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| ESRF | **Experiment title:**<br>Characterisation of oxides formed on zirconium alloys | **Experiment number:**<br>**MA- 971** |
| **Beamline:**<br>ID13 | **Date of experiment:**<br>from: 25 June 2010 to: 27 June 2010 | **Date of report:**<br>28 February 2011 |
| **Shifts:**<br>6 | **Local contact(s):**<br>Michael Reynolds | *Received at ESRF:* |


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## Report:

The aim of the experiment was to establish for the first time the variations in monoclinic/tetragonal phase distribution in the oxides of zirconium alloys as they go through a transition of their oxidation kinetics. To achieve this, cross-sectional samples were prepared from each alloy at key stages in the oxidation process. By carefully monitoring the weight gain of specimen during autoclave testing we were able to produce samples from the pre-transition and post-transition regimes as well as directly at the time where transition was taking place.

The highly focused beam available, allowed detailed grids of measurement positions on the cross-sectional samples. The diffraction patterns obtained were then analyzed to provide spatially resolved information about the relative phases present.

Due to the relatively low energy used during the experiment (~14 KeV), measurements were carried out in reflection geometry. This had the benefit of improving the depth resolution of the measurements, i.e. only material near to the sample surface contributed to the diffracting signal. However, this setup also had the downside of an elongated sampling volume, reducing resolution in the lateral direction.

The final footprint of the beam was approximately 300nm x 1500nm. Fig.1 shows an example of a map obtained for the tetragonal/monoclinic peak ratio as a function of position within the oxide. Some variation of tetragonal phase can be seen, which appears to correlate to the layered structure of the oxide.

It is interesting to note that the expected increase in tetragonal

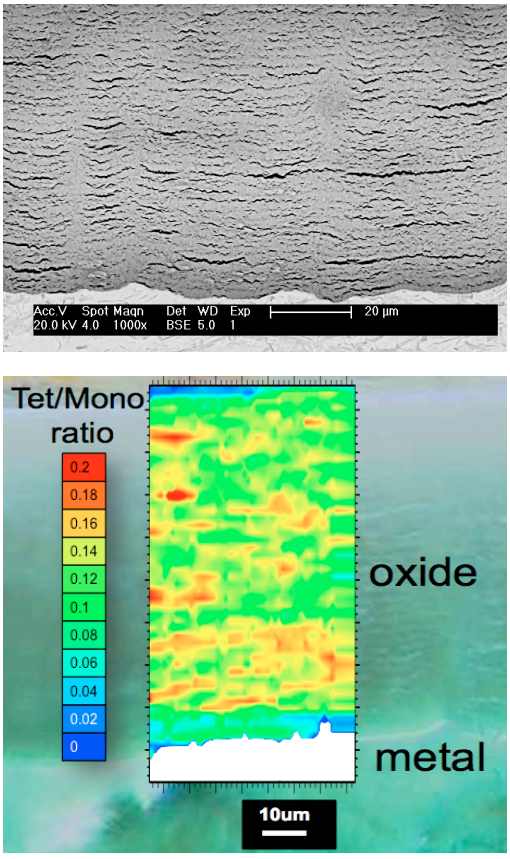


*Figure 1: SEM micro-graph of oxide layers formed on ZIRLO (top) and Map of tetragonal/monoclinic peak ratio measured on oxide cross-section at ID13*

phase near the metal/oxide interface was not observed during this experiment. Previous work has suggested that near the interface, large compressive stresses are present in the oxide, which are thought to stabilize the tetragonal phase. Indeed, when the same samples used for this experiment were investigated using through thickness measurements at higher energy (ID11, expt MA467- see Fig. 2) [1,2], this trend was observed. It is believed that the low penetration provided by the setup used at ID13, meant that the residual stress in the material sampled had been relieved and therefore any previously stabilized tetragonal oxide will have transformed to monoclinic oxide.

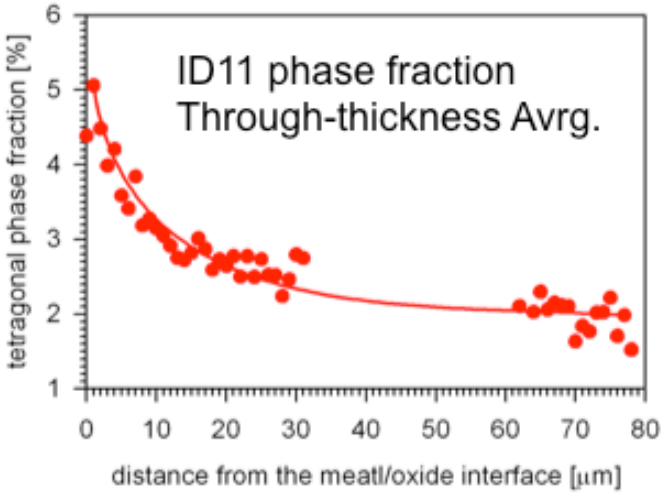


*Figure 2: Tetragonal phase fraction as measured on ID11 – MA467 in transmission (through thickness average of 1mm sample)*

If this is indeed the case, it may have important ramifications for many other investigations into the oxides formed on zirconium alloys, as many techniques require samples to be sectioned before analysis. In particular, this may explain why despite x-ray diffraction measurements reporting significant tetragonal phase fractions on bulk samples, it has often been difficult to identify similar proportions of tetragonal grains using TEM analysis [3].

Unfortunately, due to the lack of tetragonal phase near the metal/oxide interface in all the samples analyzed, it was not possible to correlate the distribution of tetragonal phase with respect to oxidation time. Thicker, multilayered oxides showed some variation in tetragonal content, which appeared to be related to the periodicity within the oxide.

The finding that tetragonal phase fraction may be affected by the sectioning of samples, may be very important in assessing future investigations into the oxidation mechanism of zirconium alloys.

It is hoped that further work will allow measurements to be carried out with similarly high resolution to the current ID13 experiment, but at higher energy, which would allow through thickness measurements. In this way the original stress state of the oxide will be preserved and the evolution of tetragonal phase fraction can be investigated.


[1] M. Preuss, P. Frankel, S. Lozano-Perez, D. Hudson, E. Polatidis, N. Ni, J. Wei, C. English, S. Storer, K.B. Chong, M. Fitzpatrick, F. Wang, J. Smith, C. Grosvenor, J. Sykes, A. Cerezo, B. Cottis, S. Lyon, L. Hallstadius, B. Comstock, in:, 16th International Symposium On Zirconium In the Nuclear Industry, 2010.

[2] P. Frankel, R. Moat, E. Polatidis, M. Preuss, B. Comstock, A. Ambard, Journal Of Nuclear Materials SUBMITTED (2011).

[3] N. Ni, Thesis: TEM Characterization Of ZrO2 Microstructure, Oxford University, 2011.