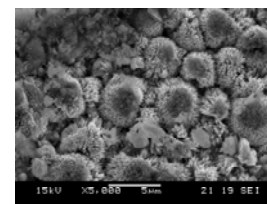


Figure 3
SEM image from the "rough" region

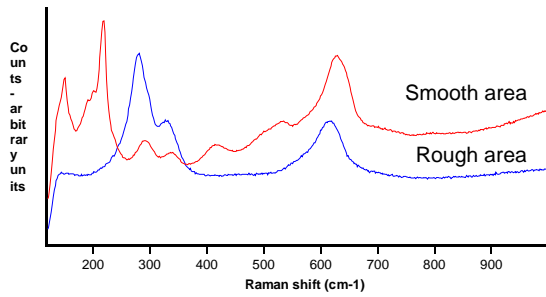


Figure 4
Raman spectra from smooth and rough areas

The SEM micrographs show clearly that there are “smooth” and “rough” areas on the wire. The latter, on inspection, at higher magnification (Figure 3), comprise agglomerated ball-like growths.

The spectrum from the smooth area has Raman bands consistent with **cuprous oxide** (Cu_2O) or **cuprite**.

The blue spectrum is similar to that of **cupric oxide** (CuO) or **tenorite** but the peaks are rather broad implying that the degree of crystallinity is low - this is consistent with the SEM observations that show a highly disordered surface. There is no evidence for the presence of hydrated copper oxides (e.g. malachite, atacamite) due to the absence of O-H bands in the spectra.

Figures 5 and 6 show SEM images of a wire sample that had been heated at 750°C . Visually it is possible to see red and black coloured regions. The SEM images are taken at the junction of these regions - “red” wire on the left, “black” on the right. Raman spectra from the areas indicated are shown in Figure 7. Several spectra were collected from random points in the red and black areas, but no localised differences in the spectra were noted.

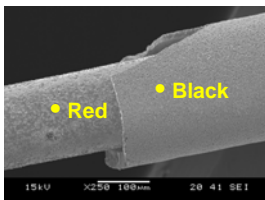


Figure 5
SEM image at x250

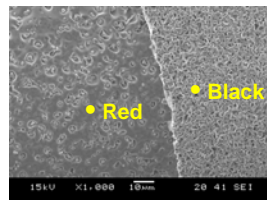


Figure 6
SEM image at x1000

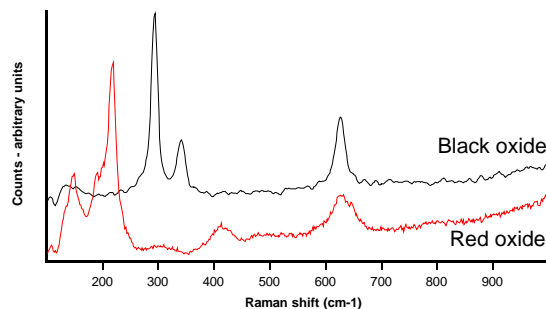


Figure 7
Raman spectra from black and red oxides

The spectrum from the red oxide is characteristic of **cupric oxide** (CuO) - the black matches **cuprous oxide** (Cu_2O).

Figures 8 and 9 show SEM images of a wire that had been heated at 900°C . The images show that the oxide film is uniform and this is consistent with visual inspection, which notes uniform blackening. The fracture revealed that there appears to be a layer structure, a sub-layer being revealed at the fracture surface.

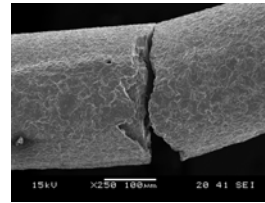


Figure 8
SEM image at x250

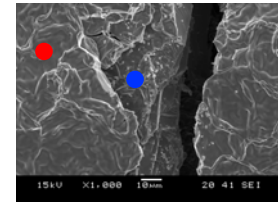


Figure 9
SEM image at x1000

Figure 10 shows spectra taken from the base of the fracture area as shown in Figure 9 (in blue), and from the oxide surface (in red).

Both spectra are characteristic of **cupric oxide** (CuO), although the spectrum from the fracture base has additional bands (at 148 cm^{-1} and 216 cm^{-1}) from **cuprous oxide** (Cu_2O).

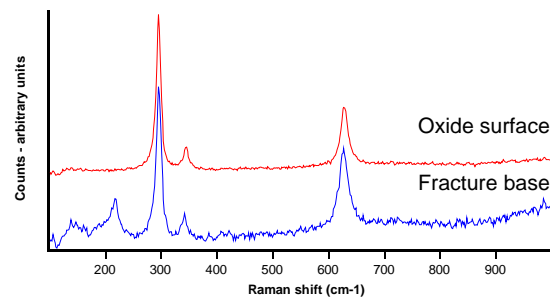


Figure 10
Raman spectra from the oxide surface and fracture base

When copper oxidises it first grows a thin adherent layer of cuprous oxide (Cu_2O) - **cuprite** - which is red. As oxidation progresses cupric oxide (CuO) - **tenorite** - forms, this is black and adherent if present as a thin film. If the CuO layer becomes thick enough it will spall away when the copper cools (Figure 5) because of differences between the coefficients of thermal expansion of copper and CuO .

The samples examined here represent various stages in the oxidation process. The wire exposed to the hydrated conditions has formed a Cu_2O layer, and CuO is beginning to form, the interesting morphology is most likely due to the hydrated environment.

The wire heated at 750°C has appears to have grown a Cu_2O layer and then a thick CuO layer much of which has subsequently spalled away. The wire heated at 900°C has an adherent CuO film, which implies it is quite thin.

If *tenorite* (CuO) forms and the material is subject to thermal cycling, then spallation can cause significant reduction of the conductor cross-section - this in turn can lead to:

- Ohmic heating - and more oxidation...
- Reduced load-bearing capacity – possible fracture

The sample wire that was provided by Renault from their test vehicle showed only *cuprite* (Cu₂O) had formed. This finding gives confidence that the potential problems associated with *tenorite* formation are unlikely to occur under normal operating conditions.

SEM-Raman investigation into oxidation of reactor steel

Nuclear reactors are an aggressive environment for materials - coolants (either gas or pressurised water) run at high temperatures and pressures. Nuclear power stations are designed to run for 25 years or more and any unforeseen materials failure during this lifetime is unacceptable since the consequences can be catastrophic.

An understanding of the corrosion and oxidation processes for the material employed is vital for implementing a planned maintenance programme to ensure lifetime safety for the station.

A steel component (Figure 11) from a high-pressure, high-temperature, high-stress region of the reactor started to show signs of cracking - this was believed to be as a result of oxidation. The part was taken out of service and provided for analysis to identify the oxides present, to understand the oxidation process, and assess its implications.



Figure 11
The image left shows the part that had been withdrawn from service and the interface between the unaffected and oxidised regions. The low power optical micrograph on the right shows a higher magnification image of the interface

Examination of the oxidised region using a conventional Raman microscope yielded valuable data (see Figure 12). It was difficult to relate the optical microscope images to the macrostructure because of the highly topographic nature of the oxide surface, and the limited depth of field of the high-power objective - this is illustrated by the inset optical micrograph.

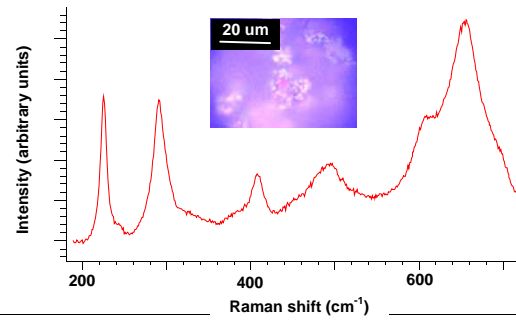


Figure 12
Raman spectrum collected from within the oxidised region, the inset optical micrograph shows the point from which the spectrum was collected

Using the SEM-SCA, spectra and SEM images were taken at the top of the crack (the topmost spectrum in Figure 15). Further spectra were collected at 1 mm intervals through the oxidised region down to the oxide/metal boundary (the bottom spectrum in Figure 15).

The micrographs in Figures 13 and 14 were collected at the top of the crack and at the oxide/metal boundary respectively. The red spots indicate the laser spot position and hence the analytical point.

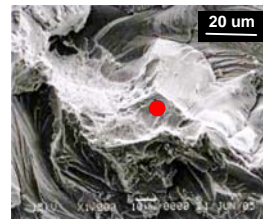


Figure 13
SEM image at crack

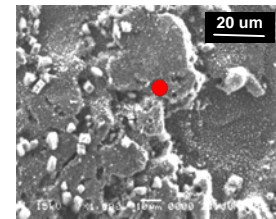


Figure 14
SEM image at the metal/oxide boundary

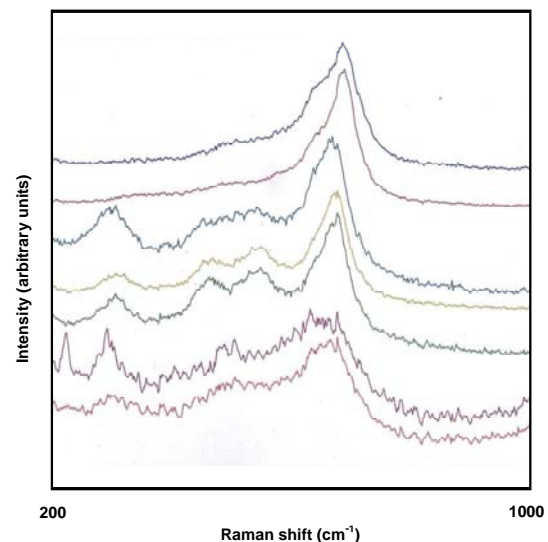


Figure 15
Raman spectra from different depths in the oxide layer

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The spectra show there is a gradual transition from **magnetite** (Fe_3O_4) to **haematite** (Fe_2O_3) – this is typical of a gradual oxidation process where a thin film of haematite forms initially, but is soon overgrown with magnetite.

It would appear that the oxide grew gradually until it reached a thickness where it could no longer tolerate the stresses imposed on it, and cracked. Cracking of course exposes a fresh metal surface, which can then oxidise; if this process is allowed to continue then, after multiple oxide growth and cracking cycles, the cross-section of the part would be so reduced that its strength could be critically compromised.

The kinetics of oxide growth on steels, however, are well characterised, and this study has confirmed that the oxidation process is conventional. A maintenance regime that involves replacing the part before oxidation compromises its performance can now be planned with confidence.

Advantages of SEM-SCA for oxidation and corrosion studies

- Raman can identify unambiguously the oxidation state and chemical composition of regions EDS only identifies as “oxide”
- SEM visualisation can often reveal subtle variations in composition that are invisible to optical microscopy
- Raman analysis can be carried out *in situ* so that the spatial context is maintained
- EDS analysis complements Raman spectroscopy by revealing either subtle variations or consistency in concentration and the presence of trace elements
- LV-SEM observation means samples can be examined “as prepared” - subsequent analyses are not affected
- Full characterisation of sample components can be carried out quickly and easily



Why choose Renishaw?

Renishaw is an established world leader in metrology, and has been providing high performance solutions for measurement and control since 1973. In 1992, Renishaw combined several new technologies, including its metrology expertise, into its Raman microscopes and rapidly became a world leader in the design and manufacture of Raman spectroscopy systems.

Renishaw has a global network of subsidiary companies, distributors, and agents, providing a level of service second to none. Its teams of highly qualified engineers and scientists can provide you with rapid and comprehensive product, technical, and application support.

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