	Experiment title: Characterisation of matrix chemistry and precipitation distribution in zirconium alloys	**Experiment number**: MA-325
Beamline: ID31	**Date of experiment**: from: 2007-02-26 to: 2007-03-02	**Date of report**: 2007-08-28
Shifts: 9	**Local contact(s)**: Alexander Evans	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Alexander Evans*, ESRF

Ms Maria Ivermark*, University of Manchester

Dr Michael Preuss, University of Manchester

Dr Joseph Robson, University of Manchester

Report:

1. Aim of study

The initial aim was to measure the lattice parameters of zirconium alloys (containing Cr, Cu, Fe, Nb, Si and/or Sn) at room temperature (ex-situ) thus detecting very small changes in the hcp-matrix due to variation in composition. The main aim was then to study the matrix compositional change during heat treatment of specific alloys (in-situ) by the study of lattice parameter changes over time.

2. Experimental

Solid cylinders of zirconium alloys (approximate dimension of 0.7 mm in diameter and 2 mm in length) were mounted in quartz capillaries. The specimens subjected to ageing were sealed in argon atmosphere to avoid oxidation during the heat treatment, whereas the samples measured at ambient temperature were mounted in air. The specimens were then loaded onto the spinner using the automated robot. The optimized beam energy for this type of sample and dimension was calculated to be 40 keV and the diffracted beam in transmission was detected where the most prominent 10 peaks of the zirconium matrix were recorded.

During the ex-situ experiment the eight working detectors each recorded a full diffraction pattern giving a scanned 2θ-range of -3° to 22° recorded over 11 minutes. During the in-situ experiments a hot air blower was placed in very close proximity to the specimen with the scanning starting immediately after. The eight detectors, 2° apart, recorded one diffraction pattern over the 2θ-range of 2-18.5° with a small pattern overlap. The increased scan rate (75s/scan) facilitated the continuous detection of small changes in the lattice parameter due to heat treatment. Each heat treatment experiment was recorded during two hours to capture the initial change in lattice parameters during ageing of zirconium alloys. Between each measurement a silicon standard was used to monitor the temperature. A calibration curve of the lattice parameter change due to thermal expansion was also recorded.

3. Results

Each diffraction pattern was fitted using a Rietveld routine (TOPAS) to determine the stress-free lattice parameters along the a- and c-axis in the zirconium matrix. Each lattice parameter was determined from the first 10 diffraction peaks in the α-Zr diffraction pattern.

3.1 Ex-situ measurements

The small variations in alloy element concentration were possible to detect, especially important was the Zr-Si system with ppm-concentrations of Si. This change has not been possible to detect using conventional XRD.

3.2 In-situ measurements

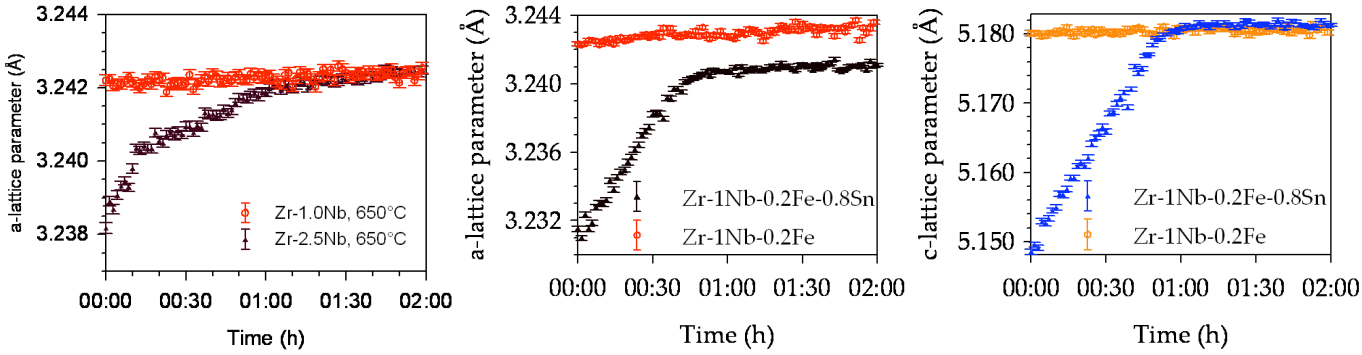

Fig 1a. Niobium binary alloys heat treated at 650 ℃. 1b-c. Aged ternary and quaternary alloys.

In figure 1 the lattice parameter evolutions during heat treatment are shown. This type of in-situ characterization of the Zr-matrix has never been performed before. There is a significant change in lattice parameter for the 2.5wt%-Nb compared to the 1.0wt%-Nb alloy. This is an effect of precipitation or formation of a second phase (SPP). Both diffraction patterns showed a new peak due to formation of β-Zr. It is commonly known that this phase usually contains dissolved niobium. To confirm this, a microscopy study is needed, or a thoroughly recorded diffraction pattern at the end of the ageing experiment. The precipitation kinetics of the SPPs can be determined from the in-situ study. This data is currently being used to test a novel model that has been developed to predict precipitation in zirconium alloys.

Two types of higher order niobium containing alloys were evaluated during heat treatment (fig 1b-c). The ternary alloy shows a lattice parameter evolution similar to the binary niobium alloy with the same niobium concentration. However, the quaternary alloy containing tin shows a remarkable increase in lattice parameters over time, due to a reduction in concentrations of alloying elements in the Zr-matrix. The diffraction pattern did not show an extra peak consistent with β-phase formation, which suggests that the change in matrix chemistry is due to the formation of a different precipitate phase, currently being investigated using electron microscopy. The successful in-situ experiments gave insight into how a single alloying element, as well as a combination of alloying elements, affects the evolution of Zr-matrix composition and precipitation kinetics of SPPs.

4. Future work

It is important to measure multiple specimens of the same alloy concentration in ex-situ to receive better statistics. Alloys of the same element concentration and with the same or very similar lattice parameters can then be chosen for the in-situ experiment. The scatter due to variation in starting lattice parameter can thus be limited.

The initial MA325 experiment proved successful to study the lattice parameter evolution during ageing of dilute zirconium alloys. The beam line set-up was ideal for this type of matrix characterization study. Fortunately, there are many more zirconium alloys interesting to study under similar conditions. It is important to compare more concentrations in order to investigate the solubility limit of Nb in α-Zr at specific temperatures, the influence of additional element to the Zr-Nb matrix and the change in lattice parameter and more.

For future synchrotron work it will also be interesting to scan slowly and thoroughly to record a diffraction pattern at the end of the heat treatment experiment in order to identify and fully characterise the precipitate phases formed during ageing. This was not done during the MA325 experiment.