Characterization of luminescence and electron transport in corroded zirconium alloys

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Abstract: Nitrogen vacancy centers in diamond are used to image electron pathways in corroded zirconium alloys, with preliminary data showing unexpected luminescence from the oxidized zirconium. Our ongoing work includes identifying the origin of this luminescence.

1. Introduction

The environment within Pressurized Water Reactors (PWRs) include temperatures that exceed 300 Celsius, pressures at roughly 150 bar, high neutron flux, and constant high-temperature water exposure. All of these contribute to an extreme oxidizing environment that severely degrades materials that are critical for reactor safety, such as the zirconium alloy cladding that surrounds the nuclear fuel pellets. Understanding the corrosion behavior, such as the charged species transport through the zirconium oxide layer, is vital to developing mitigation strategies that can avoid the onset of corrosion. Research on the charged species transport through the corroded oxide layer has thus far been limited to analyzing the ion transport (proton, oxygen anions, etc…) that result from the corrosion process [1], due to limited capabilities in characterizing electron transport at submicron length-scales. Meanwhile, recent developments in atomic-scale defects in wide-bandgap semiconductors, such as the nitrogen-vacancy (NV) center in diamond, have enabled sensitive vector magnetometry with high spatial resolution, thus making it possible to image submicron electron pathways in conductive materials [2] [3]. In this presentation, we will describe our efforts to apply vector magnetometry with NV centers in diamond to characterize the electron transport in the corroded oxide layer in zirconium alloys and correlate transport characteristics with the structural properties of the oxide (Fig. 1a). We will also discuss our analyses of the luminescent features of corroded zirconium alloy samples through confocal fluorescence microscopy and cathodoluminescence, which provide potentially promising approaches towards understanding the impact of corrosion on the electronic structure of the metal alloy. Our experimental configuration is illustrated in Fig. 1b, which shows corroded metal-oxide samples placed on top of arrays of near-surface NV centers which are used to map magnetic fields and thereby current flow (via calculation using the Biot-Savart law) across the oxide layer. This approach will allow us to correlate spatial distribution of currents with structural properties as characterized by transmission electron microscopy (TEM).

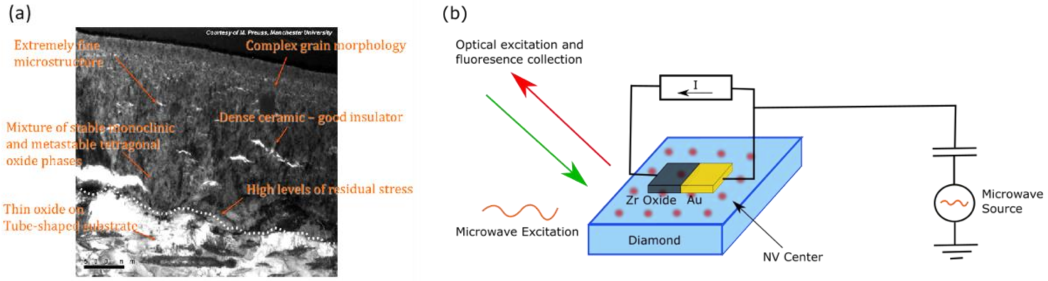

Figure 1: (a) Bright field TEM image of the thermally grown zirconium oxide obtained after corrosion of zirconium in 360 deg C high temperature at 18 MPa for 30 days. The labels indicate some of the nanoscale features of this highly defective, protective, oxide. (b) Schematic of our electron transport measurement, in which cross sections of corroded metal-oxide samples are placed on top of arrays of near-surface NV centers in diamond. Voltage is applied to induce current flow across the oxide region.

2. Experimental Method and Results

To form relatively thick oxide layers that are easily observable by optical and scanning electron microscopy, we expose samples of zirconium alloys (Zircaloy-4) to water steam at 1200 Celsius. A 500-second exposure in this environment typically results in an oxide layer of around 70 µm. Cross-sections of the oxide/metal interface and oxide layer (Fig. 2a) are then mounted and mirror polished for electron and optical microscopies. A homebuilt confocal fluorescence microscope with 532 nm excitation is used to identify NV centers and measure optically detected magnetic resonance from which we can infer the vector magnetic fields form the zirconium oxide sample (Fig. 1b). While it was expected that the wide bandgap of zirconium oxide would result in low levels of fluorescence under 532-nm excitation, our initial optical characterization of the sample revealed a broad fluorescence, shown in Fig. 2b, with intensities that are comparable to those of NV centers. This overlap in the photoluminescence will lead to poor signal contrast in our magnetometry measurements and so we are investigating the origin of the oxide fluorescence as well as implementing approaches that can mitigate its effect, including spectral filtering and time-gated fluorescence detection. It should be noted that while luminescence in doped zirconium oxides has been well-documented [4] [5] [6], its origin is still an area of active research. A study involving an ab-initio quantum chemical calculation points to the existence of oxygen vacancies in zirconium oxide as being responsible for the blue luminescence [7]. We also measured low or negligible photoluminescence from uncorroded zirconium as well as bulk yttria stabilized zirconium oxide samples, which indicate that the structured fluorescence in the corroded zirconium sample likely arises from the oxidation process. We performed cathodoluminescence in a scanning electron microscope (SEM-CL) on the corroded zirconium samples to further characterize luminescence features across the visible spectrum under electron excitation. SEM-CL facilities correlation of luminescence with structural features under the electron microscope. Our preliminary results (Figure 2c) show that the corroded layer exhibited the most luminescence with a blueish color. The alpha and beta phases of the Zirconium were relatively dark when compared to the corroded layer, which is consistent with our confocal photoluminescence findings.

3. Conclusions and future work

In summary, we have proposed an approach to map submicron electron transport in oxidized metal alloys using quantum magnetometry, which would improve our understanding of material corrosion under extreme conditions. We have described some of our preliminary data which includes observations of luminescence in the oxide, suggesting the introduction of color centers during oxide formation. Efforts are underway to identify the origin of the luminescence as well as mitigate their impact on the electron transport measurements.

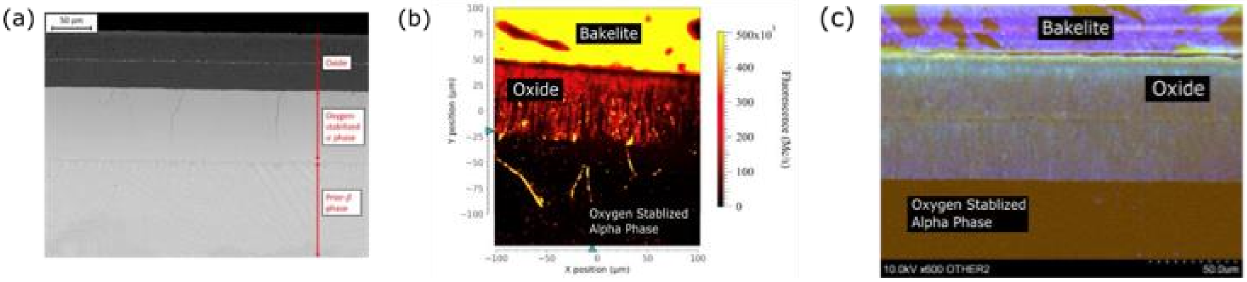

Figure 2: (a) SEM image of Zircalloy-4 sample. Shown is the oxide layer with the alpha phase, and the beta phase (b) Confocal image via 532 nm green light excitation (c) SEM-CL image produced by superimposing the SEM-CL image results from the red, blue, and green filter images

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