

## Precipitate Evolution In Zry-4 Oxidation

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The microstructure of Zr alloys has been a subject of study during the last decades due to its influence on the manufacturing of fuel elements sheaths for power reactors. In particular, Zircaloy - 4 (%wt Sn 1.45 - 1.5, Fe 0.18 - 0.24, Cr 0.07 - 0.13, O 1400ppm, Zr to balance), is widely used as fuel cladding material.

Of all the alloying elements only Sn is in solid solution. For low temperatures ( $T < 600^{\circ}\text{C}$ ) Fe and Cr are present in the form of second phase particles. These intermetallic precipitates are about 10 - 1000 nm in diameter, depending on the fabrication conditions. The structure, composition, average size and morphology of the second phase precipitates are closely related to the corrosion behavior of Zry-4.

It is known that during the initial oxidation of zirconium alloys thin coherent oxide films of  $\text{ZrO}_2$  form over the whole surface, including the intermetallic particles lying on the surface. The precipitates are accommodated in the oxide film in a non-oxidized state, and then the zirconium present inside the precipitates is gradually oxidized to either cubic or tetragonal  $\text{ZrO}_2$ . The precipitates in the oxide layer are subjected to a delayed oxidation as compared to the matrix, accompanied by the rejection of a significant proportion of their iron content. Previous works showed that precipitates undergo chemical composition changes after open furnace oxidation: EDS (Energy Dispersive Spectroscopy) showed the presence of Zr, Cr and Fe within both non-oxidized and partially oxidized precipitates, but no Fe was detected within the oxidized ones. Then, it was suggested that a progressive Fe rejection towards the oxidized Zr (Cr, Fe)<sub>2</sub> precipitate / oxidized matrix frontier takes place.

In the present work, as-received commercial Zircaloy- 4 furnished by Teledyne Wah Chang was characterised by Analytical Electron Microscopy (AEM) techniques, before and after an oxidation treatment in open furnace at  $650^{\circ}\text{C}$ . AEM analysis was carried out in a CM 200 Philips microscope with and EDAX- DX4 system operated at 160 kV.

Figure 1 shows a BF- TEM image of Zry-4 and of a non-oxidised precipitate with its corresponding EDS spectrum. The Fe / Cr atomic ratio was found to be  $\cong 1.5$ . Inside the Zry-4's oxide layer non-oxidised precipitates (i.e. original intermetallic precipitates) with a nominal Fe / Cr ratio of 1.5 were found as well as oxidized precipitates with an Fe / Cr ratio decreased to 0.5. (Figure 2).

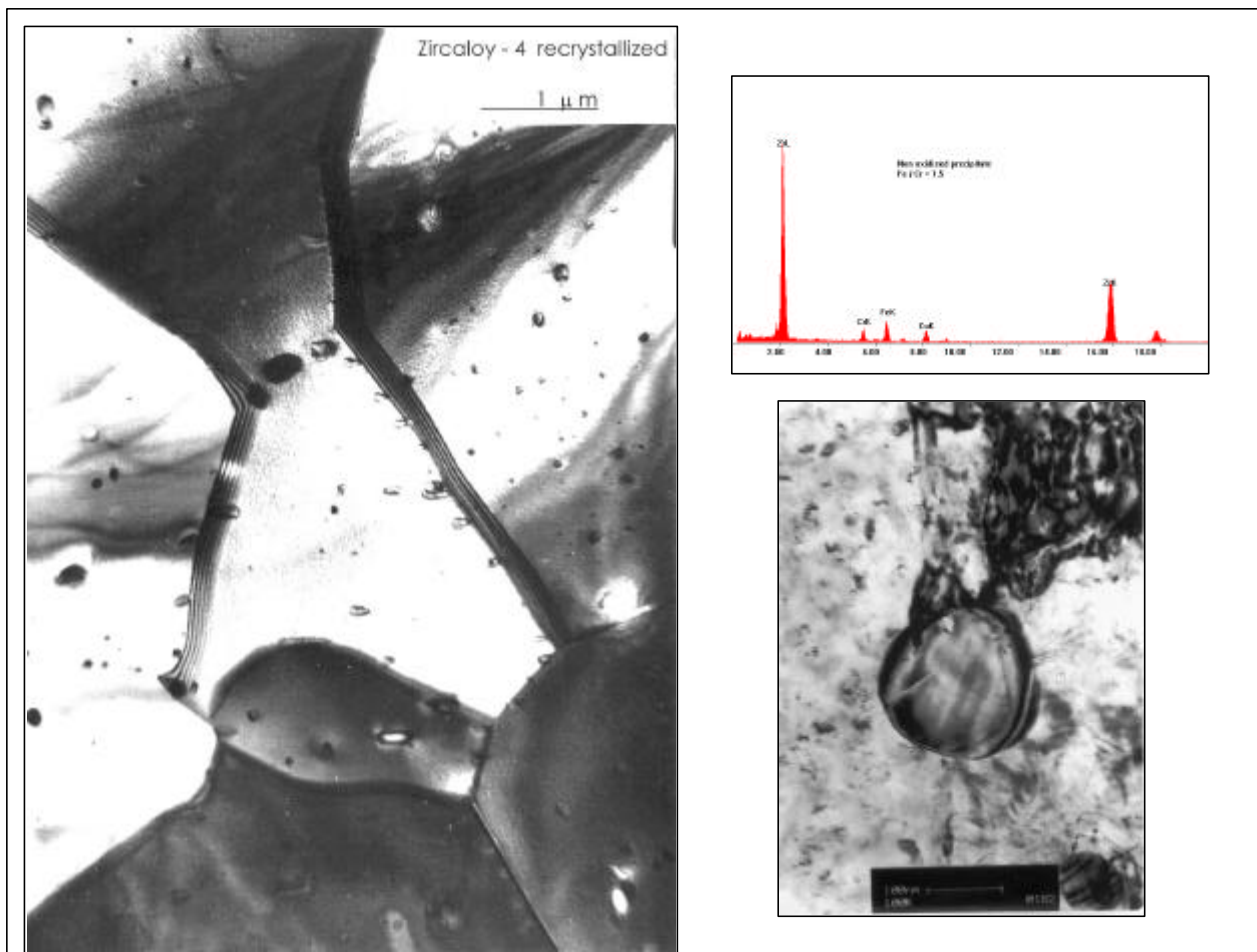


Figure 1 : BF- TEM image of non- oxidized Zry-4. The EDS spectrum corresponds to a precipitate with a Fe / Cr atomic ratio  $\cong$  1.5.

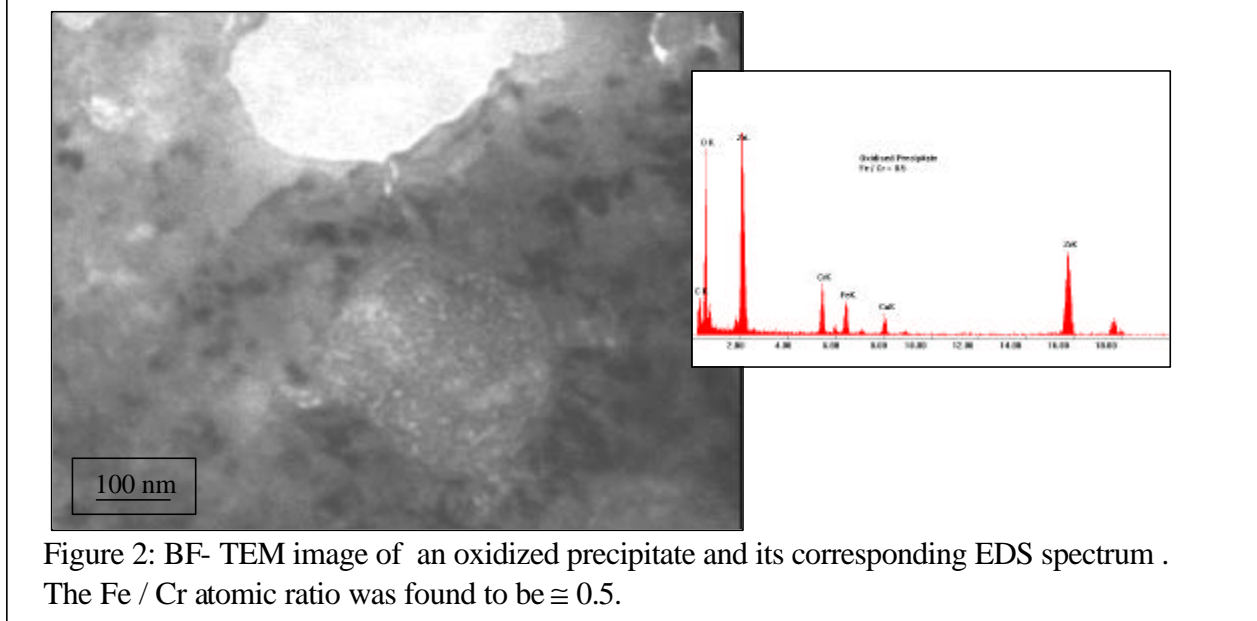


Figure 2: BF- TEM image of an oxidized precipitate and its corresponding EDS spectrum . The Fe / Cr atomic ratio was found to be  $\cong$  0.5.