

Using small x-ray beams to understand corrosion in nuclear fuel cladding

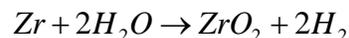
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Abstract: Uniform oxidation by the primary circuit water and associated may soon limit the service of Zr alloy fuel cladding in Light Water reactors. Understanding the differences in corrosion rate between alloys based on the microstructure of the protective oxide may allow us to design better alloying materials for severe duty cycle applications. The use of synchrotron radiation microbeam at APS allows the study of these oxide layers with an unique combination of the wealth of diffraction and fluorescence information and the level of spatial resolution obtained. We will discuss some of our experimental results and the potentials of these techniques in solving engineering problems.

Introduction

Pressurized Water Reactors (PWR) are the most common type of commercial nuclear power plants in the world. In this type of reactor, the reactor core is pressurized to 15 MPa so that in most cases there is no boiling in the coolant. The nuclear fuel is constituted of ceramic pellets of uranium dioxide (UO₂) encased in long thin tubes (called *fuel cladding*) made of zirconium alloys. These filled tubes, called *fuel rods*, are inserted into a *fuel assembly* (shown in Figure 1) and several tens of these fuel assemblies constitute the reactor core. These fuel assemblies are immersed in water that serves as coolant to remove the heat from the core and produce power. The fuel cladding has the functions of separating the fuel from the cooling water, helping maintain a coolable geometry and keeping the radioactive materials resulting from fission and absorption reactions contained. Thus in order to ensure that reactors operate safely and economically the integrity of the fuel cladding must be ensured.

To maximize thermal efficiency, the cooling water is kept at a high temperature, (inlet coolant temperature is 290-300 °C and outlet coolant temperature is 350-360 °C) thus requiring pressurization to keep it in the liquid state. The high temperature cooling water in which the fuel assemblies are immersed, promotes uniform corrosion on the outer diameter of the cladding. This corrosion can be expressed by the chemical reaction:



The hydrogen formed in this reaction can be picked up by the cladding material which leads to the formation of brittle hydrides inside the material and this can lead to a degradation of the cladding mechanical properties, thus potentially compromising the integrity of the cladding tube. Because of this, much work has been done over the last forty years to optimize the microstructure and fabrication procedures of Zr alloys so that corrosion of the zirconium alloy cladding tubing in nuclear reactors is minimized. However, this optimization work, although detailed and extensive, is based on empirical methods, and a mechanistic understanding of the influence of the role of the various alloying elements and microstructures is still lacking.

Over the last twenty years the U.S. nuclear industry has significantly increased capacity factors (the percent of power actually produced in a year to that which would be produced if the power plant operated every day at full power). This has been done by increasing the time between outages, decreasing fuel failures and increasing the overall residence time (and thus the overall energy produced, or burnup) of the fuel in the reactor. The increase in burnup necessitates changes in coolant chemistry that can accelerate the corrosion process.

Further increases in capacity factors can be obtained by power uprates, which can involve increases in the coolant outlet temperatures and can cause boiling in the coolant nearby the upper reaches of the fuel assembly, and further increases in burnup. Overall, these changes to extreme duty conditions represent a severe challenge to the current alloys used in fuel cladding, even while the performance requirements for these alloys are constantly being increased. Thus, a technical basis needs to be developed to achieve *significant* improvements in the corrosion behavior of current dilute alloys used in LWRs.

The first step in improving corrosion resistance is a clear understanding of the mechanisms of corrosion. One remarkable fact is that when autoclave tested in a given environment, different alloys can exhibit different pre-transition oxidation rates, different oxide transition times, and different post-transition corrosion rates. This is true in spite of the fact that these alloys are all 97%-plus Zr and vary only in the compositional changes within the remaining three percent. This is illustrated in Figure 2, which shows the weight gain plotted against exposure time for corrosion in an autoclave performed in pure water for three different alloys. It is seen that the weight gain associated with ingress of oxygen into the alloy and therefore used as a measure of corrosion, follows saturating kinetics as a protective oxide is formed that slows down the further ingress of the oxidizing species to the metal. At different exposure times the alloys undergo a change of kinetics to a more accelerated corrosion rate. This change is dubbed the *oxide transition*, and it is seen that the various alloys undergo the transition at different times.

The hypothesis in this work is that the differences in corrosion behavior stem from difference in the microstructure of the protective oxide. Thus, if we can characterize the microstructure of the oxide in detail, we might be able to understand the mechanisms for corrosion enhancement or decrease. Most of the oxide microstructure characterization performed previously was based mainly on transmission electron microscopy and on frontal x-ray diffraction. Because frontal x-ray diffraction averages the signal over the

whole oxide thickness, it cannot provide enough detail to allow a detailed understanding of the oxide growth mechanisms.

In this work, the structure of the oxide as a function of distance from the oxide-metal interface was studied micro-beam synchrotron radiation. These studies were performed on oxides formed on three Zr alloys that were autoclaved in pure and lithiated water in order to identify differences between oxides formed on different alloys. The ultimate objective of this project is to relate the observed differences in corrosion behavior (e.g., time to transition, post-transition corrosion rate) to the differences in oxide microstructure and in turn to relate these to the differences in alloy microstructure. The work reported here is a step in that direction.

Experimental Methods and Results

Zone plate technology is used in the 2IDD beamline to produce a micro beam that has dimensions of 0.25 x 0.35 microns. This allows to obtain all information that one can normally obtain from an x-ray beam with a spatial resolution comparable to these dimensions. We have obtained both x-ray fluorescence and x-ray diffraction information from the oxides formed on our cladding alloys. The x-ray fluorescence information has allowed us to study the distribution of alloying elements in the metal and within the oxide layer with very high degree of precision especially for the transition elements [1]. In this work, we have used fluorescence mostly to locate the beam within the oxide and allow a good positioning of the beam for the diffraction information [2].

Figure 3 shows the geometry of our experiment. The oxide is examined in cross section, and the diffraction data is recorded on a ccd camera while the fluorescence information is *simultaneously* acquired with a solid state x-ray detector. The result of a Zr L fluorescence scan is shown in the top of the figure, and it is clear that the oxide, the metal and the epoxy can be clearly distinguished using this technique. As shown in figure 4 the diffracted intensity recorded in the ccd camera is integrated in the azimuthal direction and a plot of diffracted intensity versus two-theta is obtained from where the information normally obtainable from x-ray diffraction can be extracted. This includes phases present, lattice parameters, phase fractions, grain size, texture (preferred orientation).

Figure 5 is a plot of such intensity versus two theta variations, for a series of locations, starting in the metal, travelling through the oxide and to the mounting epoxy. The pattern was obtained for an oxide formed in the alloy ZIRLO, which is one of the alloys most extensively used today in the world for nuclear fuel cladding. In the metal side of the plot, clearly seen are the alpha-zirconium peaks, along with zirconium hydrides near the oxide metal interface. When the metal side of the oxide metal interface is examined in more detail, peaks belonging to a suboxide phase Zr₃O were for the first time identified in our diffraction patterns. As the oxide metal interface is transversed, peaks belonging to the monoclinic ZrO₂ phase become quite evident, and are thus identified in the plot. The overall monoclinic orientation has a [200] plane parallel to the oxide-metal interface, but there are periodic oscillations clearly visible in several of the peaks. In addition near the oxide-metal interface there is a different structure than in the middle of the oxide layer. In

particular a highly oriented tetragonal phase appears to be present that is a precursor of the main monoclinic phase.

The oscillations in the peaks mentioned above match very well with the oscillations in corrosion weight gain shown in Figure 2, indicating the oxide reorientation is related to the corrosion process. Figure 6 plots the integrated intensities for the 020 monoclinic peaks and the 101 tetragonal peaks where the regular oscillations are clearly marked but also seen be out of phase with each other. Investigating further the reason for the oscillations, we can see that it is the variations in texture (from more random at oxide transition to highly oriented in the middle of the oxide) that account for the variation in intensity. These can be detected in our ccd recordings by the more evenly spread or more tightly angular concentrated intensity in the corresponding peaks.

Discussion and Conclusion

In this work the first spatially resolved observations of the crystal structure of oxides formed on Zr alloys, performed non-destructively, i.e. in oxides still attached to the base metal, are reported. In contrast, TEM studies, although extremely useful for studying oxide morphology, structure and the phases present (in a qualitative manner), cannot give a quantitative measure of the tetragonal fraction because the thinning process required to make a TEM foil relieves some of the stresses that help stabilize the oxide. Other techniques, such as bulk x-ray diffraction and Raman spectroscopy, examine the oxide as a whole, although some depth resolution can be achieved with glancing angle x-ray diffraction.

The objective of the study was to discern structural differences in the oxide that correlate with the oxide transition. A layered structure was evident in diffraction optical microscopy in all the alloys studied, especially in transmitted light. The layers were extremely regular (constant period) and extended over the whole oxide thickness. The regularity of the layered structures indicates that corrosion process is the same from the beginning to the end of the corrosion test. Comparing the layer periodicity from alloy to alloy, the average spacing between layers was inversely proportional to the post-transition corrosion rate, indicating a clear benefit to delaying the oxide transition.

The overall characterization performed allowed us to propose a growth mechanism for the oxide. We note that it is only the spatial resolution of the microbeam synchrotron radiation beam line that allow us to distinguish the fine detail at the oxide metal interface (normally invisible to conventional techniques) that give us insight as to the oxide growth mechanism.

If the above oxide-growth mechanism is tested and verified, and shown to be prevalent in the different oxides, it can serve as a template to compare and understand mechanistically the differences in corrosion behavior of different alloys. Different alloys could have different columnar grain sizes, for example, or different rates of oxide re-nucleation, etc. potentially resulting in different rates within the above mechanism.

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Acknowledgments

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Figures

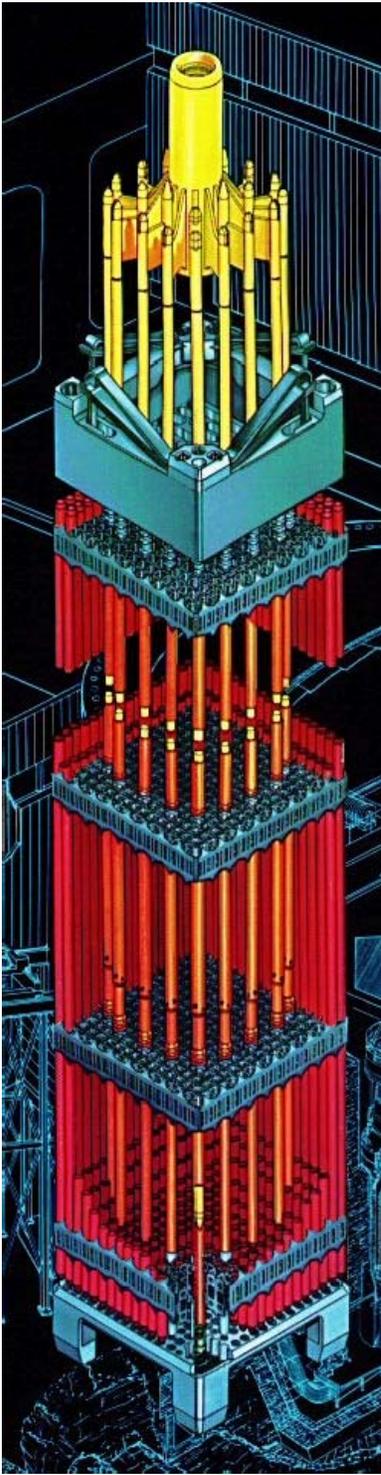


FIGURE 1: A nuclear fuel assembly used in a pressurized water reactor

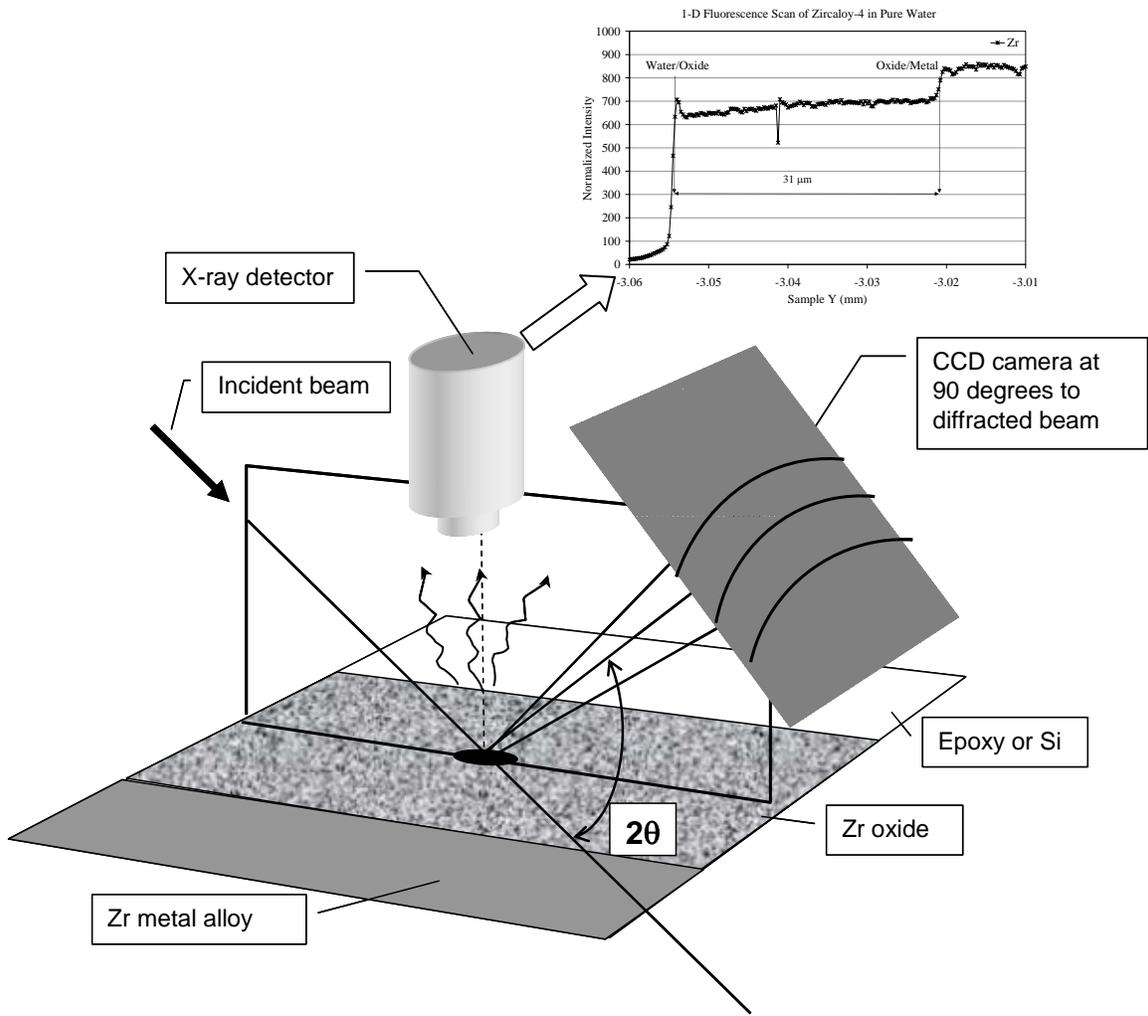


Figure 2: Schematic drawing showing the geometry of data acquisition at the synchrotron beamline.

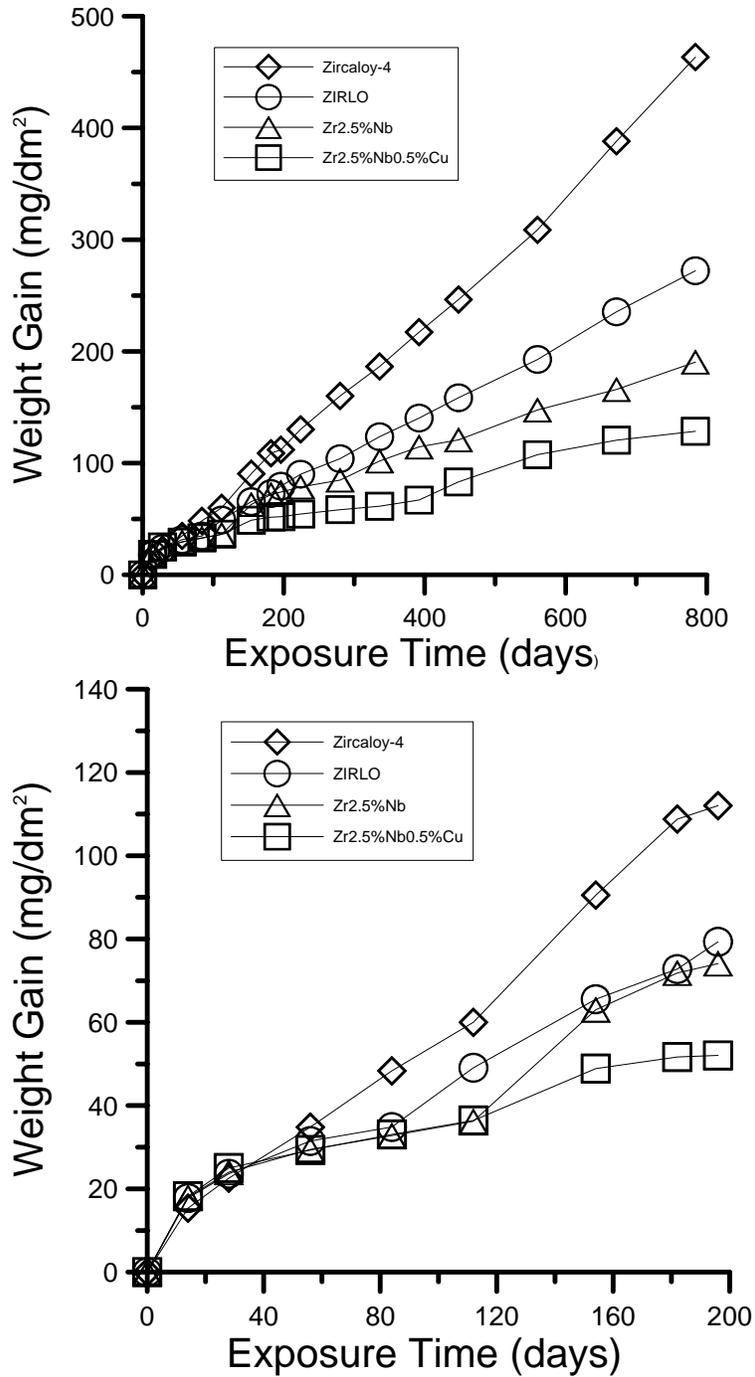


Fig.3: Weight gain in mg/dm^2 versus exposure time for the corrosion of Zircaloy-4, ZIRLO, Zr-2.5%Nb, and Zr-2.5%Nb-0.5%Cu in pure water at 360 C. (a) showing 800 days, and (b) showing initial 200 days.

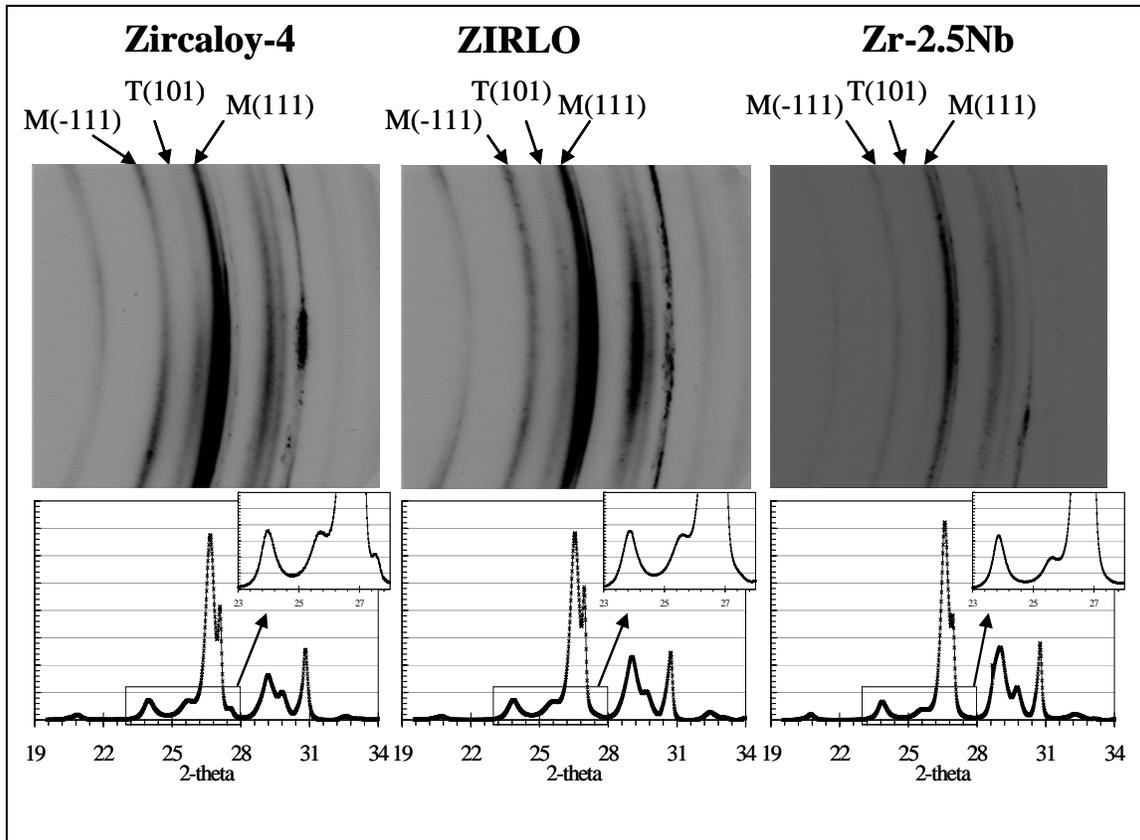


FIGURE 4: Diffraction patterns obtained with synchrotron radiation at three different oxides at a constant location (0.5 micron from the oxide metal interface) (a) Zircaloy-4, (b) ZIRLO, (c) Zr-2.5%Nb.

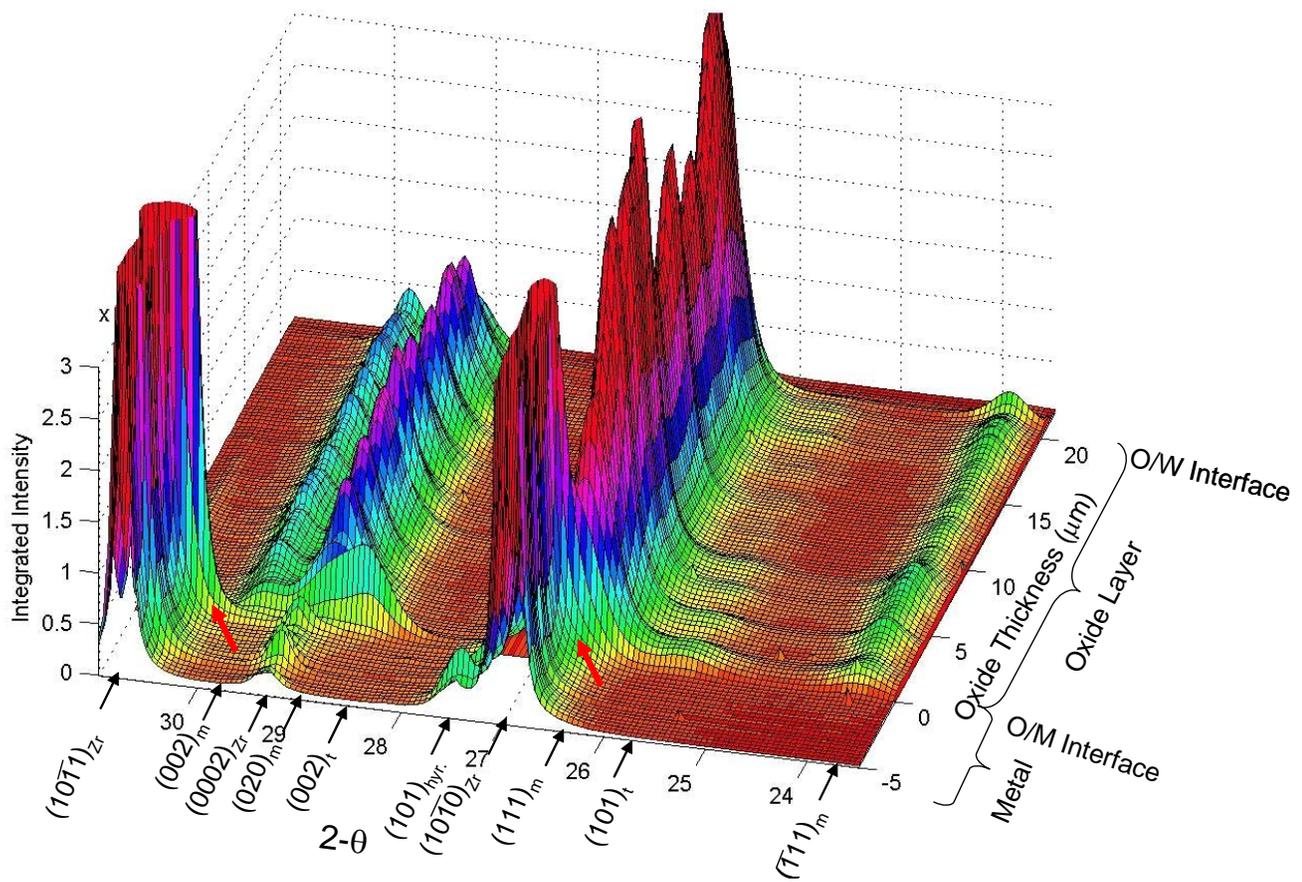


FIGURE 5: X-ray diffraction scans showing the phases that are present in oxide, from oxide-metal interface to oxide-water interface of ZIRLO oxide layer formed in 360 °C pure water environment.

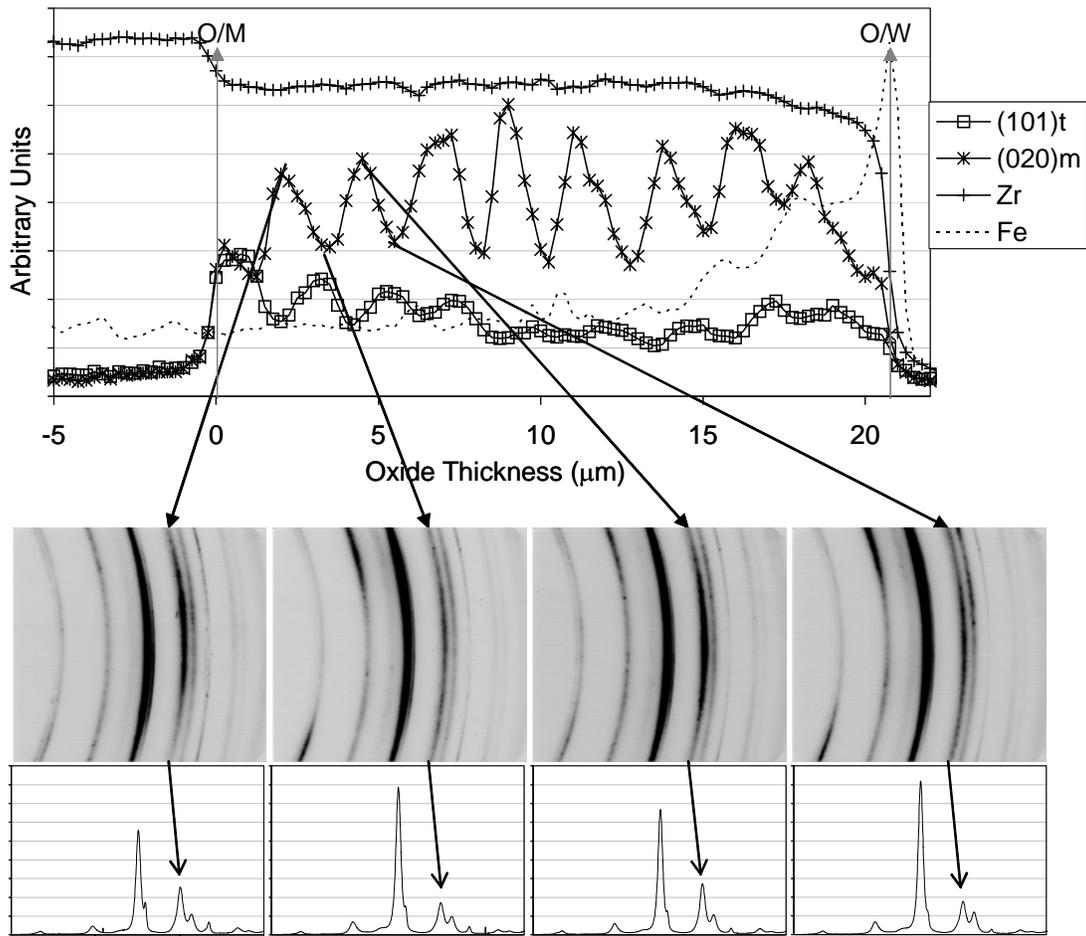


FIGURE 6: Variation of $(020)_m$ peaks with distance from oxide-metal interface in oxide layer formed on ZIRLO in 360 °C pure water environment.

References

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