

SEM and EPMA analysis of un-usual hydride structure in in-pile cracked Zircaloy-cladding

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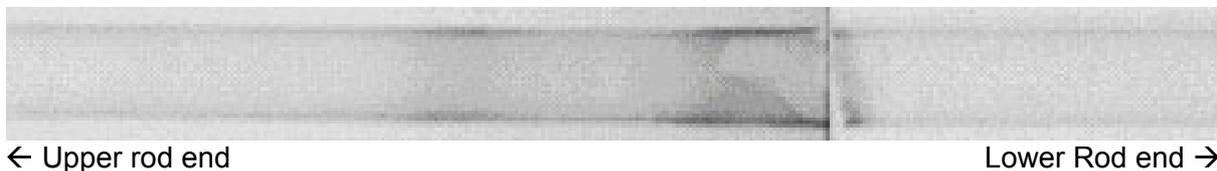
Abstract

The hydride distribution in a cracked Zircaloy cladding tube has been investigated by neutron radiography, Scanning Electron Microscopy (SEM) and Hydrogen measurements. The crack occurred during handling in the spent fuel pool. Back Scattered Electron images showed some unexpected contrasts in zones with high hydrogen concentrations near cracks. This phase has been studied by SEM and EPMA. After detailed analysis it was possible to relate the observed structure to an unexpected hydride distribution in the material.

Introduction

In the vacuum sipping of a fuel assembly a leaking rod was identified. During the transfer into the eddy current measurement equipment the defect rod broke at the lower end of the second spacer (Fig.1). The cladding material was Zircaloy-2 β -quenched with an inner liner. Post Irradiation Examination (PIE) of the broken rod have been performed in the Hotcells of the Paul Scherrer Institut. The scanning electron microscopy (SEM) analysis in backscattering mode (BSE) of polished specimens of the cladding material in spacer area revealed a strange contrast. Further analysis with SEM and EPMA (Electron Probe Micro Analysis) were realised in an attempt to explain the unusual material distribution, its formation and existing conditions.

Fig.1: Neutron radiography image of fractured spacer area (rod diameter 9.6 mm) with a very high hydrogen content (up to 8300 ppm Hydrogen in the dark areas)



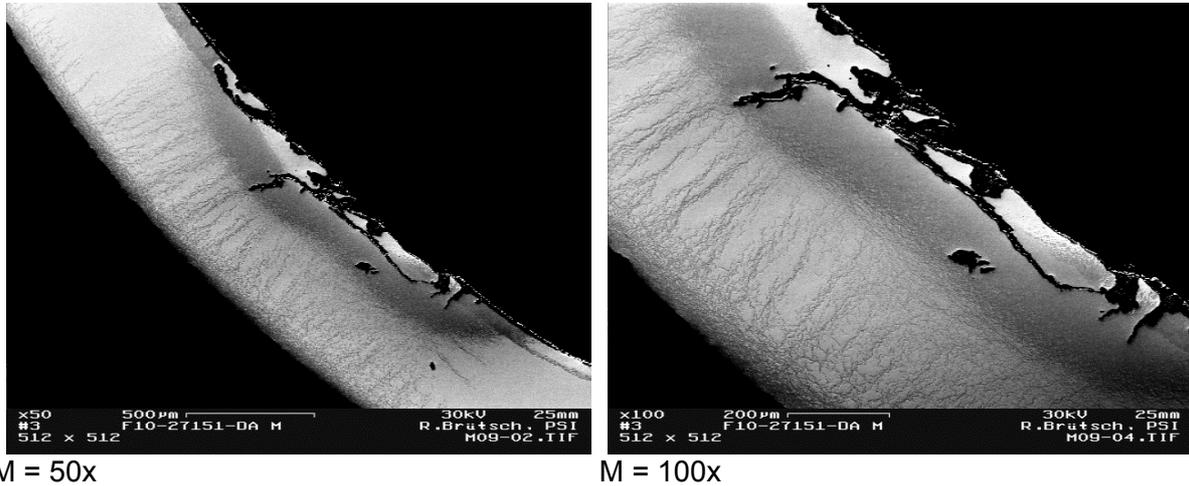
Back Scattering Mode in Scanning Electron Microscopy

Electrons of the Primary Electron Beam penetrate into the specimen material and are scattered by coulomb force. The heavier a nucleus is, the stronger is the coulomb force and therefore the scattering effect. Material with higher atomic number in the specimen produce a more intense BSE signal. Therefore, BSE-images show the elemental distribution in a flat polished specimen. The brighter an area appears the higher is the average atomic number. The crystallographic orientation may also have some influences on the BSE-signal.

Analysis

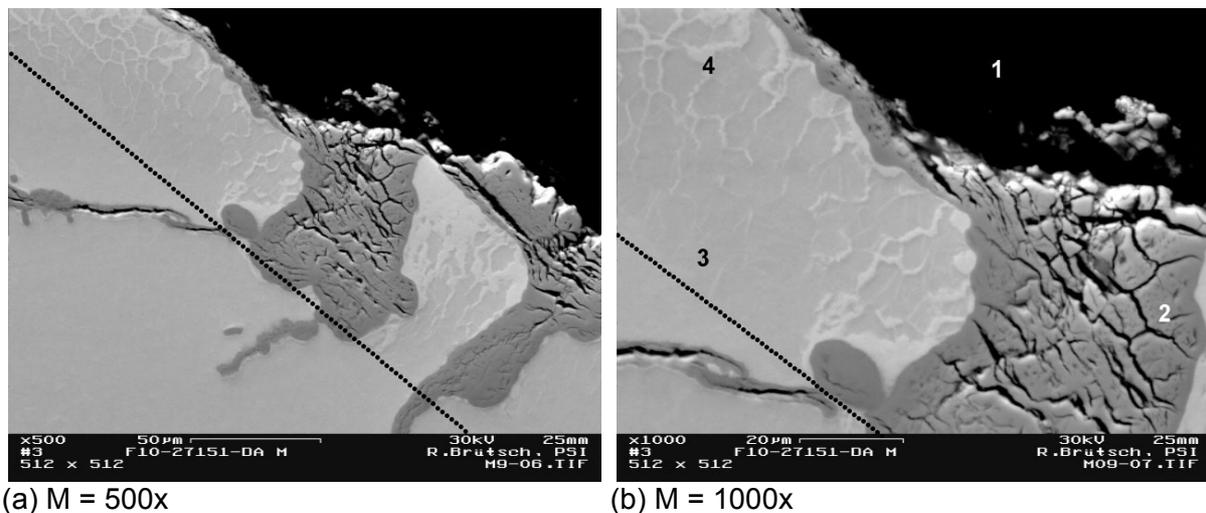
For the analysis of the hydrides in Zircaloy cladding material maximum high voltage, as high as possible beam current (depends from the requested resolution) and maximum contrast level have to be used. With these parameter settings hydrides can be made visible (Fig.2) and will appear as a darker phase.

Fig.2: Hydrides in Zry-2-Cladding near strongly oxidised cracks



With this "high contrast BSE mode" a strange contrast was found (Fig.3) in the cladding liner near oxidized cracks. The dotted line shows the border between Liner and the Zircaloy-2-Cladding. In the liner zone, directly beneath a strongly oxidised crack, bright areas appear. Three different phases are visible (Fig.3a): a dark grey phase is strongly oxidised Zry, the medium grey is the not oxidised Zry and the bright almost white area is a phase with a higher average atomic number than the medium grey Zry.

Fig.3: Details in the liner area. Three different phases are visible: the dark grey phase (2), the medium grey (3) and the bright almost white area (4). The embedding compound is almost black (1).



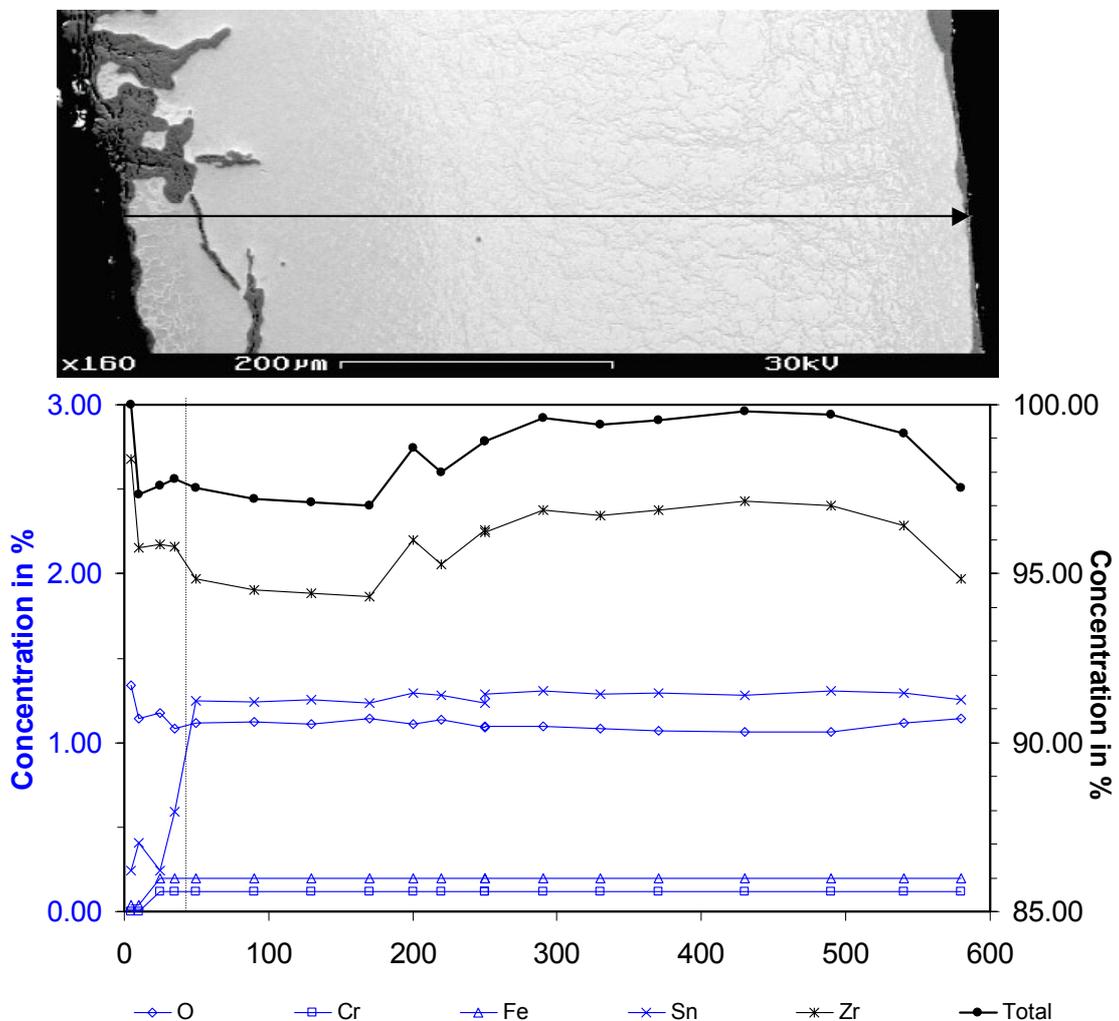
To determine the source of the observed contrast, Wavelength Dispersive X-Ray-Analysis (WDX) have been realised by EPMA to find possibly an enhancement of a heavier element in the bright phase (Fig.3b, 4). The results show no other elements present other than the

Zircaloy and Oxygen (Zr: 98.3%, Sn: 0.3%, Fe: <0.1%, Cr: n.d., O: 1.3%). The same analyses were performed in the medium grey phase (Fig.3b, 3) to analyse a local concentration increase of a lighter element. The composition in this phase is the same than in the brighter phase, with slightly lower oxygen content (O: 1.1%).

If no heavy elements are present in the observed phase, the only possibility is that the medium grey phase contains a very light and undetectable element (with X-Ray-analysis), i.e. hydrogen. Then the bright grey area consists of Zircaloy with a low hydride concentration. Compared to the strongly hydrated Zircaloy the low or not hydrated Zircaloy has a higher concentration of Zirconium, then a higher average atomic number and therefore a more intense BSE signal.

A series of analyses over the whole cross section of the cladding have been performed, every with the same analysis parameters to compare the resulting count rate in the different phases. To draw the results in a graph (Fig.4) as a line scan, the values have been standardised. For that, the sum of all measured elements of the analysis in the bright grey phase (Fig.3b, 4) was set on 100%.

Fig. 4

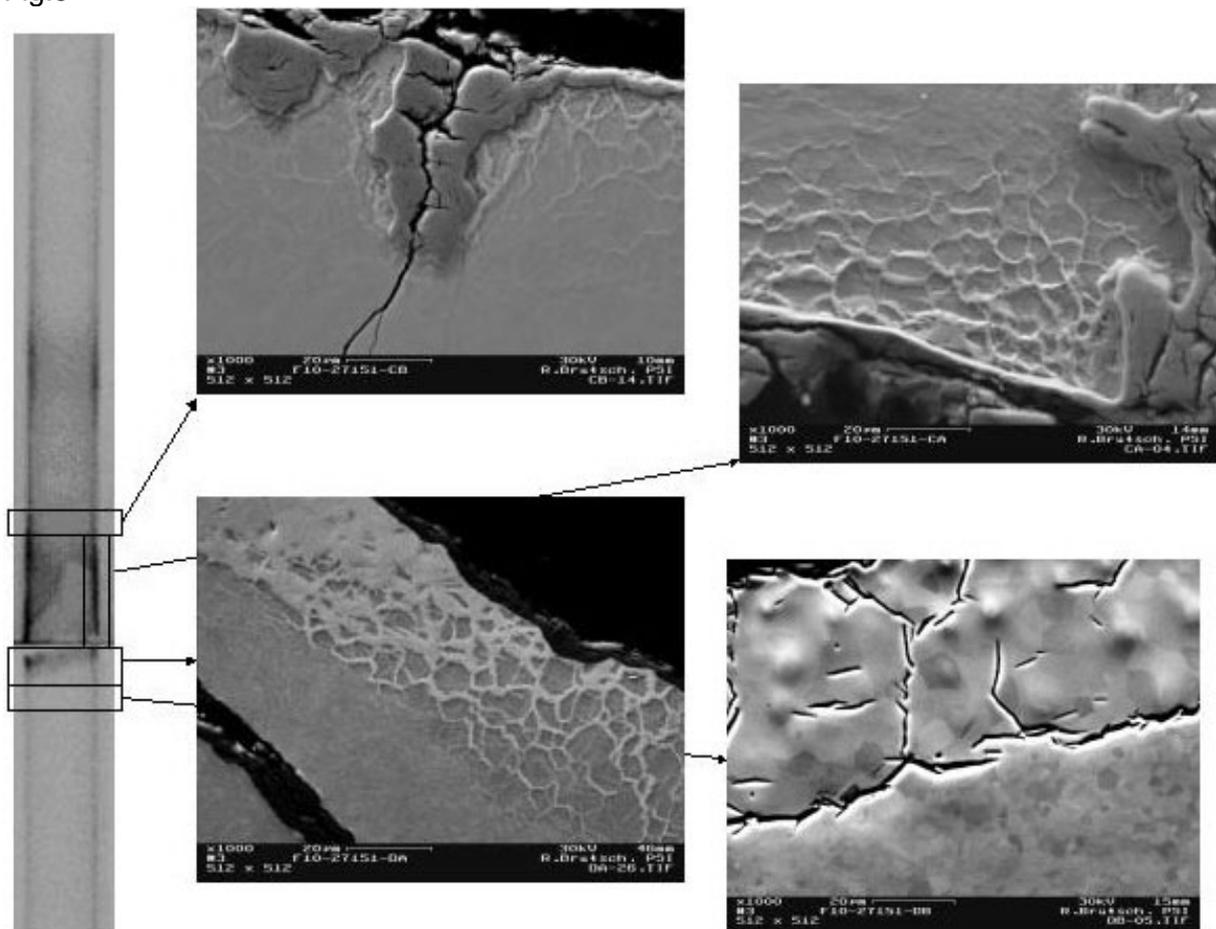


In the graph (Fig.4) the first value from left is the analysis of the bright grey phase, the second one is measured in the grey phase directly beneath. All other values are measured at the corresponding position noted on x-axis. This Linescan shows that the highest concentration of Zirconium was found in the bright grey area. Tin, Chromium and Iron have the expected concentration of the Liner and the Cladding materials and the concentration of

Oxygen increases a little bit on the very inner rim. The total of all measured elements compares very well with the BSE-Image and shows the lowest values in the highly hydrated zone in the inner third of the cladding and in the outer rim.

To check the analysis, samples of different locations of the defect rod have been taken and prepared. The locations are showed in Fig.5. Three of them are taken in the highly hydrated area of the second spacer, one is taken directly beneath this zone outside at the lower part of the spacer area. The SEM-analyses of each specimen show that the not or very low hydrated Zry-phase is observed only in the spacer area whereas outside of the strong hydrated spacer area no such contrast is visible. This phase is only found in the liner and near strong oxidised cracks.

Fig.5



Conclusion

Our analysis demonstrate that the hydrogen content is responsible for the different contrast in the BSE-Images: The bright grey phase is in fact a low hydrated Zircaloy and the medium grey area consists of highly hydrated Zircaloy.

The phase seems to follow the grain boundaries of the liner and is always found near oxidised cracks or defects. Some local conditions may have prevented hydrating of the bright grey phase in liner or hydrogen has been removed during the operation of the defect rod in the reactor.

This study allowed to analyse and to understand the unusual material distribution, but not to explain its formation and existing conditions.