

## TEM analysis of the microstructure of precipitates in binary zirconium alloys after in situ oxidation

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A series of binary Zr alloys has been studied to improve the understanding of the role of precipitates in the oxidation of zirconium alloys and the behaviour of different alloying elements during oxidation. The alloys contain 1 wt.% of the transition elements: Fe, Cr or Ni. Due to the low solubility of these elements in Zr, the entire alloying element is found in form of secondary phase precipitates (SPP) in the Zr matrix. The binary alloys were oxidized in situ in an environmental scanning electron microscope (ESEM) at 415°C in 1.3 mbar water vapour pressure. The outer surfaces of the alloys were monitored in situ and ex situ by means of atomic force microscopy (AFM), focused ion beam (FIB) and energy dispersive X-ray spectroscopy (EDS) [1]. The oxidation rates of all alloys were similar and the oxide layers were in the range of 400 nm. This study reports on the microstructure and composition of the SPPs at the metal-oxide interface and in the oxide, using transmission electron microscopy (TEM), to complete the characterisation of the oxide layers formed on each alloy.

The TEM cross-sections of the metal-oxide interface were prepared by FIB, using electron and ion assisted platinum deposition for the surface protection.

The investigation of the samples with TEM revealed different oxidation behaviours of the different alloys. For Zr1%Fe, SPPs located at the metal-oxide interface were found to be preferentially oxidized compared to the zirconium matrix (Figure 1a). The increased oxide thickness at the SPP position confirmed the accelerated oxidation of Fe containing SPPs. The structure of the oxidized SPP was examined both with electron diffraction and EDS analysis. The oxidized SPPs showed fine-grained, equiaxed and textured oxide and the neighbouring oxide of pure zirconia revealed a columnar structure (Figure 1a). Serial sections of the oxide realised by FIB confirmed that Fe containing SPPs show a preferential oxidation.

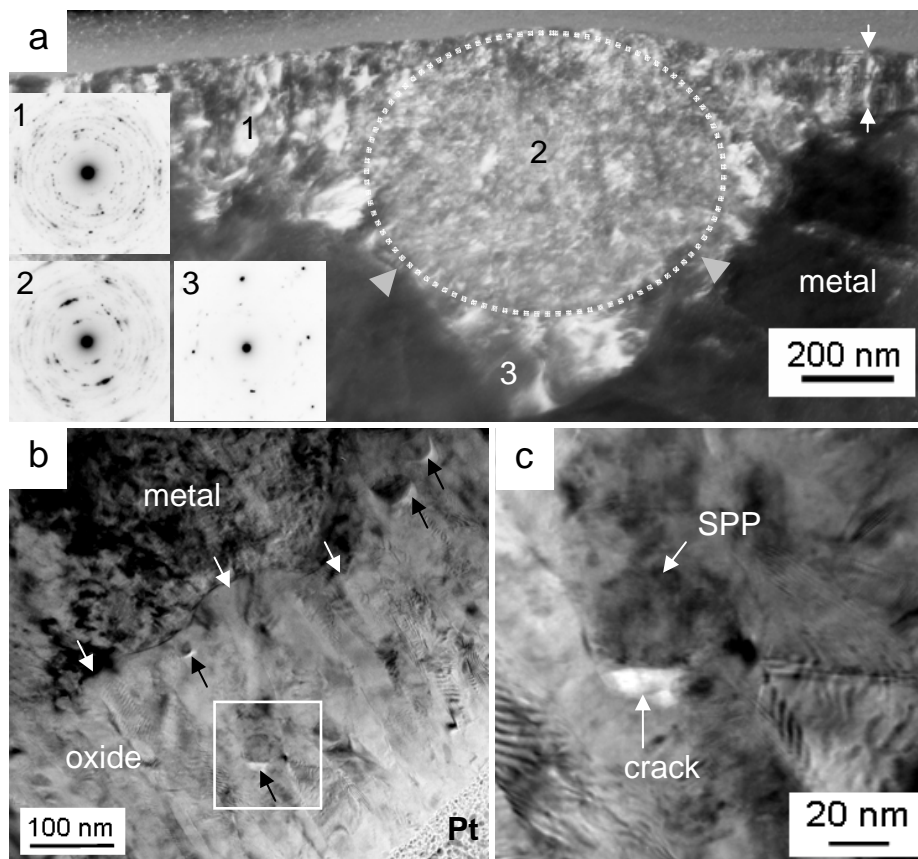
For Zr1%Ni no accelerated oxidation for the Ni containing SPPs has been found. The studied SPPs were oxidized at the same rate as the neighbouring pure oxide (not shown here), and the metal-oxide interface is not undulated as in the case of Zr1%Fe. This was also confirmed by observations of SPPs in FIB sections. The microstructure of the oxidized matrix was similar to that of Zr1%Fe.

In Zr1%Cr the SPPs are approximately one order of magnitude smaller than in the two other alloys and the oxygen content measured for SPPs in the oxide was generally low and no oxide crystals as in the case of the other two alloys could be seen in their structure (Figure 1b & 1c). Again the neighbouring pure zirconia consists of columnar grains comparable to the other alloys.

These observations reveal a difference in oxidation for the SPP from different alloying elements with respect to the zirconium matrix. The observed oxidation tendency is:  $Zr_3Fe > Zr_2Ni \approx Zr \text{ matrix} > ZrCr_2$ . The results for  $Zr_3Fe$  are in agreement with earlier findings by previous authors [2], however for  $Zr_2Ni$  a slower oxidation of SPP with respect to the matrix has been reported [3], while we observed a similar oxidation rate.

A comparison of present in situ studies with the oxidation of the same materials in autoclave in oxygen and steam is planned for the future, to study the influence of the environment on the behaviour of the alloying elements. Results of previous authors [2,3] indicate, that this tendency could at least be valid for oxidation in oxygen. Observations of metallic SPP containing the transition elements Cr, Fe and Ni in the oxide have been so far not reported for binary alloys, however in ternary and higher alloys of Zr they have been reported [4].

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**Figure 1.** TEM micrographs of SPPs at the metal-oxide interface in different binary alloys. (a) Dark Field contrast of Zr1%Fe, the oxidized SPP with fine equiaxed structure is marked. The neighbouring pure oxide shows a columnar structure (white arrows). Diffraction patterns of the oxidized SPP (2), the matrix oxide (1) and the metallic part of the SPP (3) are shown. (b) In Zr1%Cr the SPPs in the oxide often exhibit cracks (black arrows) on the side facing the outer surface and low oxygen content. The metal-oxide interface (white arrows) can be seen, the oxide layer is thin, the grain structure of the oxide is columnar and the outer surface is shown. (c) Region marked in (b) with unoxidized SPP in the oxide.