

FINAL REPORT

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Executive summary

The development of accident tolerant fuels (ATF) is aimed at avoiding the situation that occurred at Fukushima in 2011. In that station blackout condition, rapid oxidation of the Zircaloy cladding resulted in a highly exothermic zirconium-steam reaction. The rapid oxidation rate resulted in severe clad embrittlement and the production of hydrogen, which later combusted and caused damage to the secondary containment. To avoid such occurrences in LWRs, the ATF program was initiated to focus on the replacement of zirconium-based alloys with materials that exhibit slower steam oxidation kinetics.

A point of particular concern for these replacement materials is the likelihood of significantly higher general corrosion rates due to irradiation-accelerated corrosion in a reactor core. Such increases in corrosion rate may be tolerable for stainless steels or even for Zircaloy, but would be problematic for an alloy that exhibits borderline corrosion rates in the absence of irradiation. While the objective of the ATF program may be to identify fuel that is more tolerant in severe accident conditions, the fuel must first be able to function adequately under normal operating conditions.

This research plan has focused on several iron-chromium-aluminum (FeCrAl) alloys: APMT, MA956, and two experimental Fe-Cr experimental alloys. The aluminum content of these materials has been shown to impart very good resistance toward high temperature steam, by the creation of a surface layer of aluminum oxide. For comparison, we also studied T91 steel as a 9Cr alloy for which some data exists on the corrosion behavior in water in the range 300 - 600°C.

Experiments were conducted in both PWR primary water at 320°C and BWR normal water chemistry at 288°C, spanning a large range in electrochemical corrosion potential (ECP). Samples were exposed to either proton irradiation or electron irradiation to independently assess the roles of displacement damage vs water radiolysis on the corrosion rate, oxide thickness, morphology, structure and resistivity. The average dose rates in these experiments are very high relative to typical reactor conditions in order to quickly (and cheaply) assess whether the alloys might be too radiation-sensitive for reactor service.

Extensive post-test characterization has been performed to determine the oxide thickness, phases, phase morphologies and composition using a variety of techniques. In general, we find that under reducing (PWR hydrogenated water) conditions, the FeCrAl alloys are very stable, and there should be no problem with using them. In oxidizing conditions there is some tendency for the inner protective oxide to dissolve away. Such conditions may be found at the top-of-core in boiling water reactors, and engineers will need to carefully assess whether the alloys are acceptable in that situation. We find no particular effect we can ascribe to displacement damage in the proton irradiation experiments.

ACCOMPLISHMENTS

Summary: Objectives vs. Accomplishments

The original proposal was to irradiate five different steel samples with high energy protons at University of Michigan, and with high energy electrons at Notre Dame. The thin steel samples themselves are the vacuum interface between the accelerator beamline and water held at reactor conditions of high pressure and temperature. The plan was to irradiate all five samples at both PWR hydrogen water chemistry conditions (3ppm dissolved H₂ and 320°C), and with BWR normal water chemistry conditions (2ppm dissolved O₂ and 288°C). The samples were then to be dismantled, and the water-side oxide examined with microscopy both in the irradiated zone and areas upstream and downstream of the water flow. The upstream region provides an unirradiated reference, while the downstream side may be affected by water radiolysis products (e.g. hydrogen peroxide). The minimum number of samples is therefore 5 steels x 3 zones x 2 water conditions x 2 (electron vs. proton) particle beams. This program was carried out in full, with one modification. The Notre Dame electron beam high temperature water flow system is made of high-nickel Hastelloy steel alloy, and it was found that nickel oxide was coating the FeCrAl samples under 2ppm oxygen BWR conditions. To avoid this, the water condition was changed to saturation with inert Argon for these experiments at 288°C. In addition, because the protective inner oxides were found to be dissolving in irradiated zones and in the presence of oxygen, several thin samples of FeCrAl alloy were sputtered onto steel substrates and irradiated with either protons or electrons. The degree of dissolution under irradiation conditions could then be assessed directly using electron microscopy to look at the entire thin sample cross-section.

The following sections of the final report are intended to summarize the main points of our study. Detailed information was provided in Milestone reports, one for each of the alloys under investigation. The Milestone reports have been reviewed and corrected where necessary, and are included at the end of this Final report as Appendices.

Materials

Table 1. Chemical compositions of the alloys used in this study.

Alloys	Compositions wt%				
	Fe	Cr	Al	Mo	Y
T91	89.4	8.2	0.005	0.9	-
T54Y2	80.8	15.1	3.9	-	0.1
MA956	73.7	20.0	4.0	-	0.5
APMT	70.5	21.0	5.0	3.0	-
T35Y2	82.3	13.1	4.4	-	0.1

Experiment description

The experiments carried out in this study were a natural continuation of a previous study of 316 stainless and zircaloy, in which proton beam and electron beam irradiations are compared

to assess the importance of atomic displacement damage to the corrosion. The main problem to be overcome, is the limited penetration power of 5.4MeV protons available at University of Michigan. The limited penetration range requires a thin “rupture disk” geometry as shown in figures 1 and 2, with small diameter samples of only 100 microns thickness to allow all the protons to pass through into the water. The cell is made of 316 steel, and was passivated over a long period to minimize further corrosion. During experiments the water flow rate is quite low.

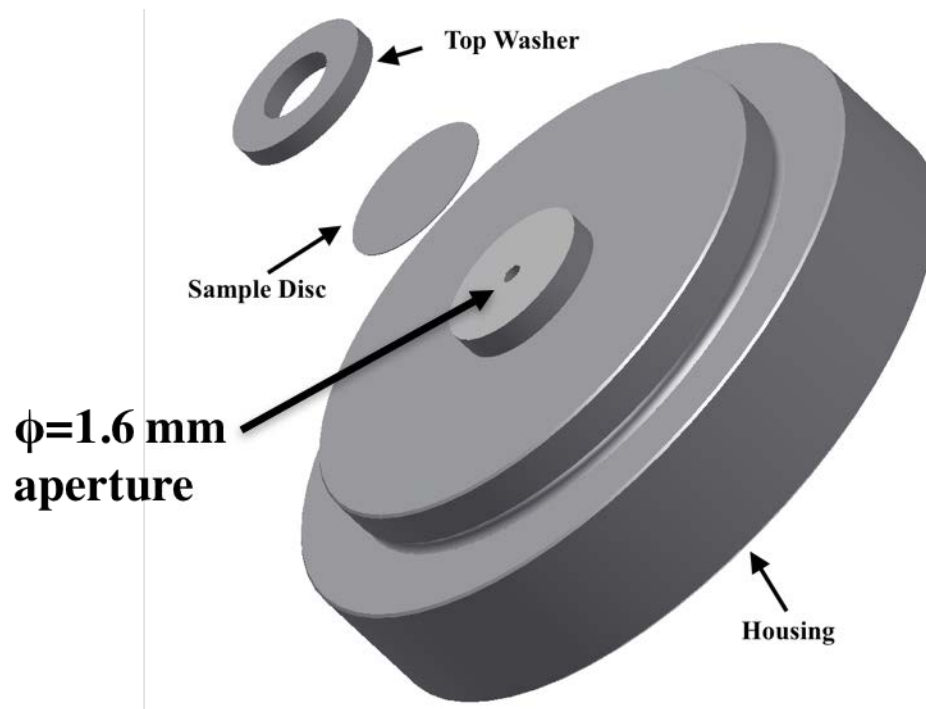


Figure 1. A schematic of the sample assembly for proton irradiations at U. Michigan.

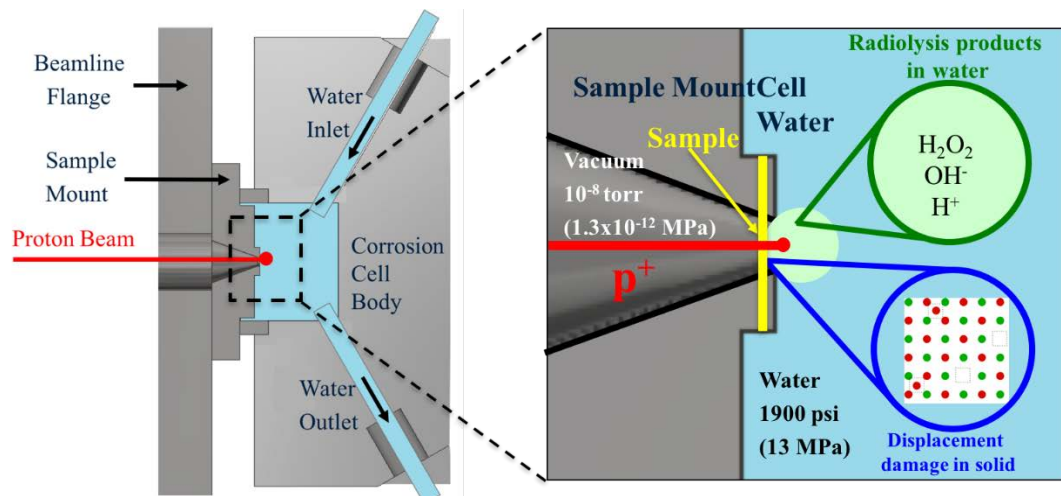


Figure 2. A schematic of the miniature corrosion cell for in-situ proton irradiation-corrosion experiment.

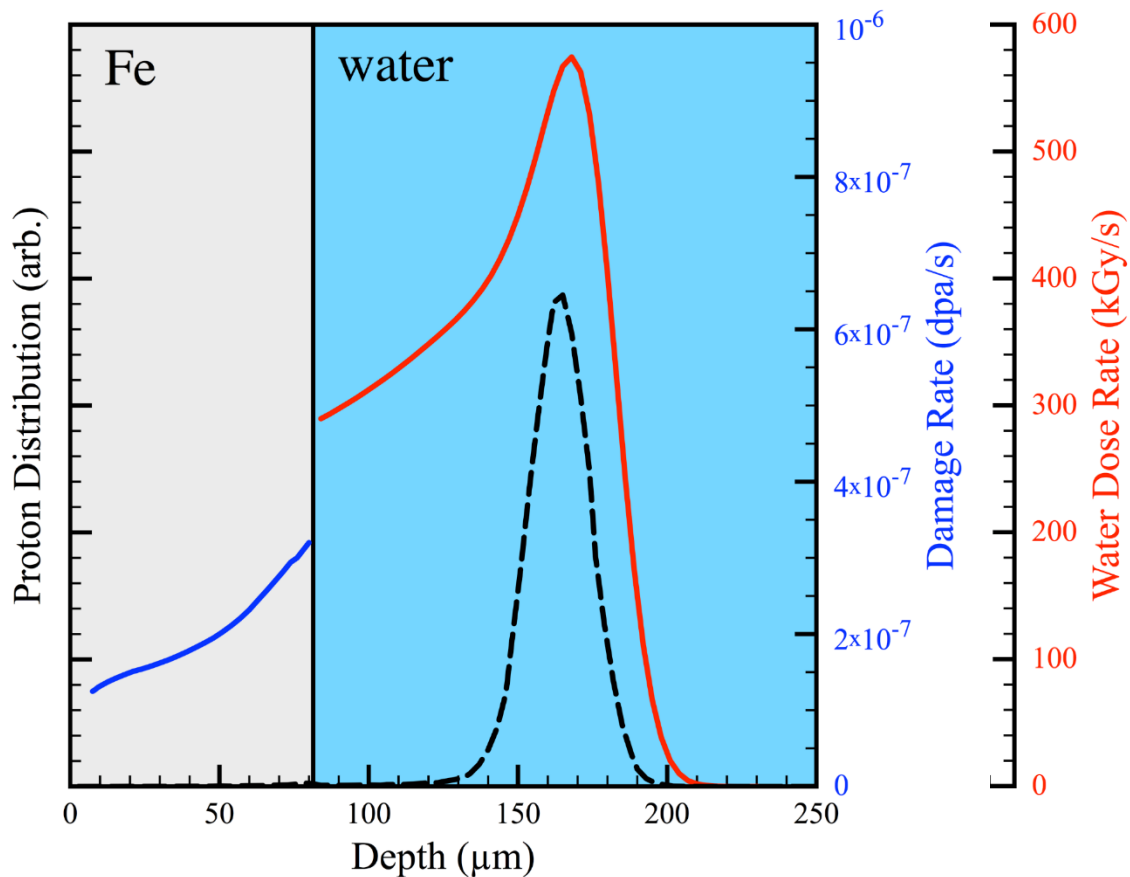


Figure 3. Proton range, damage rate and water dose rate for 5.4 MeV proton in APMT as calculated by TRIM 2013 in P-K mode with a proton flux of 1.25×10^{13} protons/cm³-s.

Figure 3 shows a simulation of the depth of 5.4MeV proton penetration, the damage rate to the metal in dpa, and dose to the water in Gy/s for this sample configuration. The desire is for a reasonable damage rate so that some effect of displacement damage might be seen in 24 hours of irradiation. However, this implies a very high dose rate to the water, on the order of 400kGy/s. (In reactor cores the dose rate to water is on the order of several kGy/s.) For electron irradiations with 2.2-2.5MeV electrons, penetration depth is not a major concern, so a thickness of 250 microns was chosen for flat samples. The 316ss sample flanges have 2mm holes to allow the electron beam access to the center of the sample, as illustrated in figure 4. The main problem is to try to match, approximately, the very high near-surface dose rate of the proton experiments. The inelastic energy scattering cross section for electrons is ca. 200x smaller than the protons, so roughly 200x larger average current density is needed to get the same dose rate. This puts a very large average heat load on the sample and cell, and requires a very high water flow rate across the sample to maintain the temperature. The flow cell geometry is illustrated in Figure 5. Hastelloy 276c was chosen for construction because this material is often recommended for high

temperature water (e.g. supercritical water) applications. Unlike in the proton experiments, the dose to the water is fairly uniform over the entire volume from the sample surface toward the sapphire window at the back of the flow cell.

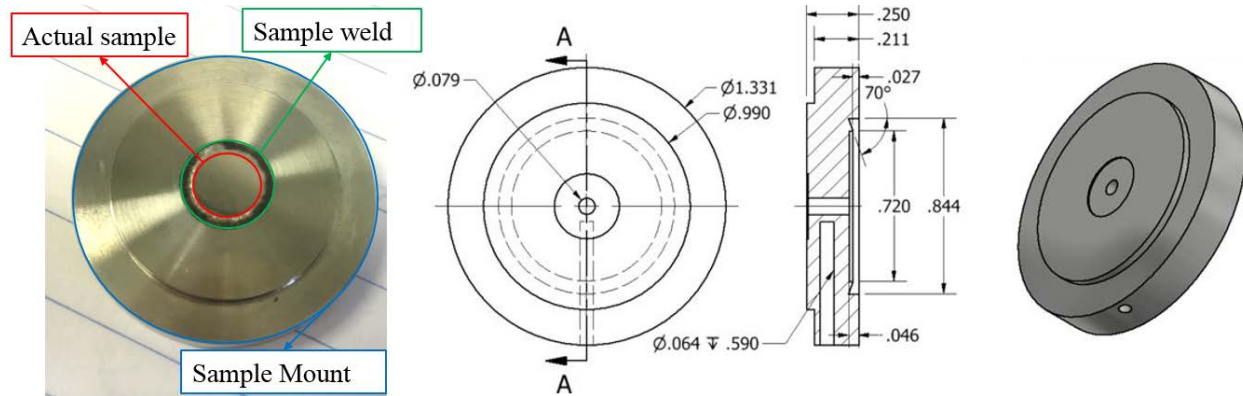


Figure 4: ND corrosion sample design: (left) Photo of a stainless steel sample with markings of components; (middle) CAD drawing of sample mount; (right) schematic of sample mount.

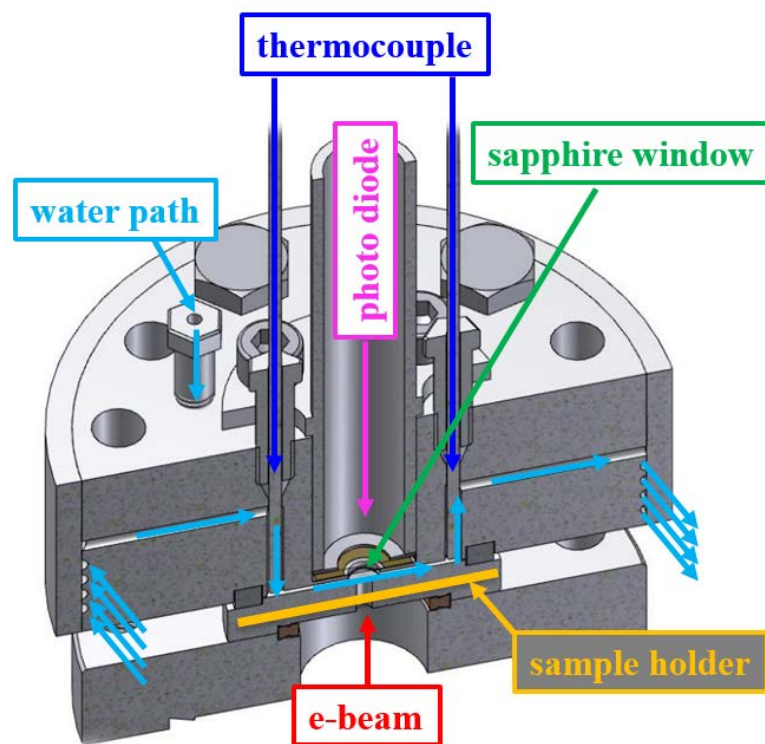


Figure 5: Cross-section of the NDRL electron beam irradiation corrosion cell design.

The high dose rate to the water, on the order of 400kGy/s, has serious implications for interpretation of our experimental results, as will be seen below. In figure 6 we present the result of a kinetics simulation of proton radiolysis of 300°C water with 3ppm H_2 at this dose rate, based on a standard radiolysis reaction model as used for reactor modeling. The simulation “turns on” the radiation at time zero and then “turns off” the radiation after one second. Steady state of the radiolysis transients is established within milliseconds. The radical species, $(e^-)_{aq}$, $(H)_{aq}$, and $(OH)_{aq}$ react away immediately after the radiation is turned off. The large H_2 concentration remains unchanged throughout. Even in the presence of 3ppm H_2 , there is significant H_2O_2 remaining (ca. 1 μ M) after the radiation turns off. (At typical reactor conditions, of ca. 4kGy/s, the H_2O_2 produced is almost negligible in hydrogenated water.) One micromolar H_2O_2 has been shown to produce corrosion potentials on the order of +200mV vs. NHE at 300°C. (The calculation reported here should be considered qualitative only, because proton radiolysis product yields have not been measured experimentally at high temperature.)

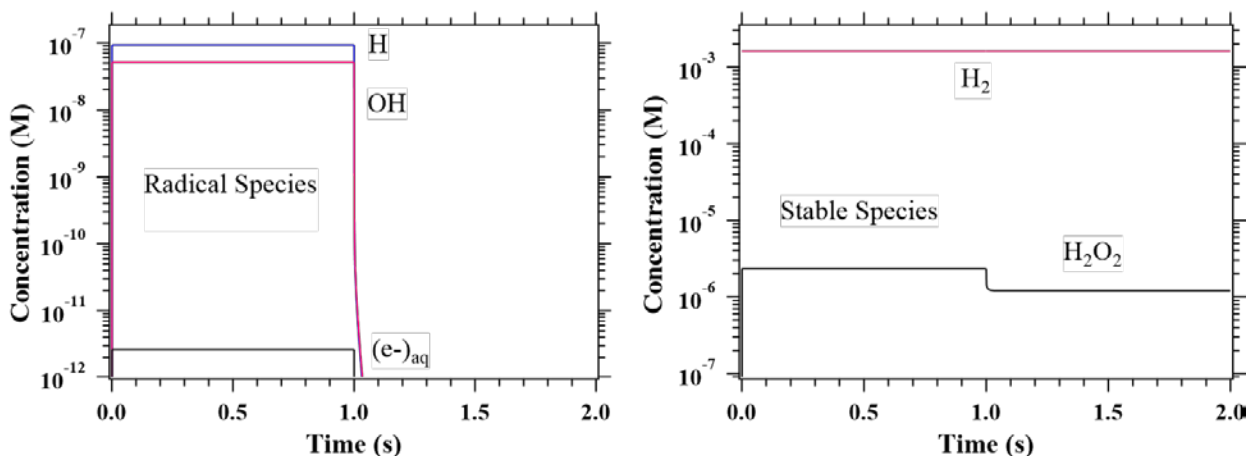


Figure 6. Simulation of water radiolysis with 1.4MeV protons at 300°C, in presence of 3ppm H_2 . Micromolar H_2O_2 survives after the radiation is turned off after 1 second.

In both the proton and electron beam irradiations, water quality was monitored in a dedicated recirculation flow system, including an inline deionizer to remove corrosion product and maintain neutral pH. Figure 7 illustrates some data collected in a 24 hour electron beam irradiation of T35Y2 alloy under 3ppm H_2 . Conductivity is monitored at both inlet and outlet of the cell. The sample temperature is first ramped up to 320°C causing a slight increase in conductivity at the cell outlet. When beam is turned on, a large conductivity is induced at the outlet, probably mostly acid produced in the radiation-accelerated corrosion. This induced conductivity monotonically decreases throughout the irradiation. After 24 hours the beam and heater are turned off, sample returns to room temperature, and the outlet conductivity becomes the same as the inlet.

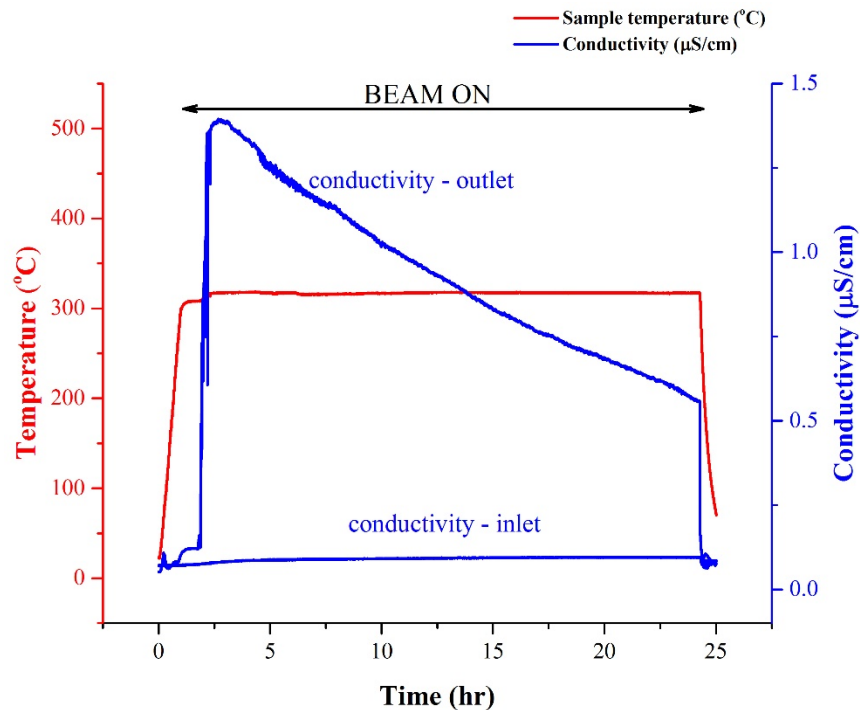


Figure 7. Temperature and water conductivity monitored during irradiation of T35Y2 alloy with 3ppm H_2 and neutral pH.

RESULTS

As in most previous studies of oxide layers resulting from aqueous corrosion of steel, we have found in our experiments an inner oxide tightly adhering to the base metal, and an outer oxide precipitation layer that is characteristic of the metal ions dissolved in the water. These latter ions may come from the sample, or from elsewhere in the high temperature flow system. We first describe our general observations of the precipitation layers and follow with description of the more important protective inner oxide layer.

Outer oxides

Proton irradiations

The general observations on the proton irradiated samples are illustrated in figures 8-11 for the T35Y2 alloy. A low resolution SEM image of the sample (left) irradiated in hydrogenated water in figure 8 shows the central irradiated region (IR), an outer unirradiated region (UR, on the bottom), and a radiolysis affected region (RAR, on the top). The radiolysis affected region results from convective flow of hydrogen peroxide generated with water radiolysis in the irradiated region. The three regions are also present in the oxygenated water (NWC) sample on the right, and are faintly visible to the eye from optical scattering, but the structural differences are nearly invisible by low resolution SEM.

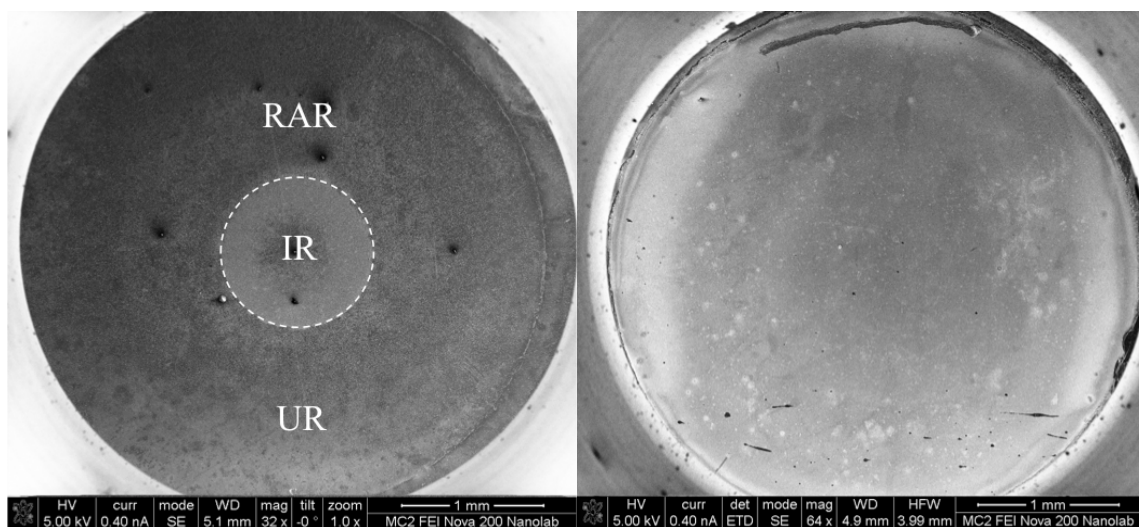


Figure 8. SEM images of T35Y2 in HW and NWC water after 24 hr irradiation-corrosion experiments

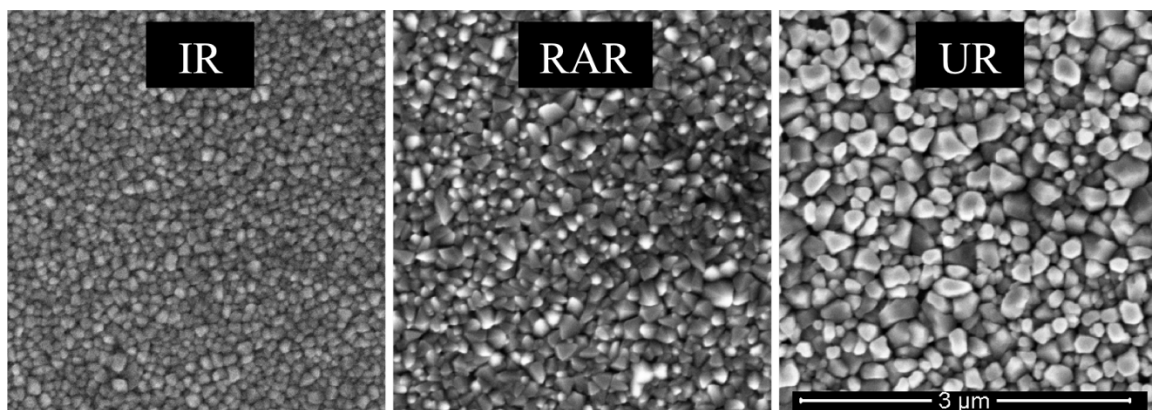
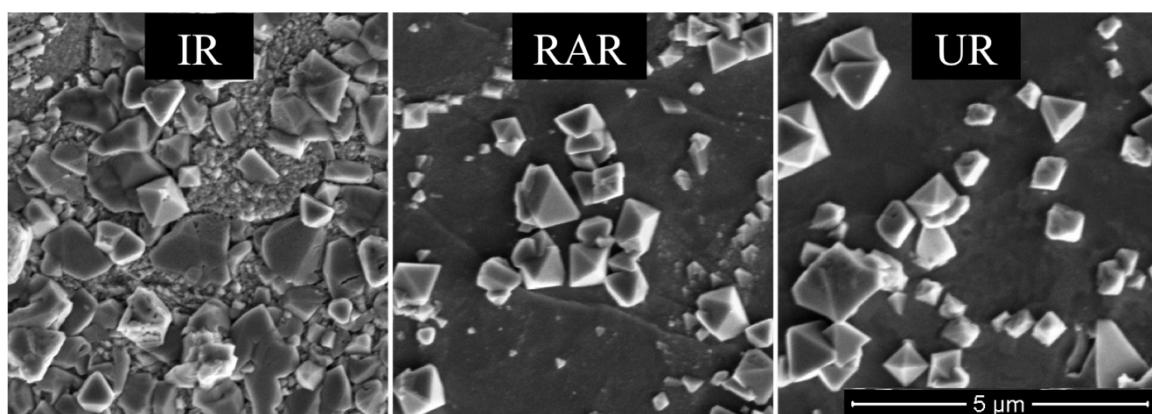


Figure 9. High magnification SEM image of the three regions observed on sample T35Y2 in HW (top) and NWC (bottom) environment after 24 h.

Typical structures seen with higher resolution SEM are shown in figure 9. In hydrogenated water in the UR and RAR regions, oxide precipitation crystals are relatively large and sparse. In the hydrogenated water IR region (leftmost picture), crystals are much smaller and more densely packed. High resolution SEM of the NWC irradiated sample shows the oxide crystals are somewhat smaller in the irradiated zone than the unirradiated zone, but there is no qualitative difference.

Differences in the several zones of the two samples are characterized with Raman spectroscopy in figures 10 and 11. In general the Raman spectra can be understood in terms of three species, magnetite (Fe_3O_4), a chromium-substituted magnetite (chromite, FeCr_2O_4), and hematite (Fe_2O_3). It is well established that in oxygenated solutions, with corrosion potential more positive than +35mV relative to NHE, the hematite structure is the most stable iron oxide form at 288°C. At less positive corrosion potentials, the magnetite structure is most stable. The Raman spectrum found in all three regions of the oxygenated NWC sample shows the characteristic peaks of hematite. Both the Raman spectrum in NWC conditions, and the small poorly defined crystals observed on this sample are consistent with previous observations.

In the hydrogenated water sample, the large crystals of the UR and RAR regions are certainly magnetite, Fe_3O_4 , as illustrated by the characteristic Raman spectrum in figure 10. This would also conform to numerous previous observations under reducing conditions. Given the sparse coating of this sample in the UR and RAR, the Raman spectrum may also show up the underlying stable chromite layer FeCr_2O_4 of the inner oxide. The RAR spectrum also shows some hint of the hematite peaks, and this may indicate a mixture of precipitated oxides due to some H_2O_2 presence.

The central irradiated region of the hydrogenated water sample shows the very characteristic Raman spectrum of hematite, Fe_2O_3 . As noted above this form of iron oxide is only stable for positive values of the corrosion potential vs. NHE. It makes sense in terms of the very high dose rate of these experiments, with proton dose to the water on the order of 400kGy/s. Simulation of the water radiolysis suggests H_2O_2 concentrations will reach on the order of one micromolar, and possibly higher. This is easily sufficient to generate a positive local corrosion potential, where hematite would be the most stable iron oxide.

This general picture of the outer precipitation layer was consistent throughout the proton-irradiated FeCrAl samples.

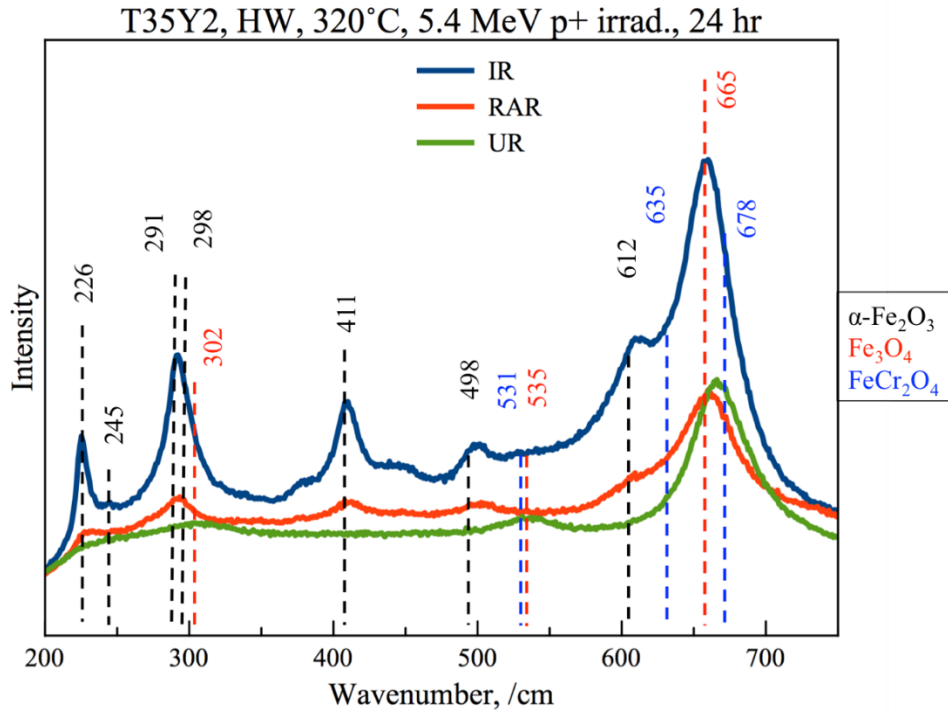


Figure 10: Raman spectra collected from IR, RAR and UR region on the 24 hr irradiated T35Y2 sample in primary water condition.

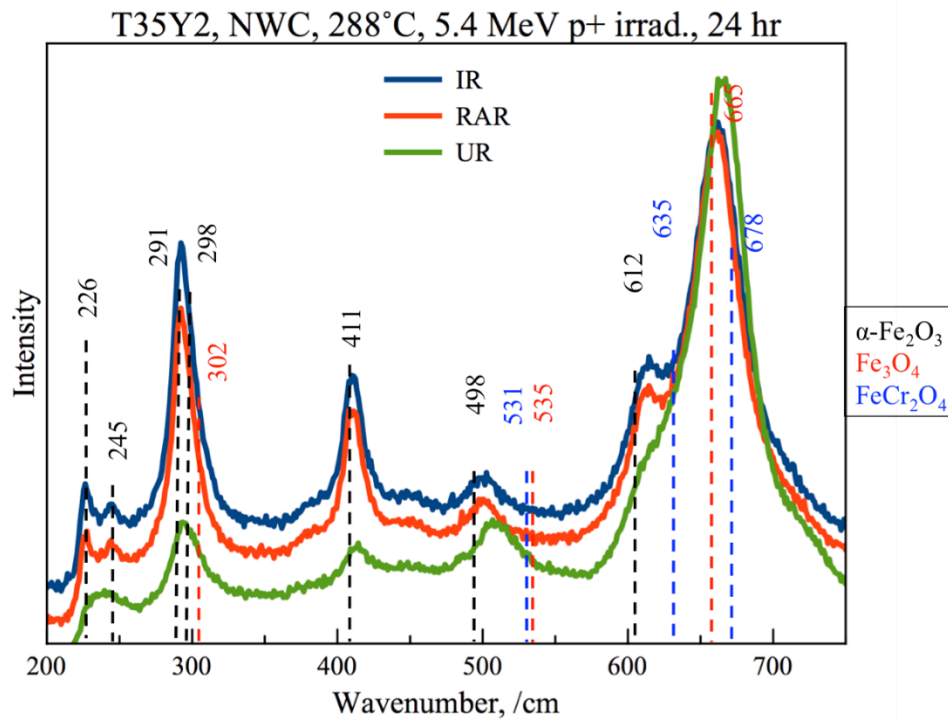


Figure 11: Raman spectra collected from irradiated region, unirradiated regions and the radiolysis affected region on the 24 hr irradiated T35Y2 sample in NWC water condition.

Electron beam irradiations

The electron beam irradiations in hydrogenated water can be understood in much the same way as the proton beam experiments. The average dose rate to the water was on the order of 200kGy/s. This results in production of a large amount of hydrogen peroxide in the irradiated region, and this can also be carried downstream to the radiolysis-affected region. High resolution SEM pictures are shown in figure 12 for e-beam irradiations of the T54Y2 alloy in PWR HWC and in BWR NWC conditions. The unirradiated regions look roughly similar to those found in the proton irradiation experiments, but the crystal morphology is different in the IR and RAR regions. The reason for this shows up in the Raman spectra as well as x-ray fluorescence.

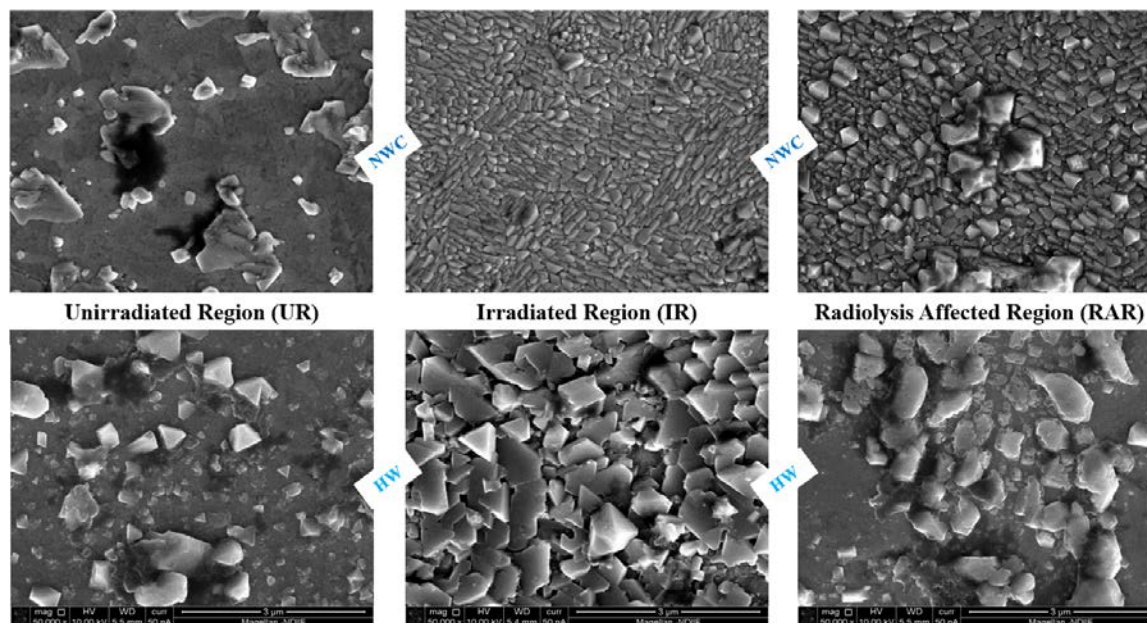


Figure 12: Post-Irradiation SEM images of 24-hour electron-beam T54Y2 sample in NWC (top) and HW (bottom). Representation of the three different regions, UR, IR and RAR.

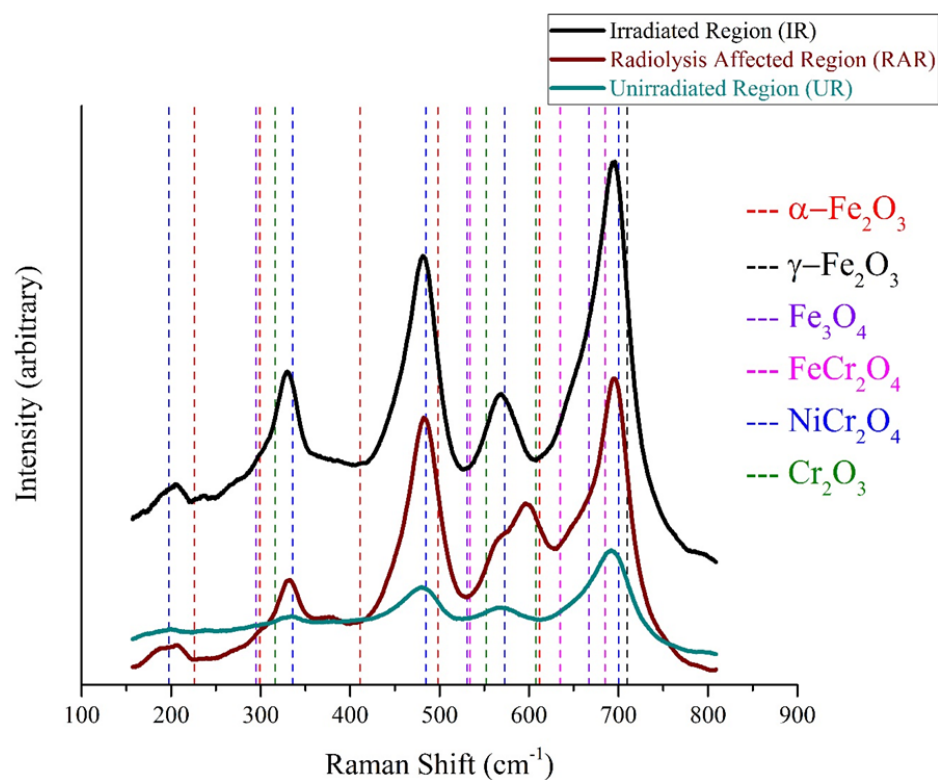


Figure 13: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated T54Y2 sample in Hydrogen-saturated water

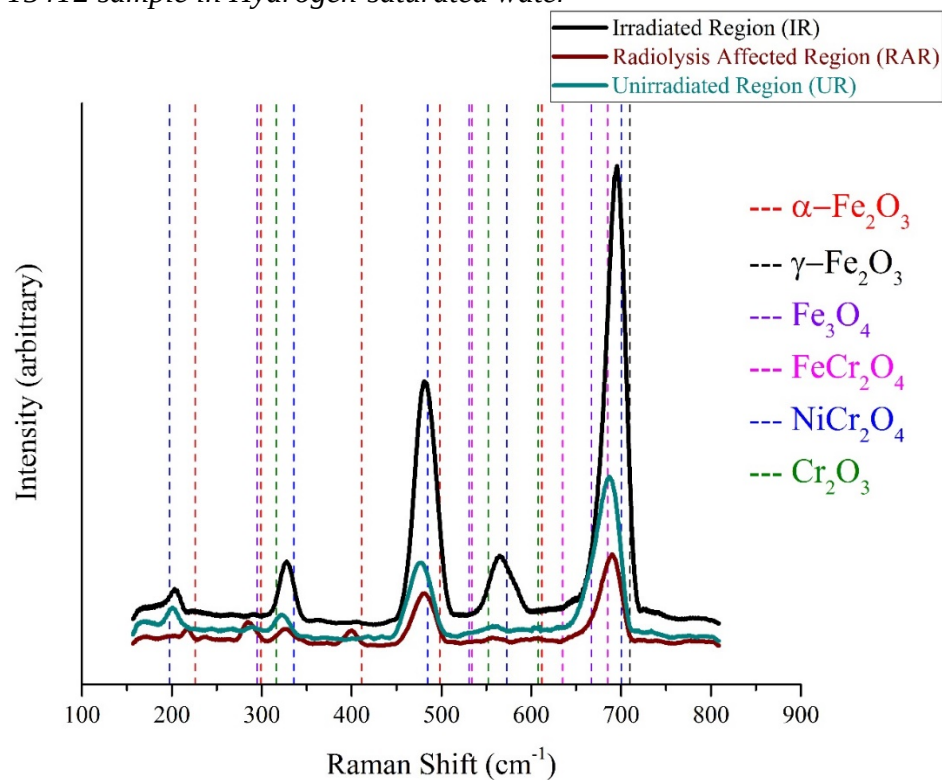


Figure 14: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated T54Y2 sample in Oxygen-saturated water.

Raman analysis in all three regions of the T54Y2 HW sample (Figure 13) showed that the corrosion products are mainly composed of a mixture of chromium oxide, iron chromite and nickel chromite. The chromium oxide associated peaks are presented by the green dashed lines in the plot, the iron chromite peaks by the pink dashed lines and the nickel chromite peaks by the blue dashed lines.

Raman analysis in all three regions of the T54Y2 NWC sample (Figure 14) showed that the corrosion products are mainly composed of nickel chromite. The nickel chromite associated peaks are presented by the blue dashed lines in the plot. The presence of nickel is confirmed in the EDX data. Given that the sample contains no nickel, this nickel oxide must come from corrosion of the hastelloy body or inconel thermocouple sheaths of our flow cell. It makes questionable the utility of this cell for the NWC chemistry conditions, in particular. The cell was passivated for a week at high temperature before attempting any further irradiation. It was decided at this point to carry out further experiments with Ar saturated water rather than 2ppm O₂ at 288°C.

A final example of the precipitation layer generated in the e-beam experiment is given for the T35Y4 irradiations in figures 15- 17.

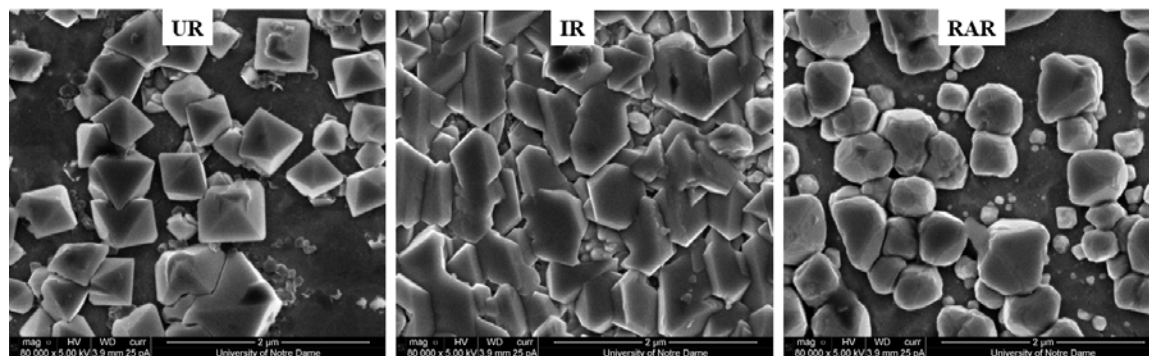


Figure 15: Post-Irradiation SEM images of 24-hour electron-beam T35Y2 sample in HW. Representation of the three different regions, UR, IR and RAR.

The high magnification SEM images in Figure 15 and Figure 16 represent the oxide particles of the three different regions (UR, IR and RAR) in the T35Y2 Hydrogen-saturated sample and T35Y2 Argon-saturated sample, respectively. There are similarities in the population density of the particles when comparing the regions of the different irradiating conditions; the IR region features the most densely populated particles, then the RAR region and the UR region. In both cases, the IR region features small particles that tend to grow in different direction, forming something similar to a “zig-zag” pattern.

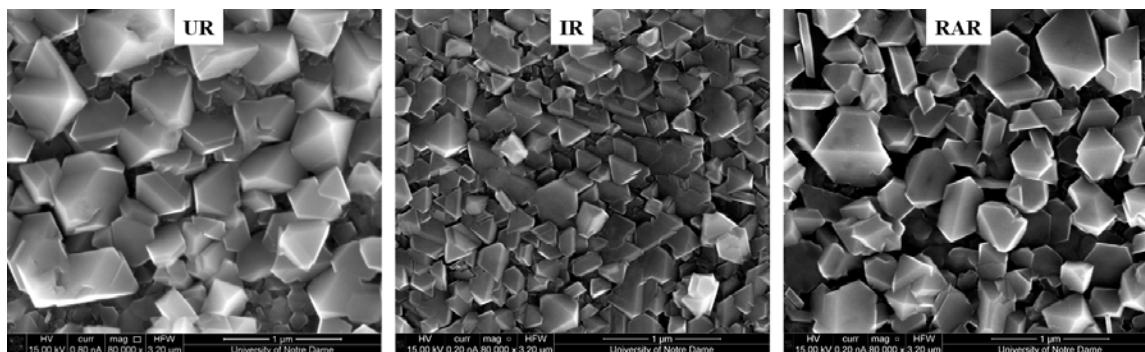


Figure 16: Post-Irradiation SEM images of 24-hour electron-beam T35Y2 sample in Ar-saturated water. Representation of the three different regions, UR, IR and RAR.

Raman analysis of the IR region of the T35Y2 HW sample (Figure 17) showed that the corrosion products are mainly composed of a mixture of chromium oxide, iron chromite and nickel chromite. The chromium oxide associated peaks are presented by the green dashed lines in the plot, the iron chromite peaks by the pink dashed lines and the nickel chromite peaks by the blue dashed lines. The UR and RAR regions of the HW sample feature a strong magnetite peak and there is no presence of nickel spinels.

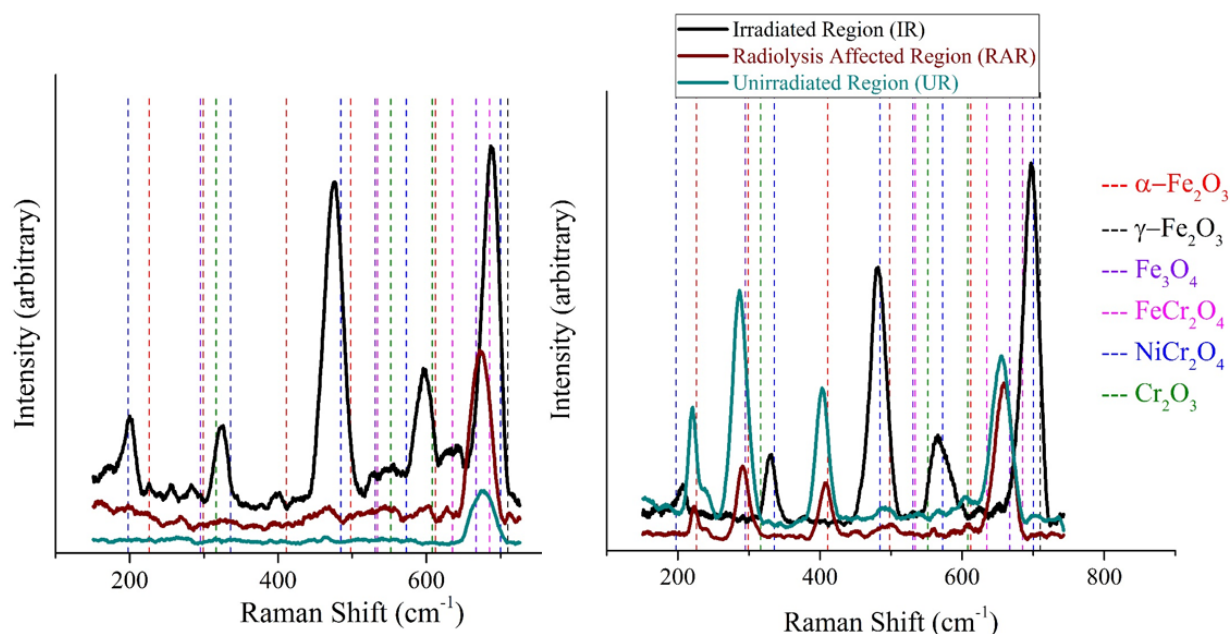


Figure 17: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated T35Y2 sample in Hydrogen-saturated water (left) and T35Y2 sample in Argon-saturated water (right). Representation of the three different regions (IR, RAR and UR) and associated Raman peaks;

Similar to the HW case, Raman analysis (Figure 17) of the IR zone of the T35Y2 Ar-saturated sample showed that the precipitation layer is mainly composed of nickel chromite. The nickel chromite associated peaks are presented by the blue dashed lines in the plot. The presence of nickel is confirmed in the EDX data. Given that the sample contains no nickel, this nickel oxide must come from corrosion of the hastelloy flow system. The UR and RAR regions of the Ar-saturated sample feature both hematite and magnetite peaks.

The different precipitation layers formed in the U-Michigan corrosion cell vs. the nickel-containing layers formed in the Notre Dame cell makes it obvious, if proof were needed, that the nature of the porous outer oxide has little to do with the essential protective function associated with the inner oxides. The inner oxide hopefully forms a passive protective layer independent of metal ions present in the solution.

Inner oxides

The most striking observation regarding the inner oxide layers is the degree to which the original very flat polished surface is preserved in unirradiated (UR) and radiolysis affected regions (RAR) of the hydrogen-saturated PWR samples. Figure 18 illustrates this behavior for the proton-irradiated samples of T35Y2 using HAADF-STEM to provide contrast. The UR and RAR regions show a very thin dark line which is the protective inner oxide. It demonstrates that the oxide grows inward and preserves the original polished-flat surface. In contrast, in the irradiated (IR) zone the very thin inner oxide boundary is very uneven, suggesting that the original surface has dissolved away. The oxygen-saturated NWC proton irradiation samples are shown immediately below the hydrogen-saturated samples. Here too, the inner oxide is very thin and very uneven, suggesting dissolution over the entire surface regardless of irradiation.

The structure and composition of the oxide layers in the irradiated region (IR) of the hydrogenated water sample is shown with an EDS linescan in figure 19. The inner oxide is just a narrow transition region, on the order of 50nm width or less, between the base metal and the outer oxide precipitation layer. The outer oxide precipitation layer is dominated by iron oxide, as already indicated by the Raman spectra. The structure and composition of the stable inner oxide in the unirradiated portion (UR) of this sample is shown with an EDS linescan in figure 20. The narrow inner oxide layer, again less than 60nm wide, is greatly enriched in chromium and aluminum, and depleted in iron. The precipitation layer above is almost entirely iron oxide.

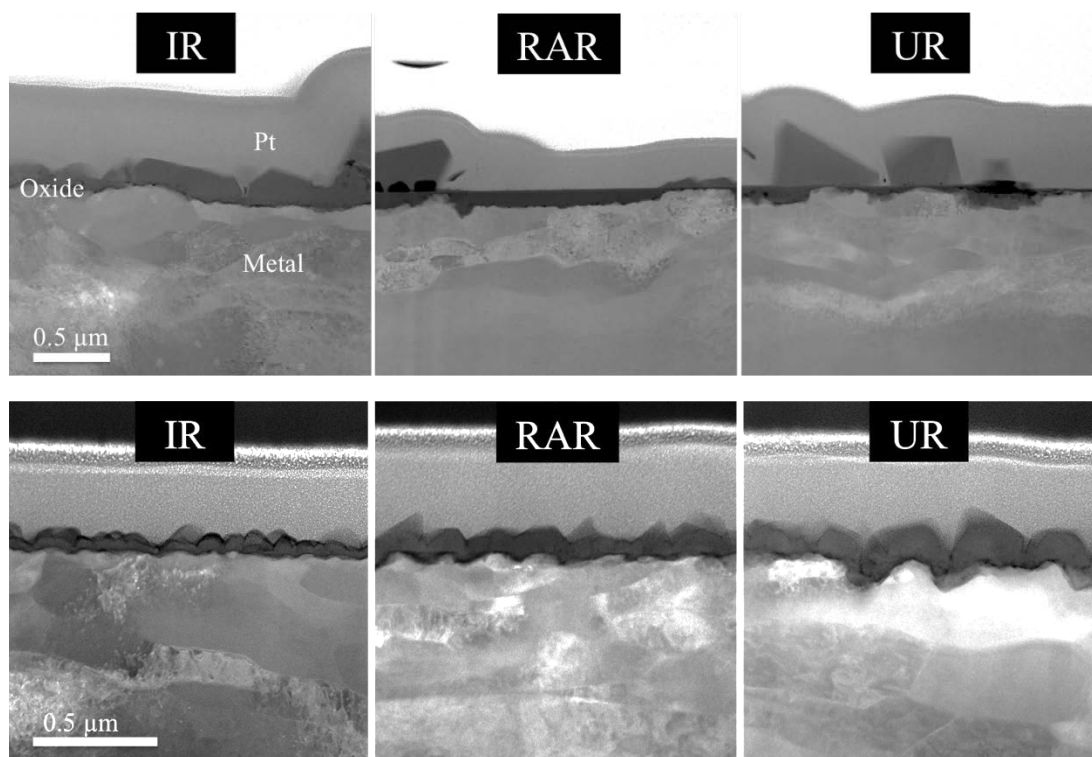


Figure 18. HAADF-STEM images of the FIB lamellas taken from the proton-beam irradiated sample T35Y2 in HW (top) and NWC (bottom) environment after 24 h of proton irradiation.

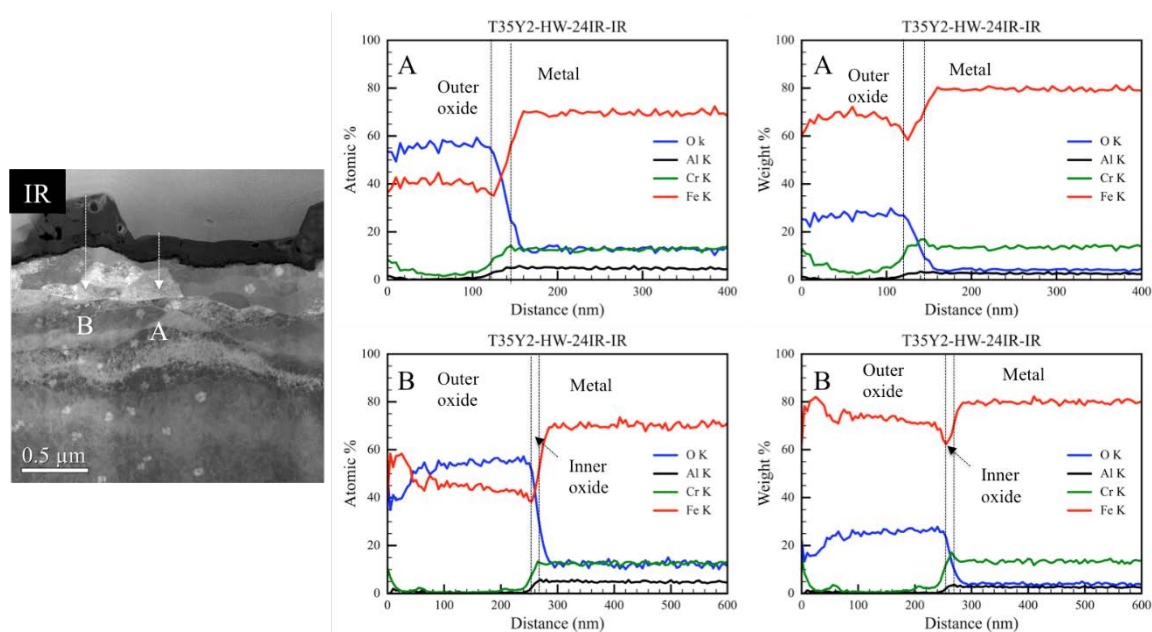


Figure 19: EDS line scans of oxide regions formed in irradiated zone (IR) on sample T35Y2-HW-24IR with 3ppm H_2 PWR water.

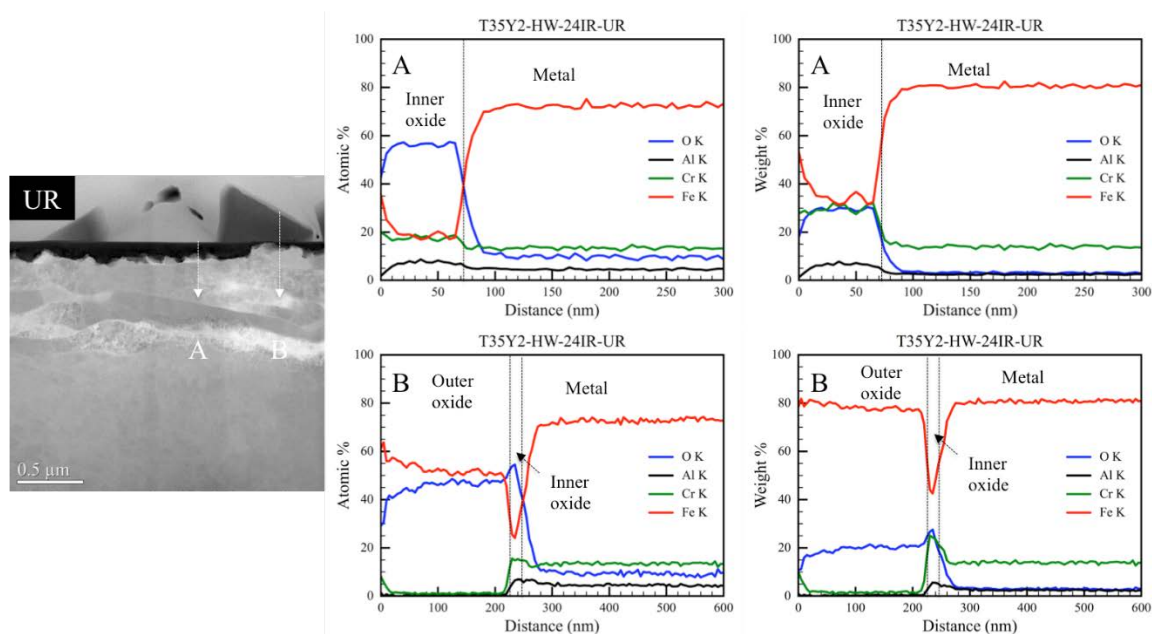


Figure 20: EDS line scans of oxide regions in the unirradiated zone (UR) formed on sample T35Y2-HW-24IR in 3ppm H_2 saturated PWR water.

Exactly the same behavior can be seen in the electron-beam irradiated samples. For example, the surface of APMT is illustrated in figure 21 for the H_2 -saturated PWR case. The IR zone boundary between metal and oxide is uneven, suggesting dissolution, but the UR and RAR regions preserve the very flat original surface. In figure 22 the Ar-saturated sample of APMT irradiated at 288°C shows that the inner oxide is uneven, and dissolution seems to have occurred in all regions of the sample.

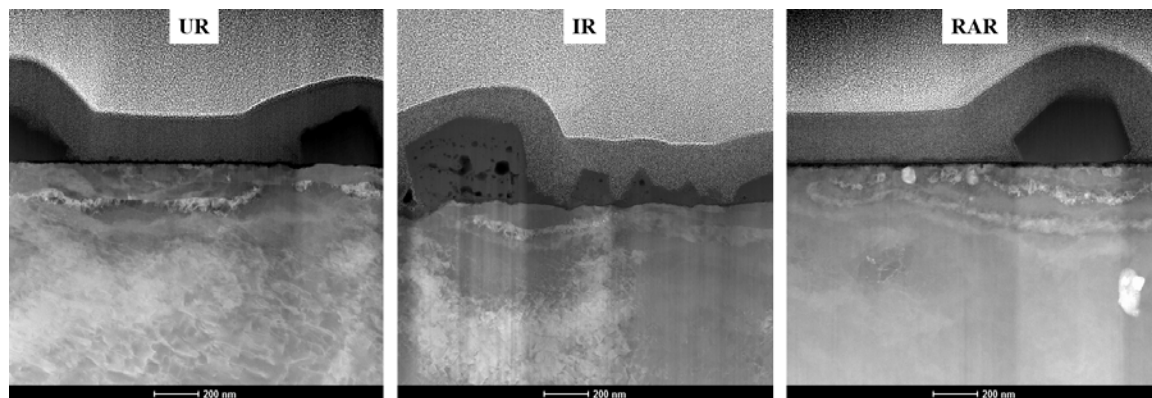


Figure 21: Post-Irradiation TEM images of 24-hour electron-beam APMT sample in Hydrogen-saturated water. Representation of the three different regions (UR, IR and RAR).

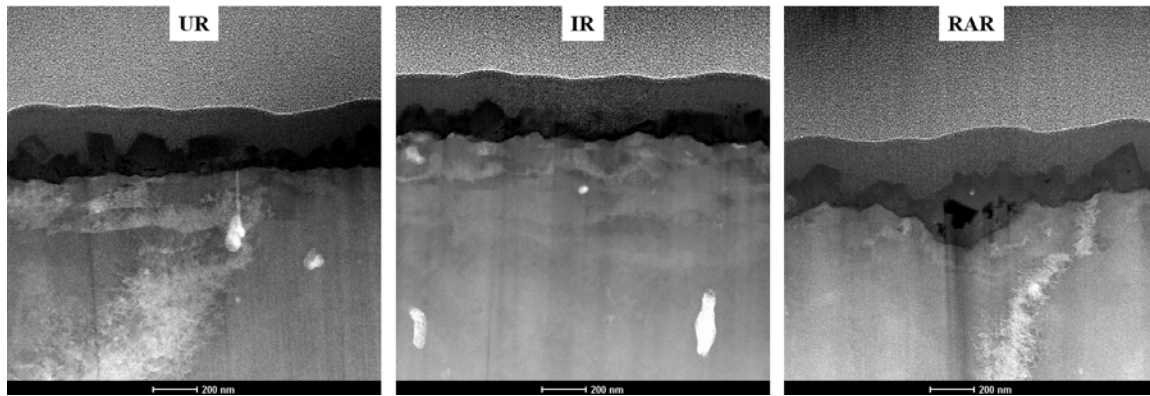


Figure 22: Post-Irradiation TEM images of 22-hour electron-beam APMT sample in Argon-saturated water. Representative of the three different regions (UR, IR and RAR).

A summary of this inner oxide dissolution behavior is reported in Table 2 for all samples of our study. It seems fairly clear that the dissolution behavior of the inner oxide correlates with more positive values of corrosion potential. Oxygen, or even Argon, saturation of the water is sufficient to promote the dissolution without radiation. Hydrogen saturation stabilizes the inner oxide in the UR and RAR zones, but the very high dose rate irradiation of the water produces a very positive corrosion potential in spite of the hydrogen. The fact that both proton and electron beam irradiation do the same thing, implies any effect of displacement damage from the protons is smaller than the effect of water radiolysis. It is interesting to note that the T91 alloy, without any Al content, suffered almost no dissolution in the hydrogenated water under irradiation, but did dissolve in oxygenated water.

Table 2: OBSERVATION OF APPARENT INNER OXIDE DISSOLUTION

PWR (reducing) conditions	proton beam irradiation:			electron beam irradiation:		
	UR	IR	RAR	UR	IR	RAR
APMT	-	x	-	-	x	-
MA956	-	x	-	-	x	-
T54Y2	-	x	-	-	x	-
T35Y2	-	x	-	-	x	-
T91	-	?	-	-	-	-

BWR (oxidizing) conditions	proton beam irradiation:			electron beam irradiation:		
	UR	IR	RAR	UR	IR	RAR
APMT	x	x	x	x	x	x
MA956	x	x	x	x	x	x
T54Y2	x	x	x	x	x	x
T35Y2	x	x	x	x	x	x
T91	x	x	x	x	x	x

Thin Film Irradiations

The dissolution of the FeCrAl steel in oxidizing conditions is potentially a very important problem in the industrial use of these materials. However, we have no way of knowing in our standard experiment exactly how much of the surface has dissolved away during the 24 hour experiments. To answer this question we arranged to sputter deposit several hundred nanometers of FeCrAl material onto steel or zircaloy substrate. These were irradiated in the standard fashion for 24 hours and then examined with HAADF-STEM imaging to determine the remaining thickness of the thin film. Pictures are shown in figure 23 showing the pristine deposited film and the several sample zones. The thickness of remaining oxide is plotted in figure 24. It appears that for both a 20%Cr and a 13%Cr FeCrAl sample layer, roughly 100nm of the material has dissolved in one day.

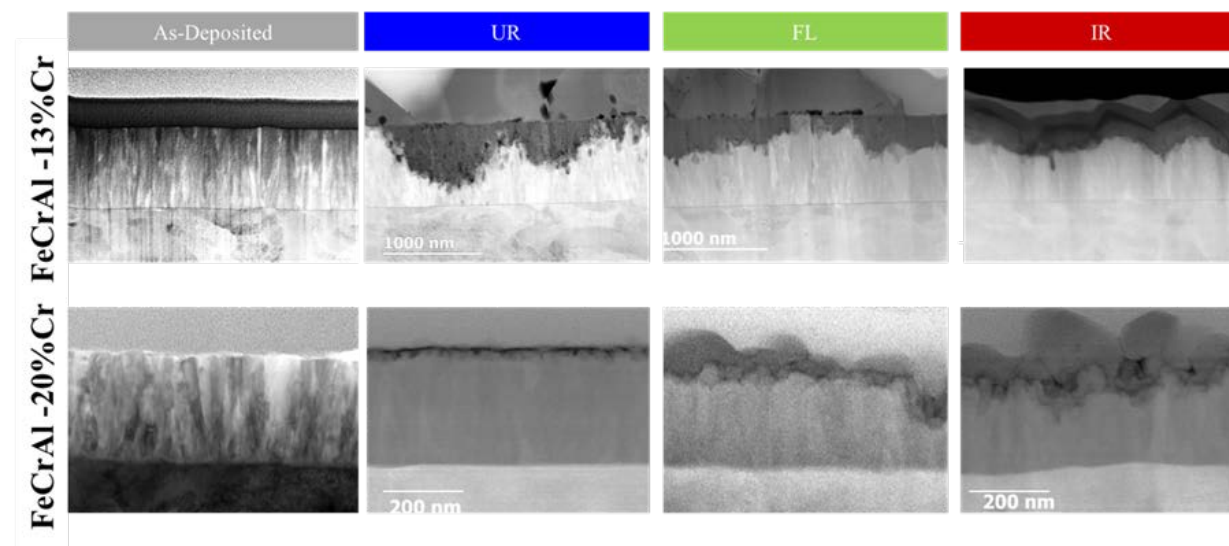


Figure 23. HAADF-STEM images of FeCrAl films (13%Cr on top, 20%Cr on bottom) before and after irradiation with protons for 24 hours in 3ppm H_2 at 320°C.

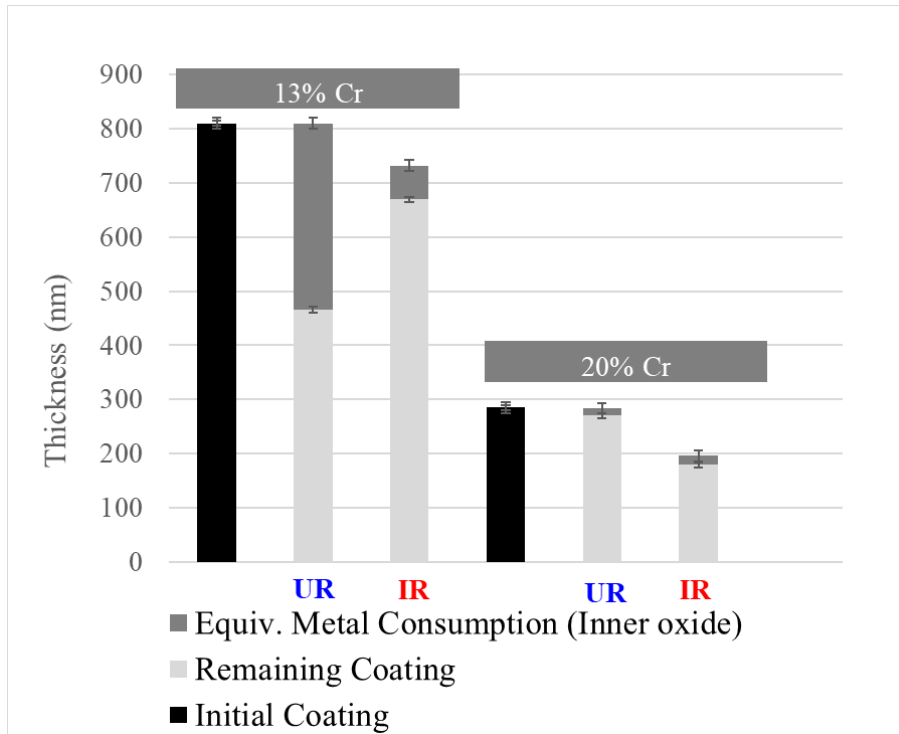


Figure 24. Thickness of the deposited metal and oxide films for the samples pictured in Figure 23.

Conclusion: potential for industrial use

The purpose of our study, as stated at the outset, is to quickly evaluate the potential sensitivity of the FeCrAl alloys to corrosion in a radiation environment. We have no problem recommending these materials for use in a PWR environment with hydrogen water chemistry. The corrosion we observe in unirradiated and downstream zones of the samples was minimal, with performance superior to other stainless steels we have examined. We did observe high temperature dissolution of the FeCrAl materials in oxidizing environments, either from direct saturation with O₂ gas, or from production of hydrogen peroxide and oxidizing radicals by the radiation. Even with use of hydrogen water chemistry, oxidizing conditions can be found at top-of-core in boiling water reactors, and some further analysis may be warranted before using these FeCrAl materials for cladding in BWRs.

PRODUCTS / DELIVERABLES

Products / Deliverables:

Journal Papers

In preparation

Conference Papers

Irradiation Accelerated Corrosion of Stainless Steel and Ferritic-Martensitic Steel in Simulated Primary Water

S Raiman, P Wang, G Was

CORROSION 2017

<https://www.onepetro.org/conference-paper/NACE-2017-9131>

In-Situ Proton Irradiation-Corrosion Study of ATF Candidate Alloys in Simulated PWR Primary Water

P Wang, GS Was

Environmental Degradation of Materials in Nuclear Power Systems, 245-258

https://link.springer.com/chapter/10.1007/978-3-319-68454-3_21#citeas

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

S Grdanovska, P Wang, G Was, D Bartels

Microscopy and Microanalysis 23 (S1), 2226-2227, St. Louis, Missouri, 2017

<https://www.cambridge.org/core/journals/microscopy-and-microanalysis/article/assessment-of-corrosion-resistance-of-candidate-alloys-for-accident-tolerant-fuel-cladding-under-reactor-conditions/4626C64D8DB5A283BB7C8DA290CF397C>

Conference Talks

Assessment of Corrosion Resistance of Candidate Alloys for ATF Cladding under Reactor Conditions

D. Bartels

Nuclear Plant Chemistry Conference (NPC2018), San Francisco, CA, September 14, 2018

Corrosion product of FeCrAl Alloys in Simulated LWR Environments during In-situ Proton Corrosion-irradiation Experiments

P Wang, GS Was

Symposium of Accident Tolerant Fuel for Light Water Reactor - Cladding Materials, TMS 2018, 18 March 2018

Irradiation accelerated corrosion of cladding and core structural materials

P Wang, G Was, S Raiman, R Hanbury

EuroCorr 2017

Irradiation accelerated corrosion of core structural materials and cladding

G Was, P Wang, S Raiman, R Hanbury
ICG-EAC 2017

Assessment of Corrosion Resistance of Candidate Alloys for ATF Cladding under Reactor Conditions

D. Bartels

DOE Advanced Fuel Campaign Integration Meeting, Oak Ridge National Lab, March 28, 2017

Irradiation accelerated corrosion of 316L stainless steel, T91, and Zircaloy-4 in simulated primary water

S Raiman, P Wang, G Was

Corrosion Conference 2016

Oxidation of FeCrAl alloys in simulated LWR environment during in-situ corrosion irradiation experiment

P Wang, G Was

TMS 2016 - 145th Annual Meeting & Exhibition, Nashville, TN, USA

Poster Presentations

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

S Grdanovska, P Wang, G Was, D Bartels

Microscopy and Microanalysis, St. Louis, Missouri, August 10th, 2017

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

S Grdanovska, P Wang, G Was, D Bartels

4th Midwest Imaging and Microanalysis Workshop, University of Notre Dame, Indiana, May 9th, 2017

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

S Grdanovska, P Wang, G Was, D Bartels

International Conference on Ionizing Processes (ICIP 2016), Brookhaven National Laboratory, Upton, New York, October 13th, 2016.

Evaluation of T91 steel for use as nuclear fuel cladding material

S Grdanovska, P Wang, G Was, D Bartels

3rd Midwest Imaging and Microanalysis Workshop, University of Notre Dame, Indiana, May 17th, 2016

Patents: none

APPENDICES: Updated/Corrected Milestone Reports for each Alloy

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

April 2016 Milestone report for T91 steel

Four T91 steel sample irradiations were completed to assess the corrosion behavior of this steel under reactor-like conditions. In this experiment the thin samples actually serve as the interface between the accelerator vacuum system on one side, and water at high pressure and temperature on the other. The samples irradiated at the University of Michigan used high energy protons while at University of Notre Dame an electron beam was used. The protons have energy of ca. 1.7MeV as they pass through the oxide into the water, and electrons have energy of ca. 1.5MeV. The protons have much higher momentum, and so (like high energy neutrons) are capable of causing significant atomic displacement damage in the oxide layer. They also move much more slowly than the relativistic electrons, so their LET (linear energy transfer) is ca. 200x larger than the electrons. To compensate and give nearly the same average energy dose to the sample and water near the surface, the electron beam flux (amps/cm²) is adjusted to be ca. 100x greater than the proton beam. Electrons do essentially no displacement damage to the solid.

Detailed analysis of the several T91 samples is shown below in sections A-C. A summary of oxide thickness generated in the 24 hour irradiated samples is presented in Figure 1. The plot shows comparison between three different regions of interest: the directly irradiated region (IR), unirradiated region upstream of the radiation (UR), and a radiolysis affected region (RAR) downstream of the sample. Samples were irradiated at 320°C (HWC) and 288°C (NWC). (The e-beam irradiated sample at 288°C proved to be badly contaminated by graphite packing material from a pressure seal, and so is omitted from consideration, though the corrosion was qualitatively similar to the proton beam result.) In general we find no very large difference in the corrosion properties between irradiated and unirradiated zones, beyond those to be expected from typical stainless steels under these extreme conditions of irradiation. We conclude that T91 steel is a viable candidate material for nuclear fuel cladding.

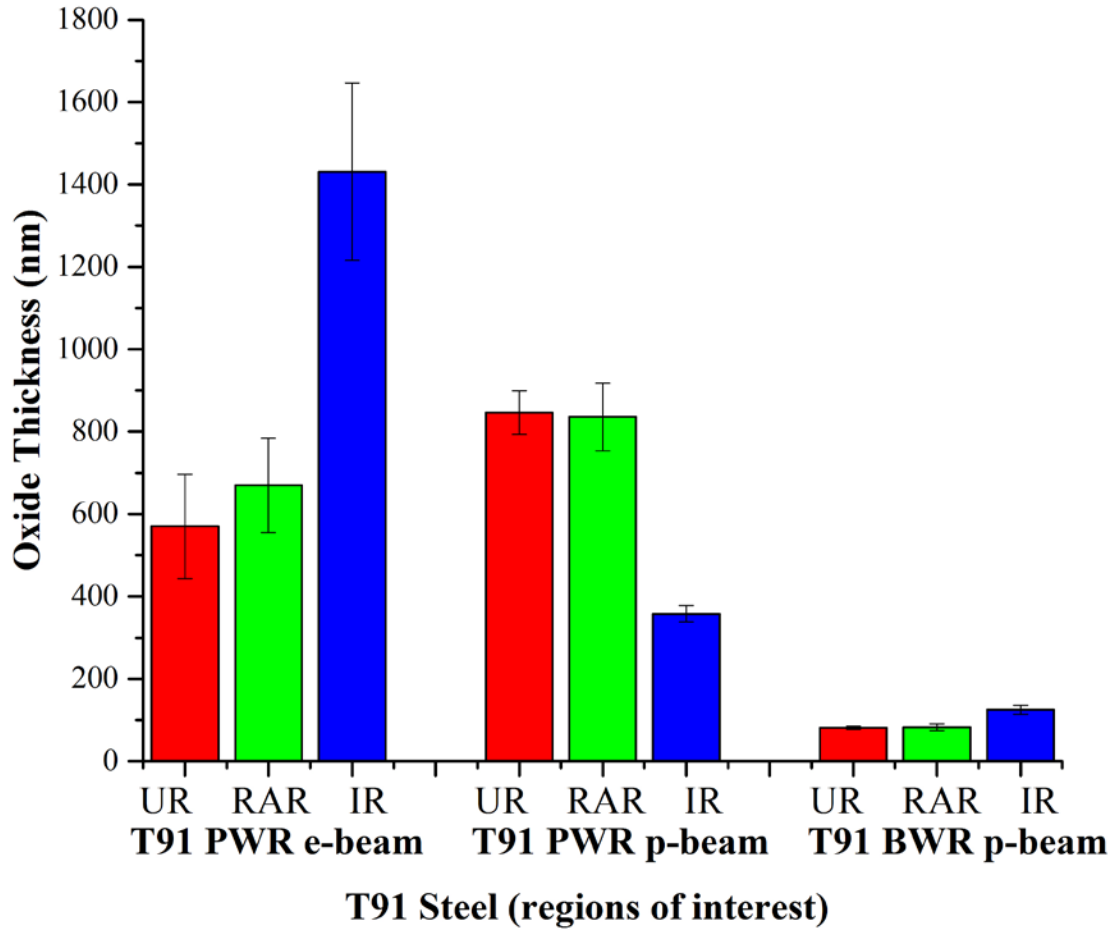


Figure 1: T91 Oxide thickness comparison between ND and UM 24 hour irradiated samples.

A. T91 Base Metal Characterization

The bulk material was obtained from InduSteel (Belgium) by American Alloy and Steel (AAS), and chemical composition is listed in Table A1.

Table A1. Chemical composition of as-received T91, supplied by American Alloy and Steel.

Heat	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
40473	0.106	0.428	0.018	0.0027	0.210	0.044	0.221	8.872	0.958
	Al	Nb	Zr	V	Ti	N	Fe		
	0.019	0.076	0.006	0.204	0.002	0.0518	Bal.		

EDS element analysis was carried out on a FEI NOVA SEM/FIB with EDAX detector. EDS spectrum is shown in Fig. A1. Atomic and weight percentage of each alloy element was shown in Table A2. The concentration of major alloying elements were consistent with the reference received from AAS, however the Mo content was slightly lower than standard.

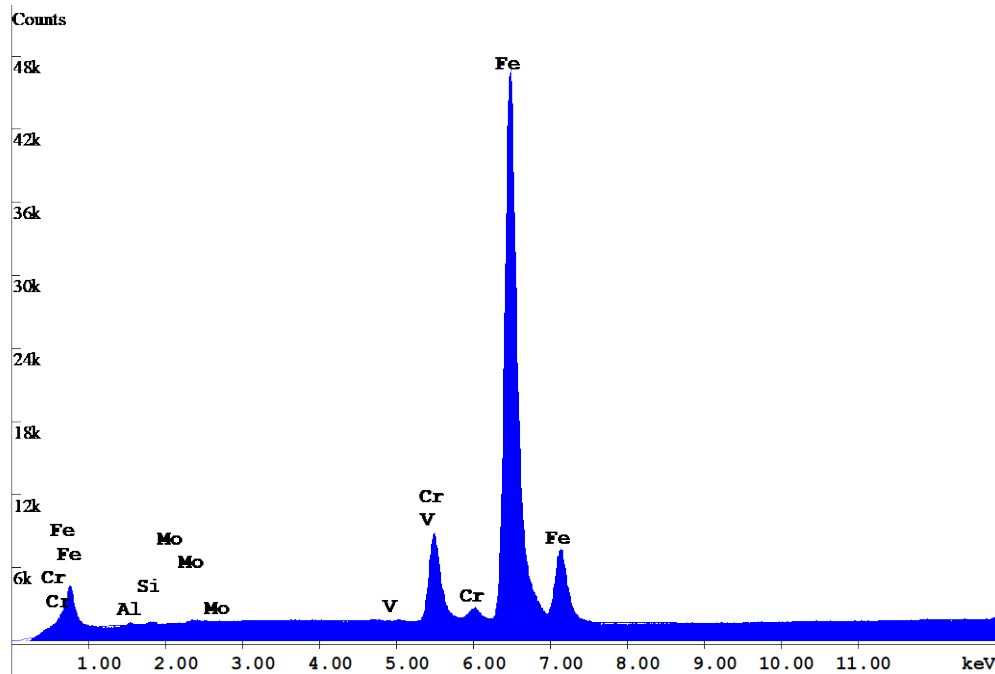


Figure A1. EDS spectrum of as-received T91.

Table A2. Alloy element analysis by EDS.

Element	Wt %	At%
Fe	90.84	90.22
Cr	8.23	8.77
Mo	0.50	0.29
Si	0.23	0.45
V	0.15	0.17
Al	0.05	0.1

TEM analysis was performed using a JEOL 2100F STEM on twin-jet polished samples. The sample showed a typical T91 microstructure with martensite laths and the dislocations in the grain. Average grain size was about 1 μm , however, majority of the grains have a very large aspect ratio due to the martensitic transformation that produce laths as subgrains in a ferrite matrix. Carbides (e.g. M_{23}C_6) were found at subgrain boundaries, with a size of 50-100 nm.

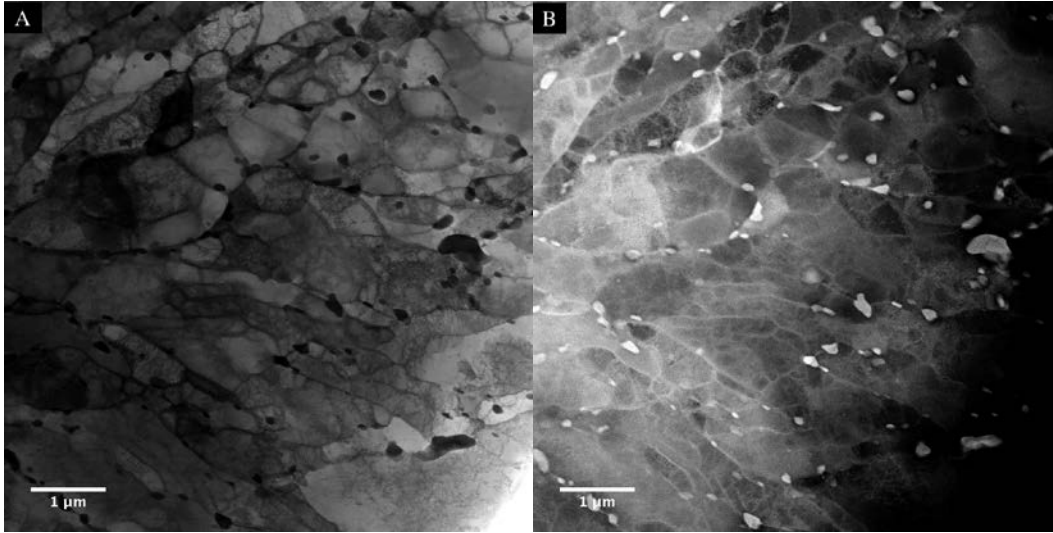


Figure A2. TEM images of T91 base metal. a) bright-field image b) annular dark field image of the sample.

B. Proton Irradiation Experiments (U. Michigan)

B1. Summary

Proton irradiations of T91 were completed in PWR primary water (PWR-PW), and in BWR normal water chemistry (BWR-NWC) at 320°C and 288°C, respectively. A 5.4 MeV proton beam at 2μA/cm² current density was used for these irradiations. The sample thickness was 80 microns, and the energy of the protons as they cross the oxide layer and enter the water is 1.7MeV. The LET in water is 5.6×10^{-11} J/cm/e⁻. The dose rate to the water directly at the interface is 500kJ/kg/s. Various regions of the irradiated sample were analyzed using SEM and Raman Spectroscopy and characterizations of the oxide microstructure were carried out on the TEM.

Table B1: List of irradiation experiments completed for T91.

Sample ID	Proton energy (MeV)	Temp (°C)	Water chemistry	Water dose rate (kGy/s)	Damage rate (dpa/s)	Duration (hr)
T91-PW-24IR	5.4	320	PWR-PW (3 ppm H ₂)	500kGy/s	2.2×10^{-7}	24
T91-NWC-24IR	5.4	288	BWR-NWC (2 ppm O ₂)	500kGy/s	2.2×10^{-7}	24

B2. Proton Irradiation Experimental conditions

Two T91 samples were irradiated for 24 hr under the experimental conditions listed in Table B1. Water loop data and beamline data are shown in Figures B1 and B2 for PWR-PW condition and Figures B3 and B4 for BWR-NWC condition.

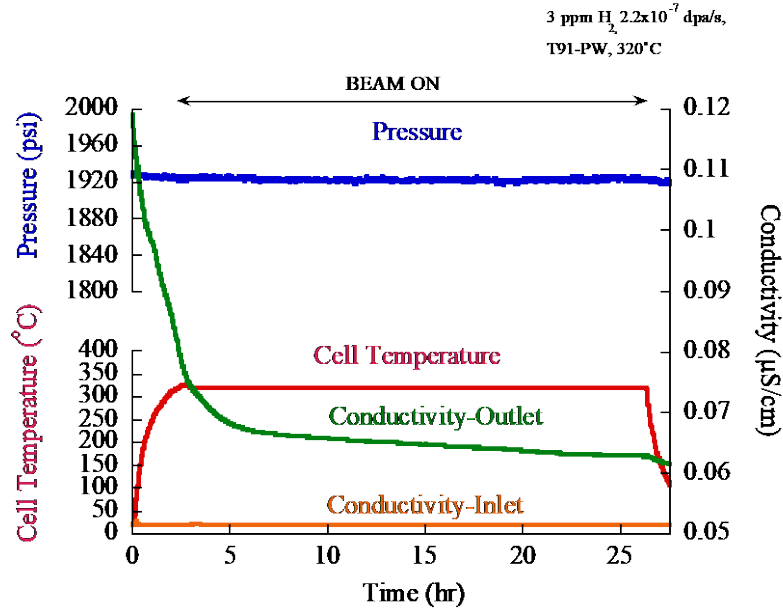


Figure B1: Water loop data of 24 hr proton irradiation of T91 in 320°C 3 ppm H_2 water at a damage rate of 2.2×10^{-7} dpa/s.

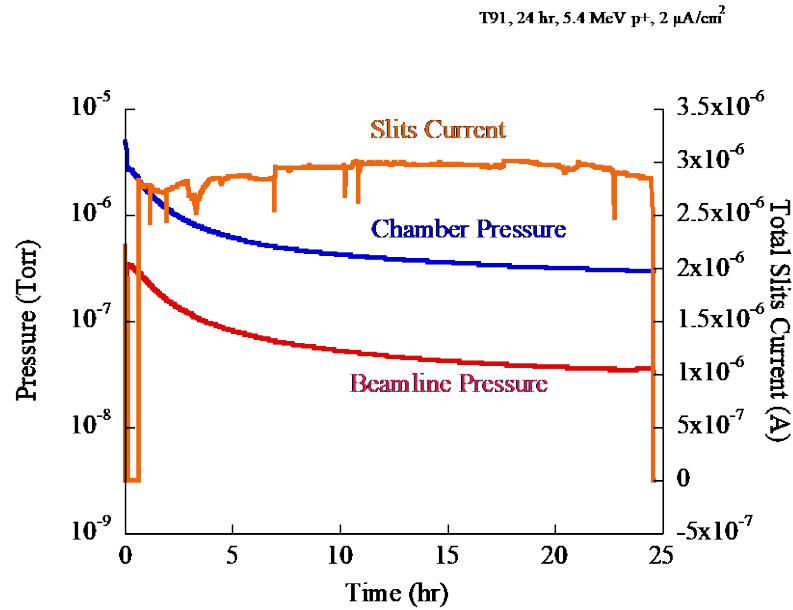


Figure B2: Beam current and pressure in the beamline and target chamber for the T91 proton irradiation experiment in PWR-PW condition.

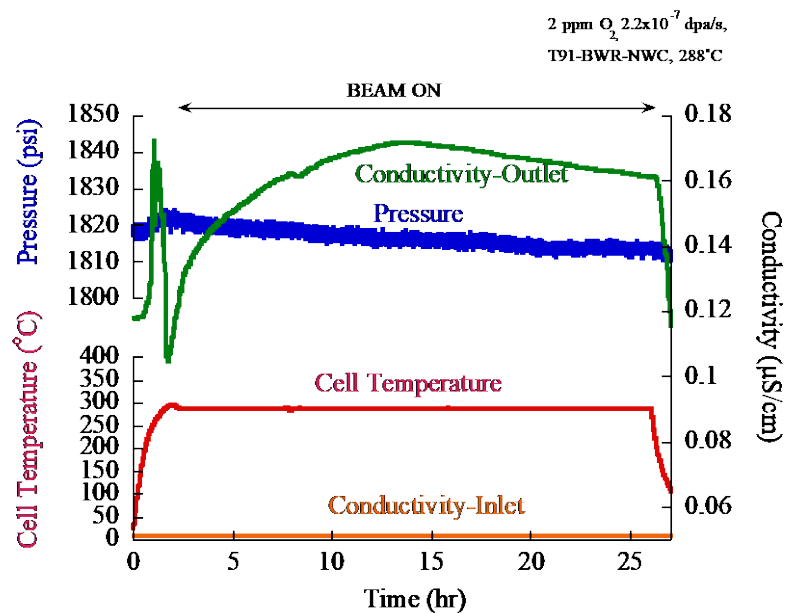


Figure B3: Water loop data of 24 hr proton irradiation of T91 in 288°C 2 ppm O_2 water at a damage rate of 2.2×10^{-7} dpa/s.

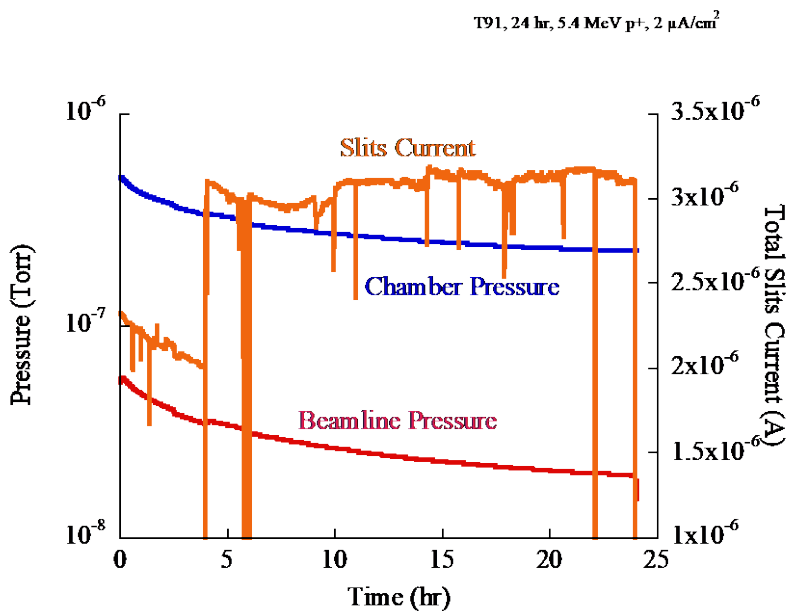


Figure B4: Beam current and pressure in the beamline and target chamber for the T91 proton irradiation experiment in BWR-NWC condition.

B3. Post Irradiation Characterization

Three distinctive regions of the sample surface were characterized, namely the Irradiated Region (IR), Radiolysis Affected Region (RAR) and the Unirradiated Region (UR).

Surface Oxide Morphology Analysis

Sample T91-PW-24IR has a matte gray appearance after 24 hr exposure in primary water condition; an SEM image with circles outlining each region is shown in Figure B6. Oxide morphologies in IR and RAR regions were similar. In both regions an irregular shaped outer oxide was observed with particle size of ~ 500 nm. In the UR region oxide particles were faceted with a size of ~ 1 μm as indicated in Figure B5.

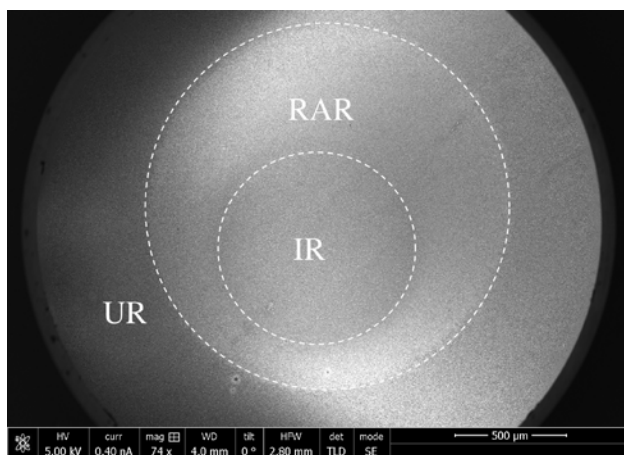


Figure B5: SEM image of sample T91-PW-24IR. The irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR) are indicated by the dotted line.

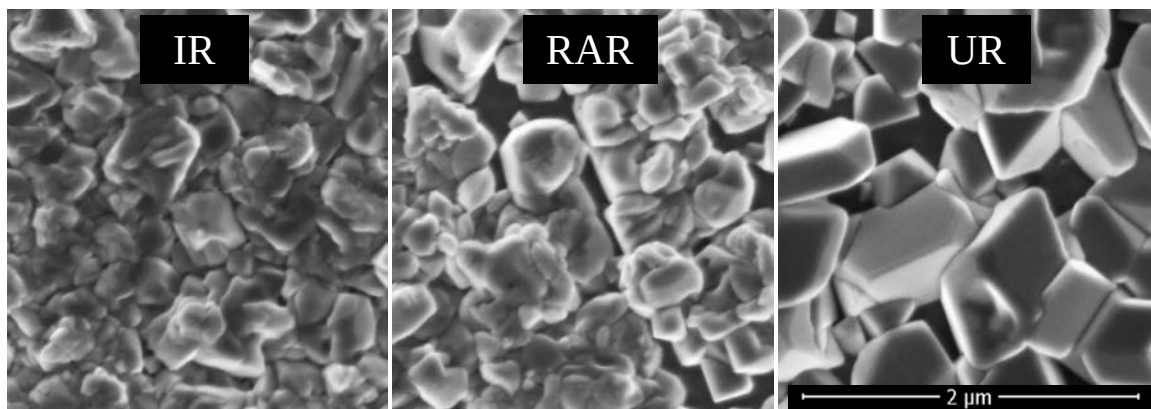


Figure B6: High magnification SEM images of the three regions observed on sample T91-PW-24IR.

Sample T91-BWR-24IR was slightly discolored after 24 hr of exposure in BWR-NWC water chemistry. In Figure B7, the IR and RAR regions can still be observed on the surface of the sample. However, the high magnification SEM images shown in Figure B8 indicated that there was no significant difference in terms of oxide particle size and morphology.

FIB lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared and TEM analysis was carried out on these TEM lamellas.

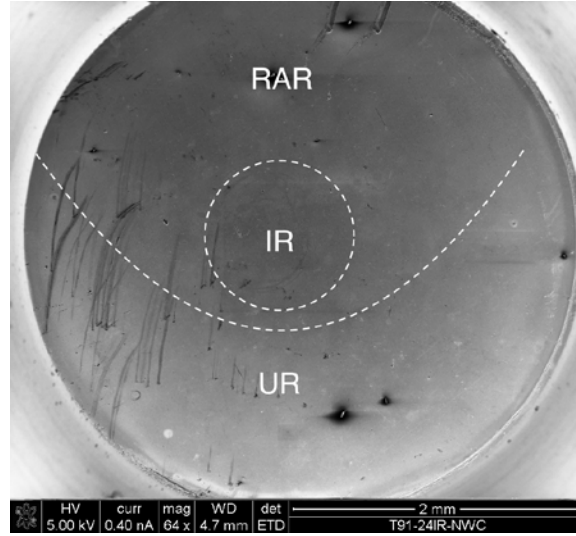


Figure B7: SEM image of sample T91-BWR-24IR. The irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR) are indicated by the dotted line.

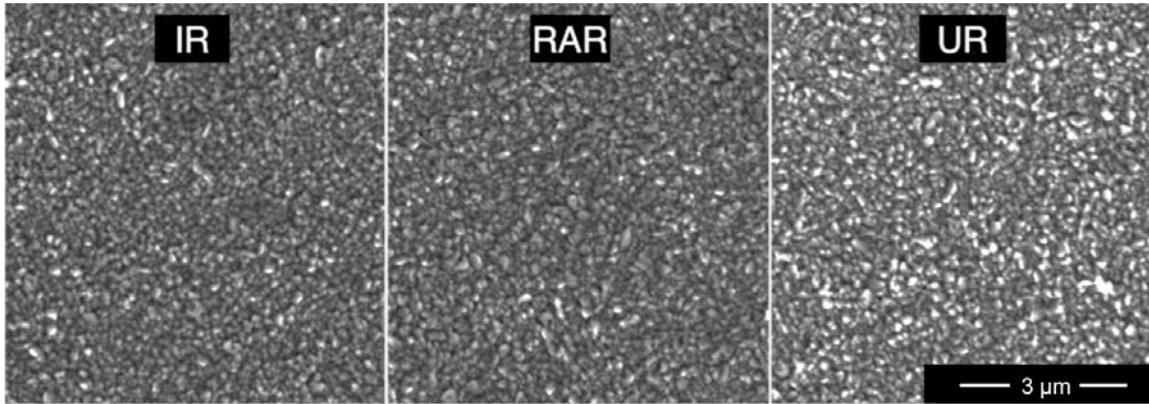


Figure B8: High magnification SEM image of the three regions observed on sample T91-BWR-24IR.

Oxide Phase Analysis with Raman Spectroscopy

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated samples. Spectra were recorded using a Renishaw inVia microscope with a RenCam CCD detector. The spectra were collected using a 633 nm wavelength red laser, at a typical laser power of 50 mW, during a total of 500 s of acquisition time.

All three regions (IR, RAR and UR) on the irradiated samples were measured using Raman spectroscopy. Three individual spectra were also taken in each region for data consistency check.

For **sample T91-PW-24IR**, the Raman peaks related to α -Fe₂O₃ were observed in the IR and RAR regions as shown in Figure B9. This observation indicated that when the sample surface was in contact with the radiolyzed water, the corrosion potential must be high enough for the formation of hematite. The cause of hematite formation could be the presence of short- and long-lived radical species and hydrogen peroxide. The short-lived radiolysis products (e.g. OH radicals) cannot escape the IR region, however, the product species H₂O₂ can be carried away from the IR region into the RAR region by convection flow of the heated water. The UR region showed a typical Raman spectrum of magnetite (Fe₃O₄). In primary water chemistry (HWC), the only stable iron oxide is magnetite which was observed in the UR region only. However, the 665 cm⁻¹ peak which was related to Fe₃O₄ was observed in all regions, indicating that the inner layer may also consist of magnetite phase. However, further compositional analysis of the inner oxide layer is required to confirm identity of the inner oxide. In the IR region, the oxide consisted of a spinel Fe_xCr_{3-x}O₄ inner layer and a Fe₂O₃ outer layer. Possible dissolution of Cr³⁺ could have occurred in the inner layer and substitution of Cr with Fe would result in an oxide that it is close to Fe₃O₄, which could be the reason for the presence of 665 cm⁻¹ Fe₃O₄ peak.

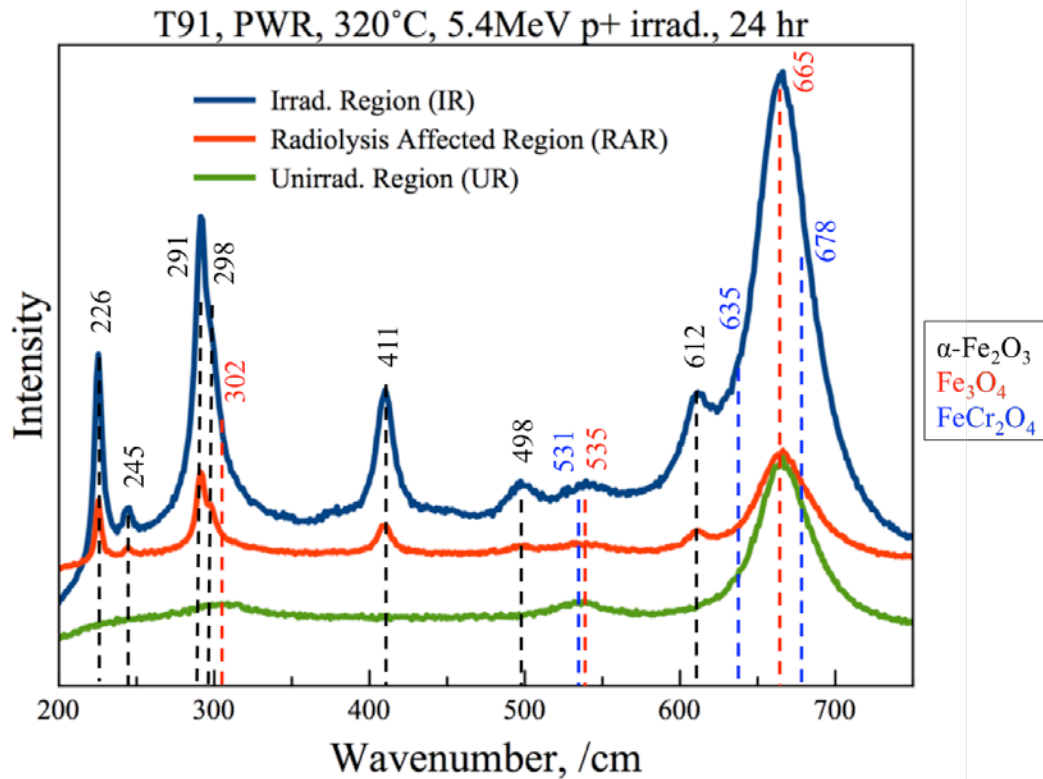


Figure B9: Raman spectra collected from IR, RAR and UR region on the 24 hr irradiated T91 sample in primary water condition.

For **T91-NWC-24IR**, the Raman peaks related to Fe₂O₃ are more intense in the IR and RAR region as shown in Figure B10. This indicates that oxide in those regions maybe thicker compared with the UR region. Also some of the peaks cannot be fitted by a single peak of Fe₂O₃ or Fe₃O₄, which suggests both oxide phases maybe present in the spectra. However, in BWR-NWC water chemistry, Fe₂O₃ is still the dominant oxide, with possible

Fe substituting Cr in FeCr_2O_4 . A weak shoulder peak at 635 cm^{-1} for FeCr_2O_4 could be the evidence for the Cr dissolution mechanism.

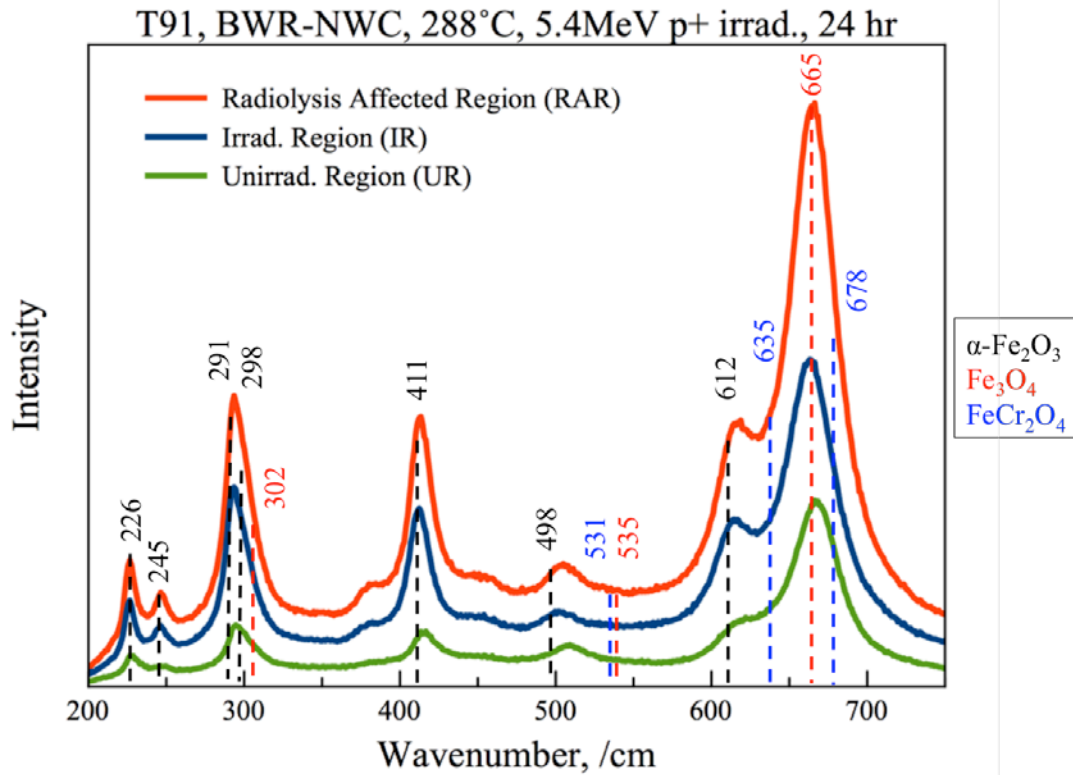


Figure B10: Raman spectra collected from irradiated region, unirradiated regions and the radiolysis affected region on the 24 hr irradiated T91 sample in BWR-NWC water condition.

Oxide Morphology with TEM

TEM lamellas from all three regions (IR, RAR and UR) were prepared using FIB, and a JEOL 3100R05 TEM/STEM was used for TEM analysis.

The high angle annular dark field (HAADF) images were collected for oxide thickness analysis. Under such imaging conditions, the oxide would have a dark contrast compared to metal substrate or platinum protective coating.

On **sample T91-PW-24IR**, as shown in Figure B11, the oxide layers appeared to have a double layer structure. The outer layer consisted of large faceted crystals that were grown by precipitation; while the inner layer consisted of finer grain oxides. The boundaries between inner and outer oxide were clearly visible, which could represent the original metal surface if inward diffusion of oxygen was assumed as the only corrosion mechanism for inner oxide growth. Average total oxide thickness, individual inner and outer layer thickness were listed in Table B2.

For **T91-NWC-24IR**, the HAADF STEM images shown in Figure B12, had indicated that the oxide layers were much thinner compared with the hydrogenated (and

higher temperature) condition. The inner and outer oxide layer became indistinguishable since the oxides were only 100-200nm thick.

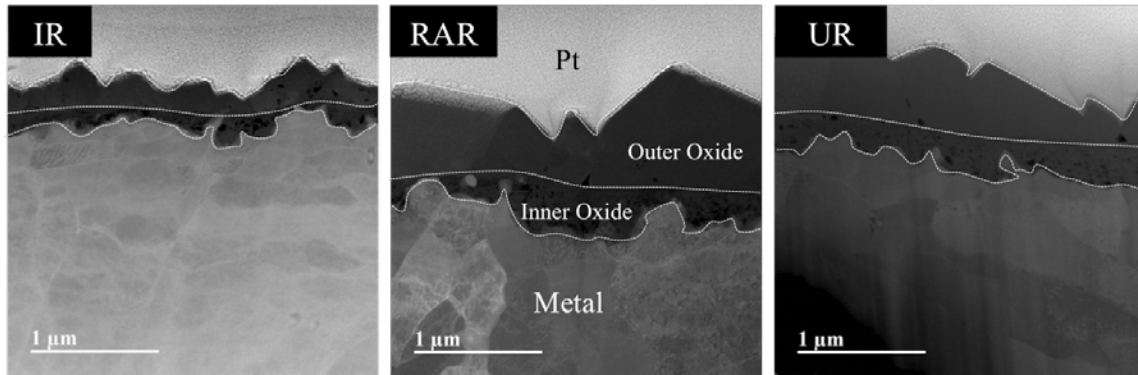


Figure B11: High Angle Annular Dark Field STEM (HADF-STEM) images of the FIB lamellas taken from the irradiated sample T91-PW-24IR.

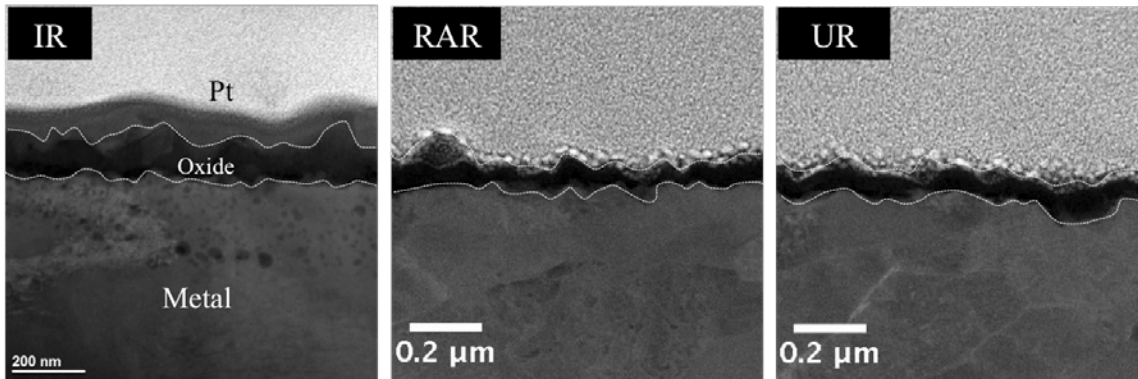


Figure B12: HAADF-STEM images of the FIB lamellas taken from the irradiated sample T91-NWC-24IR.

Table B2: Oxide thickness of outer and inner layers observed on samples irradiated in both PW and NWC conditions.

Sample	Region	Outer Oxide (μm)	Inner Oxide (μm)	Total Oxide (μm)
T91-PW-24IR	IR	0.239 ± 0.022	0.118 ± 0.008	0.358 ± 0.020
	RAR	0.560 ± 0.081	0.275 ± 0.050	0.836 ± 0.082
	UR	0.585 ± 0.056	0.253 ± 0.024	0.846 ± 0.053
T91-NWC-24IR	IR	-	-	0.125 ± 0.011
	RAR	-	-	0.083 ± 0.008
	UR	-	-	0.082 ± 0.004

Oxide Composition Analysis with EDS

Energy Dispersive x-ray Spectroscopy (EDS) was used to determine the oxide compositions. The EDS spectra were collected on JEOL 2010F STEM with EDAX detector.

For hydrogenated water conditions in **sample T91-PW-24IR**, EDS results of IR and UR region are shown in Figure B13. The IR region oxide composition was consistent with Fe_2O_3 , which is 40 at% Fe and 60 at% O for the outer oxide, and iron rich $\text{Fe}(\text{Cr},\text{Fe})_2\text{O}_4$ spinel for inner oxide. The spinel oxide was expected to be a mixture of FeCr_2O_4 and Fe_3O_4 inverse spinel oxides. This mixed phase oxide layer would give an iron rich appearance in the EDS spectrum. The presence of two phases in the inner oxide was also supported by the Raman data shown in Figures B9 and B10, where the peaks between $600 - 700 \text{ cm}^{-1}$ cannot be completely fitted with 612 cm^{-1} ($\alpha\text{-Fe}_2\text{O}_3$) and 665 cm^{-1} (Fe_3O_4) peaks, the 635 cm^{-1} and 678 cm^{-1} peaks have to be added to completely fit the spectrum. EDS result from the UR region had confirmed that the outer oxide was Fe_3O_4 (theoretical values for Fe_3O_4 is 43 at% Fe and 57 at% O), and the UR region inner oxide was also made up by two spinel oxides.

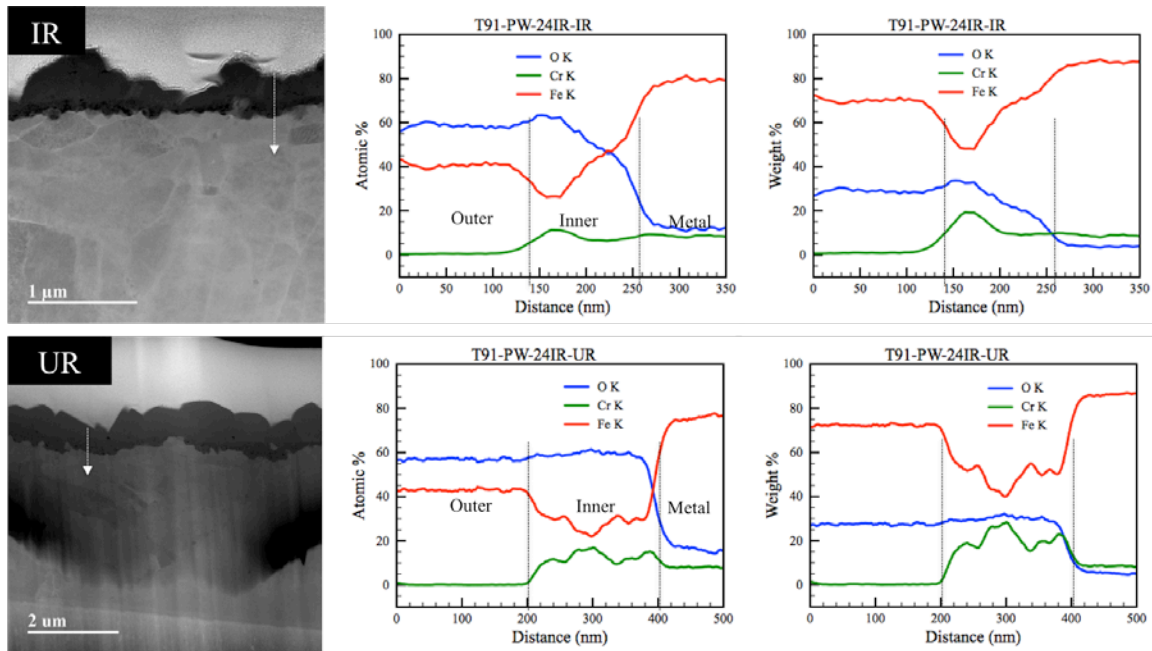


Figure B13: EDS line scans of oxide regions (IR and UR) formed on sample T91-PW-24IR.

For the NWC condition of **sample T91-NWC-24IR**, EDS results of IR and UR region are shown in Figure B14. In the IR and UR regions, Fe was slightly enriched in the outer oxide (almost 50 at% Fe and 50 at% O was shown in both case) and Cr enrichment was only observed in the IR region inner oxide. In the inner oxide, Cr enrichment could be caused by outward diffusion of Fe, but without irradiation, the Fe loss in the UR region seem to be much less.

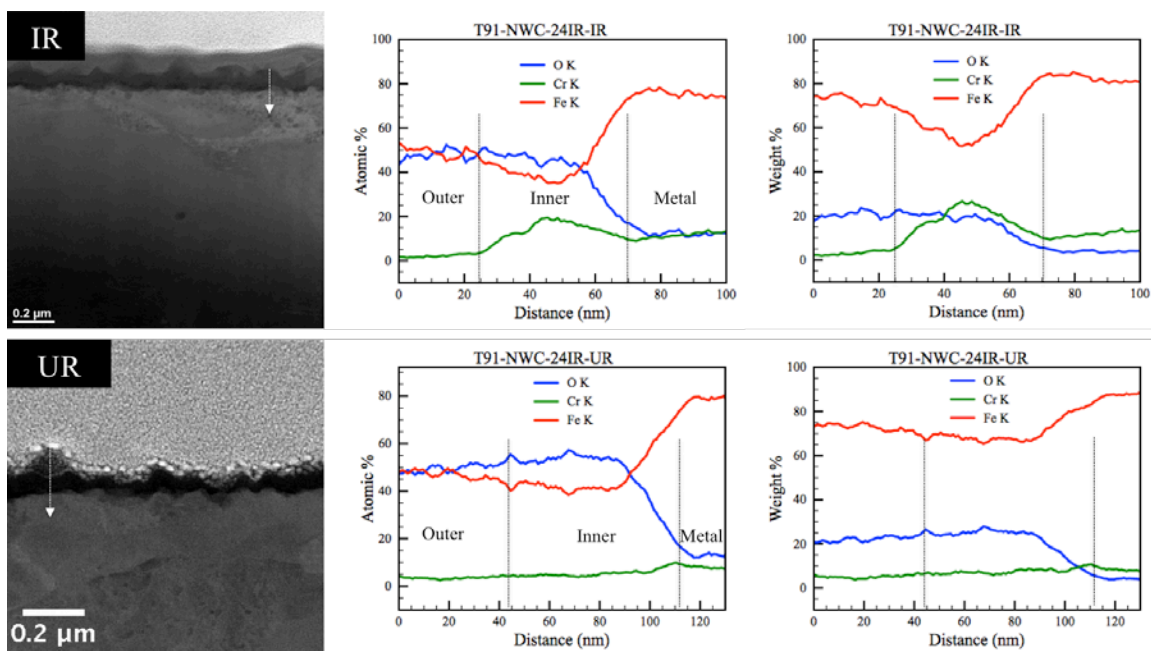


Figure B14: EDS line scans of oxide regions (IR and UR) formed on sample T91-NWC-24IR.

Oxide Phase Identification with Selected Area Electron Diffraction (SAED)

SAED analysis was carried out on the outer oxide of **sample T91-PW-24IR**, to support the Raman results of identifying different oxide species. Electron diffraction patterns from individual outer oxide particles in IR and UR regions were taken. Oxide particle from the IR region was identified as α -Fe₂O₃ particle, with rhombohedral crystal structure as shown in Figure B15, while the particle in the UR region was identified as Fe₃O₄ particle with face centered cubic crystal structure as shown in Figure B16. As a result, oxide species identified by Raman spectra was consistent with SAED diffraction results. The oxide that formed in NWC condition produced the same Raman spectrum as the IR region on the PW sample. Based on the assumption that only same oxide species would give the same Raman response, the oxide particle was not analyzed on the NWC sample.

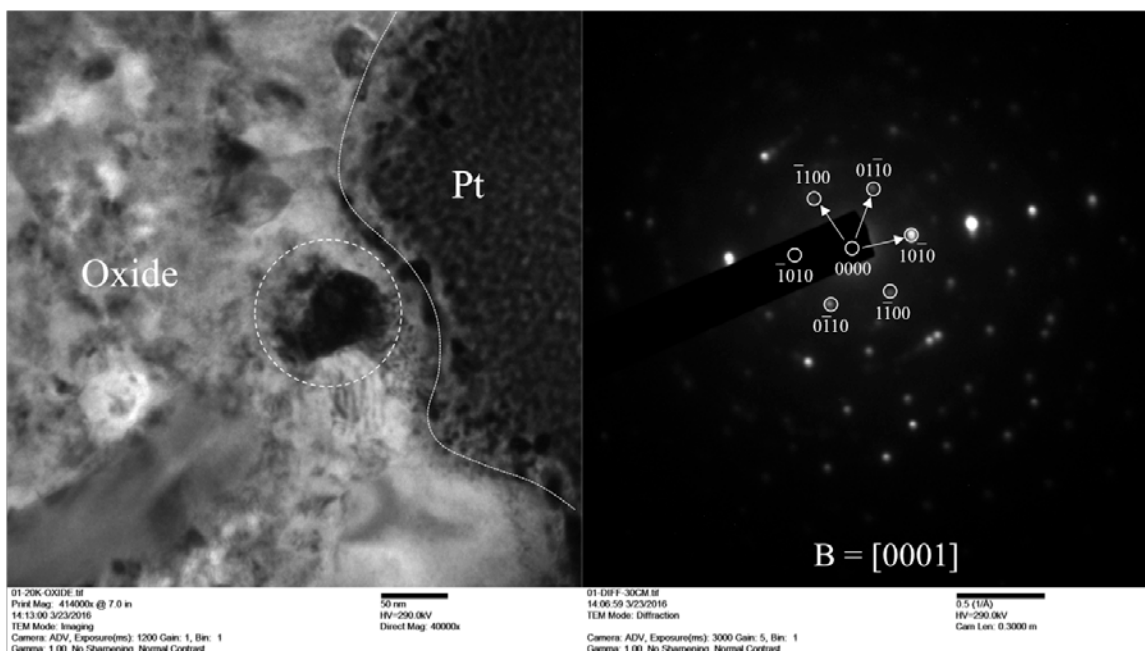


Figure B15: TEM image of the IR region outer oxide particle where the SAED pattern was taken and diffraction pattern of the [0001] zone axis.

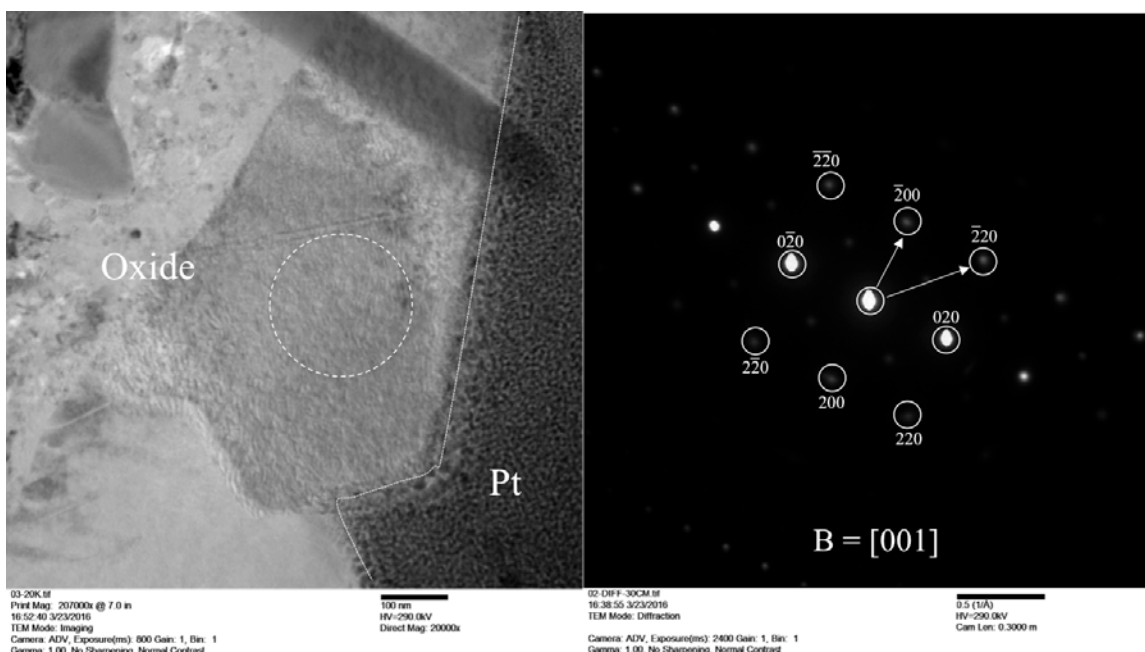


Figure B16: TEM image of the UR region outer oxide particle where the SAED pattern was taken and diffraction pattern of the [001] zone axis.

Proton Post Irradiation Characterization Summary

The oxide species found on irradiated samples under different conditions were confirmed using Raman and SAED and the findings were summarized in Table B3.

Table B3: Summary of the oxide species found on T91 in PW and NWC conditions under proton irradiation.

Samples	Regions	Outer Oxide/Inner Oxide	
		NWC 288°C, 2 ppm O ₂	PW 320°C, 3 ppm H ₂
T91	IR	$\alpha\text{-Fe}_2\text{O}_3$ $/\text{Fe}(\text{Cr}, \text{Fe})_2\text{O}_4$	$\alpha\text{-Fe}_2\text{O}_3/\text{Fe}(\text{Cr}, \text{Fe})_2\text{O}_4$
	RAR		
	UR		$\text{Fe}_3\text{O}_4/\text{Fe}(\text{Cr}, \text{Fe})_2\text{O}_4$

C. Electron Irradiation Experiments (ND)

C1. Summary

Electron irradiations of T91 were completed (samples ID and conditions are listed in Table C1) in PWR primary water (PWR-PW), and in Argon saturated water chemistry at 320°C and 288°C, respectively. An additional irradiation of T91 steel using a 2.5 MeV electron beam in 288°C water containing 2 ppm O₂ for 24 hrs was completed later on in the year. A 2.5 MeV electron beam at 120 $\mu\text{A}/\text{cm}^2$ current density was used for these irradiations. Given 250micron sample thickness, energy of electrons as they cross the oxide layer and enter the water is ca. 1.5MeV, so that they are still relativistic, and have LET of 1.9×10^6 eV/cm/e-. Dose rate to the water at the surface is ca. 170 kGy/s. Post-irradiation characterization of various regions of the irradiated samples was completed by means of Raman spectroscopy, SEM, TEM imaging and EDX line scans.

Table C1: List of irradiation experiments completed in this quarter.

Sample ID	e- Energy (MeV)	Temp (°C)	Water chemistry	current density (mA/cm ²)	Water dose rate (kGy/s)	Duration (hr)
T91-320H2- 24IR	2.5	320	3 ppm H ₂	120	170	24
T91- 288Ar-24IR	2.5	288	Ar Saturation	120	170	24
T91-NWC	2.5	288	2 ppm O ₂	120	170	24

C2. Summary of Irradiations

- a) PWR conditions. A T91 sample was irradiated 24 hours at temperature 320°C. The pressure of water was 158 bar and flow was equal 15 ml/min. The water was saturated by 3 ppm H₂ (ultra-high purity). Inlet conductivity was stable (0.05-0.06 $\mu\text{S}/\text{cm}$) during the experiment.



Figure C1: Photo of the 24 hour electron-beam irradiated T91 in 3 ppm H₂ saturated water.

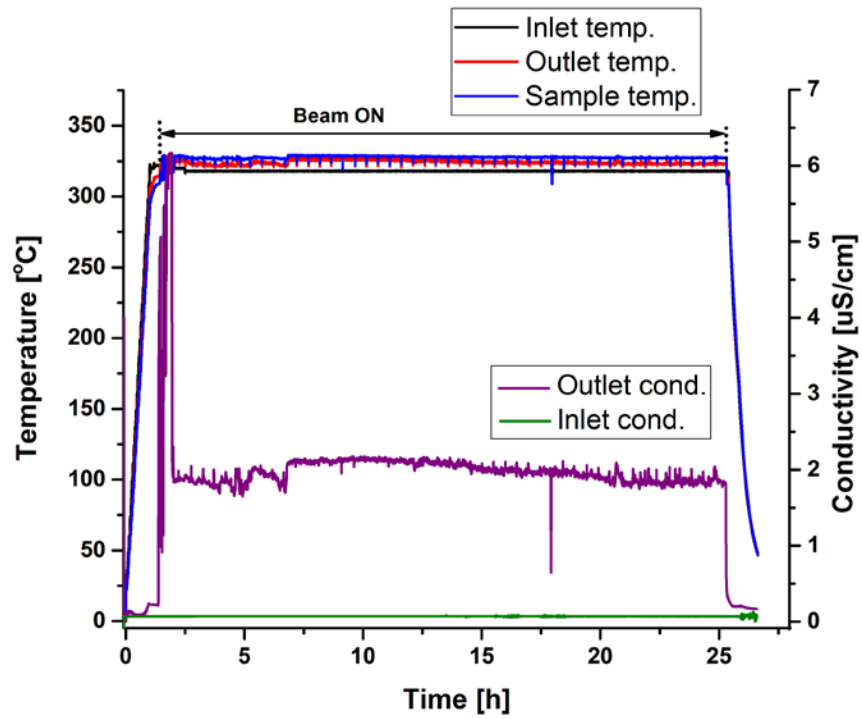


Figure C2: Temperature of water on Inlet, Outlet and Sample (left axis) during irradiation. Inlet and Outlet conductivity of water (right axis).

- b)** BWR condition. The T91 sample was irradiated 24 hours at temperature 288°C. The pressure of water was 155 bar and flow was equal 15 ml/min. The water was saturated by Argon (ultra-high purity). Inlet conductivity was stable (0.05-0.06 $\mu\text{S/cm}$) during experiment.

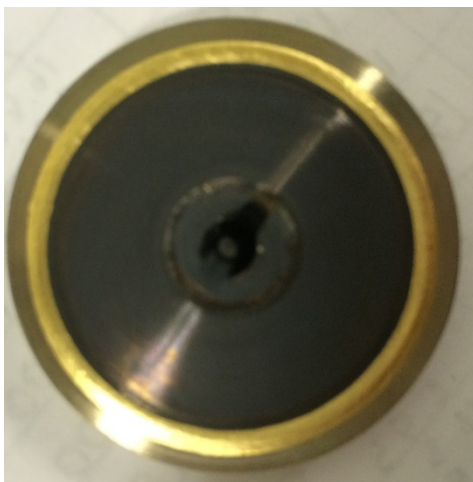


Figure C3: Photo of the 24 hour electron-beam irradiated T91 in Argon saturated water.

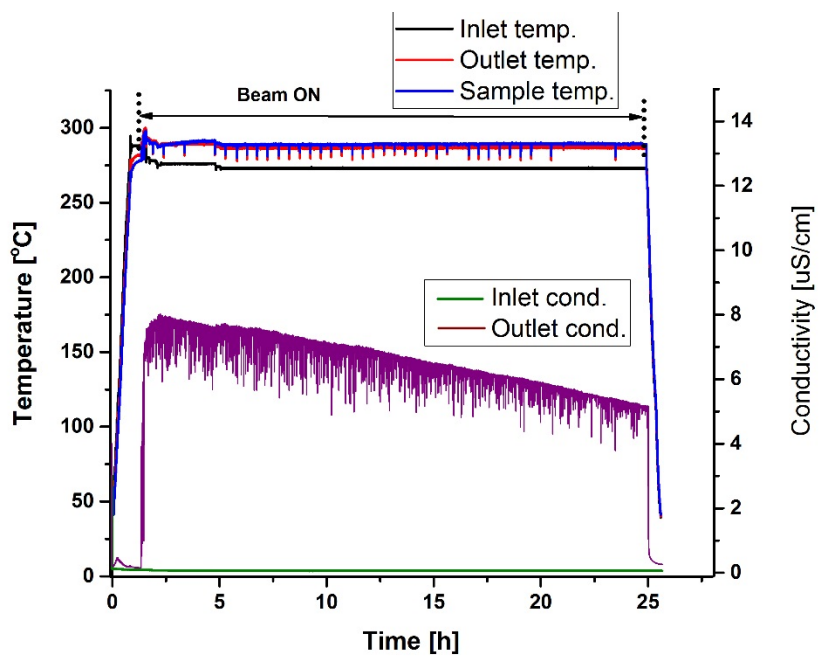


Figure C4: Temperature of water on Inlet, Outlet and Sample (left axis) during irradiation. Inlet and Outlet conductivity of water (right axis).

C3. Post Irradiation Characterization of T91 H₂ sample

Optical microscopy and SEM Imaging – Oxide Morphology

All T91 steel samples (e-beam irradiated) were analyzed via microscopy. Both samples were slightly discolored after 24 hr of e-beam exposure. The sample irradiated in Ar condition was found to be contaminated with an over-layer of carbon. It was subsequently confirmed that this came from the graphite packing material used to seal the sapphire window above the sample. Measures are being taken to modify the cell to avoid this in the future. Consequently this part of the post-irradiation characterization report focuses entirely on the T91 H₂-saturated sample at PWR conditions. Section C4 at the end of this milestone focuses on the T91 sample irradiated in O₂ saturated water.

Under the optical microscopy, three distinctive regions can be identified on the sample surface, Irradiated Region (IR), Radiolysis Affected Region (RAR) downstream of the radiation, and Unirradiated Region (UR) upstream of the radiation zone. These are shown in Figure C5 for the T91 H₂-saturated sample. The irradiated area of the sample is defined as a circular-shaped area with diameter of about 2 mm.

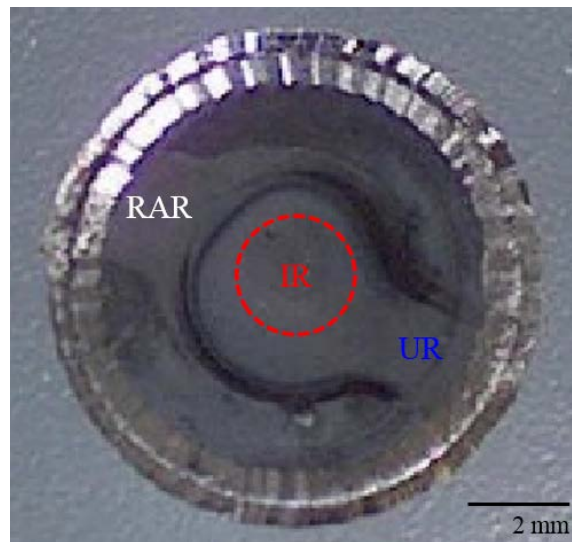


Figure C5: Post-irradiation optical image of 24-hour electron-beam irradiated T91 sample in H₂ saturated water. Representation of unirradiated region (UR), irradiated region (IR) and radiolysis affected region (RAR).

The high magnification SEM images in Figure C6 represent the oxide particles of the three different regions (UR, IR and RAR) in the T91 H₂-saturated sample. The particles in the UR and RAR region look very similar, however, the oxide particles in the RAR region seem more densely packed. Also, the oxide particles in the UR region have sharper edges than the oxide particles in the RAR region. In comparison to both UR and RAR region, the IR region particles are much larger in size and well defined in shape.

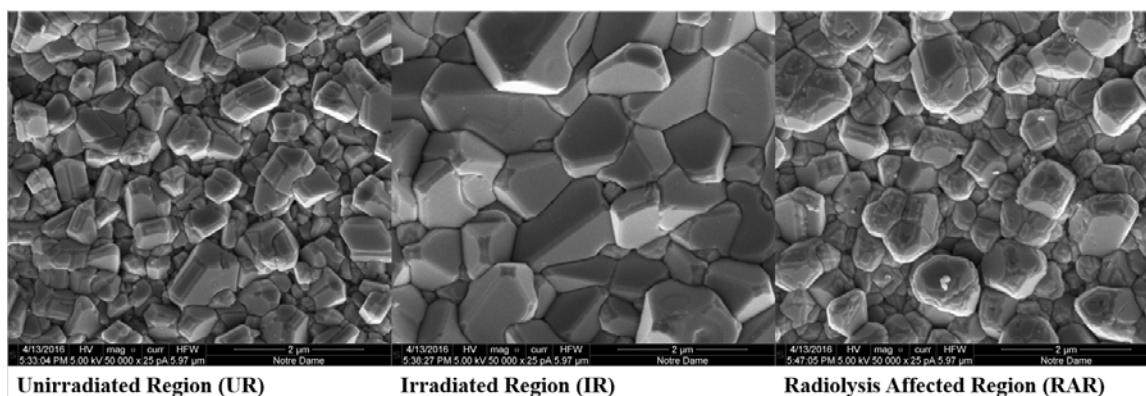


Figure C6: Post-Irradiation SEM images of 24-hour electron-beam T91 sample in Hydrogen saturated water. Representation of the three different regions, UR, IR and RAR.

TEM Imaging and EDX Line scans – Oxide Thickness

Focused ion beam (FIB) lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared for transmission electron microscope (TEM) analysis of the oxide layer thickness and morphology. The FIB lift-outs were prepared using the FEI-HELIOS dual beam FIB and the samples were further investigated via high magnification TEM images and EDX linescans, performed with the Titan TEM (FEI Titan 80/30 TEM) that is equipped with an energy-dispersive X-ray system by which line profiles can be measured. Both instruments are located at the Notre Dame Integrated Imaging Facility.

Illustration of the different layers (IR, RAR and UR) via TEM imaging is demonstrated in Figure C7 for the T91 H₂-saturated sample.

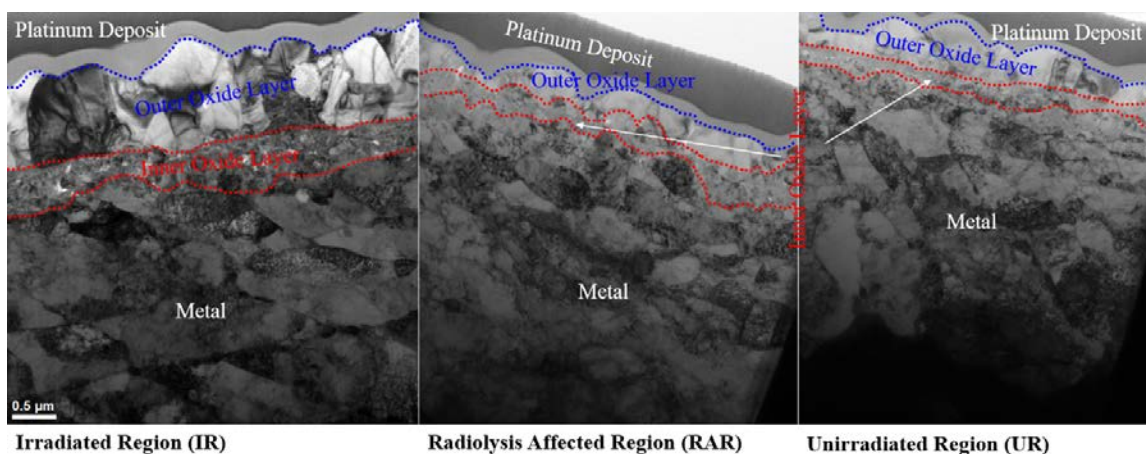


Figure C7: Post-Irradiation TEM images of 24-hour electron-beam T91 sample in Hydrogen saturated water. Representative of the three different regions (IR, RAR and UR).

The plot presented in Figure C8 compares the thickness between the different regions of interest in the T91 H₂-saturated sample. The plot provides the results obtained from measuring the distance from the top to the bottom of the oxide layer where approximately 50 different lines were considered in the measurements. The plot shows a slight increase in the outer oxide thickness from UR to RAR region and a larger increase in the oxide thickness of the IR region. The inner oxide thickness is represented by almost a linear increase through the different regions of interest, from UR inner thickness of approximately 200 nm to RAR inner thickness of approximately 300 nm to IR inner thickness of approximately 480 nm.

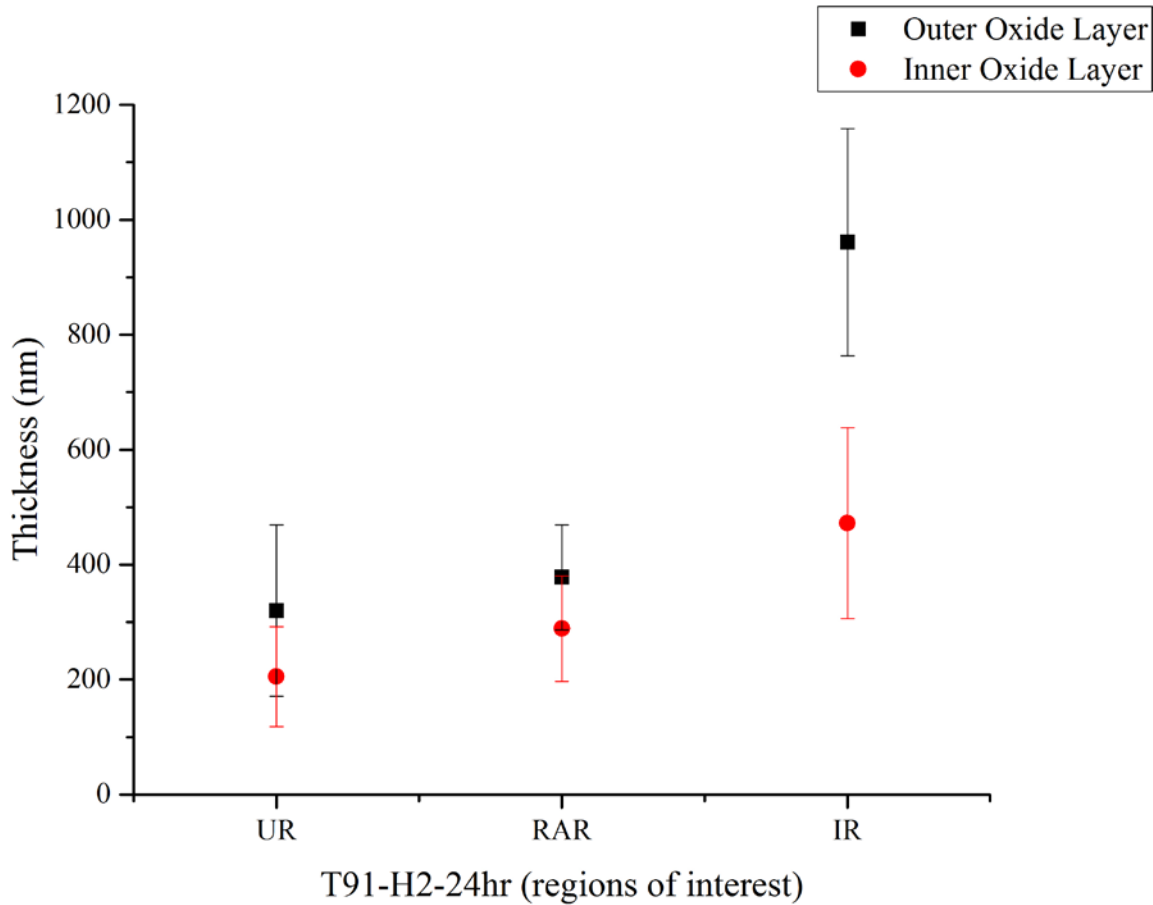


Figure C8: Oxide thickness comparison in the T91 sample in the Hydrogen saturated water. The plot represents the average oxide thickness (outer layer-black, inner layer-red) over the three different regions (UR, RAR and IR). The error bars indicate the 90% confidence limit associated with the thickness measurements.

EDX line scans were performed to reveal elemental distribution information about the sample. Multiple EDX line scans were completed on each sample and are shown in the following figures.

The EDX line scans of the UR region of the T91 sample in the H₂ saturated water are presented in Figure C9. It is apparent that the outer layer is filled with iron oxides. As suggested from the figure, there is iron depletion in the inner oxide layer, but chromium is

stable. In regards to the T91 metal region, the EDX line scans show spikes of either Oxygen or Chromium near the interface of the inner oxide layer and the metal layer. Since the interface region is rich with grain boundaries, Oxygen could easily diffuse towards the top parts of the metal region.

The EDX line scans of the RAR and IR region of the T91 sample in the H₂ saturated water are presented in Figure C10 and Figure C11, respectively. Similarly to the UR region, presence of iron oxides is apparent in the outer layer, and iron is depleted in the inner oxide layer. In regards to the T91 metal region, the EDX line scans show the highest content of Iron with small amount of Chromium and Molybdenum as they are constituents of the original metal.

Similar to the EDX results of the proton irradiated T91 sample in H₂ saturated water, the oxide composition in the IR and RAR regions was almost consistent with Fe₂O₃, which is 37 at% Fe and 63 at% O for the outer oxide, and iron rich Fe(Cr,Fe)₂O₄ spinel for inner oxide. EDX lines from the UR region had confirmed the presence of Fe₃O₄ in the outer oxide.

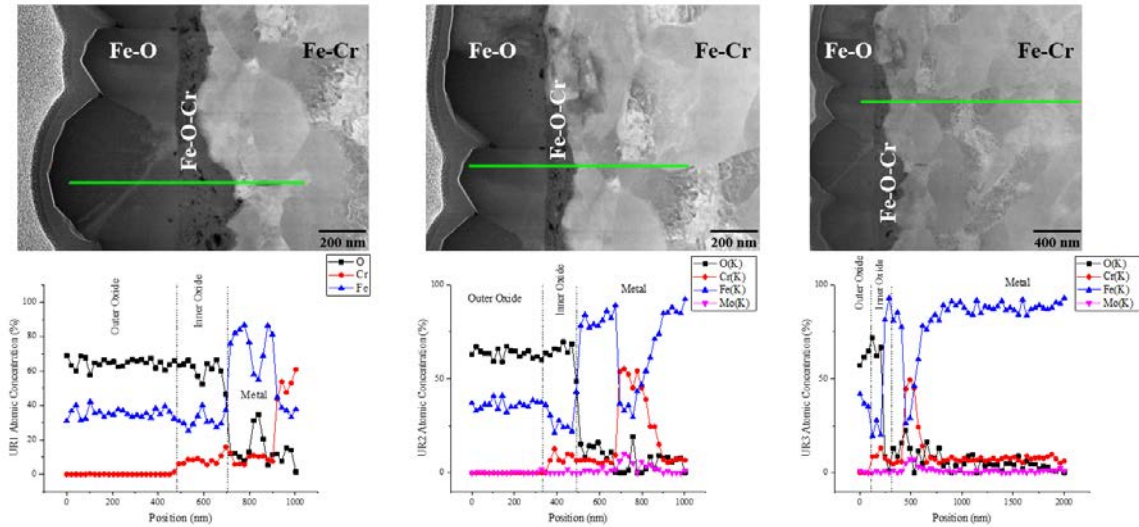


Figure C9: TOP: STEM bright field images of UR region of the T91 sample in the Hydrogen saturated water (the thin arrow shows the length of the EDX line scan and the direction is from left to right) BOTTOM: STEM EDX line scan results across the different layers of T91 sample in the Hydrogen saturated water (Outer, Inner Oxide layer and the T91 metal).

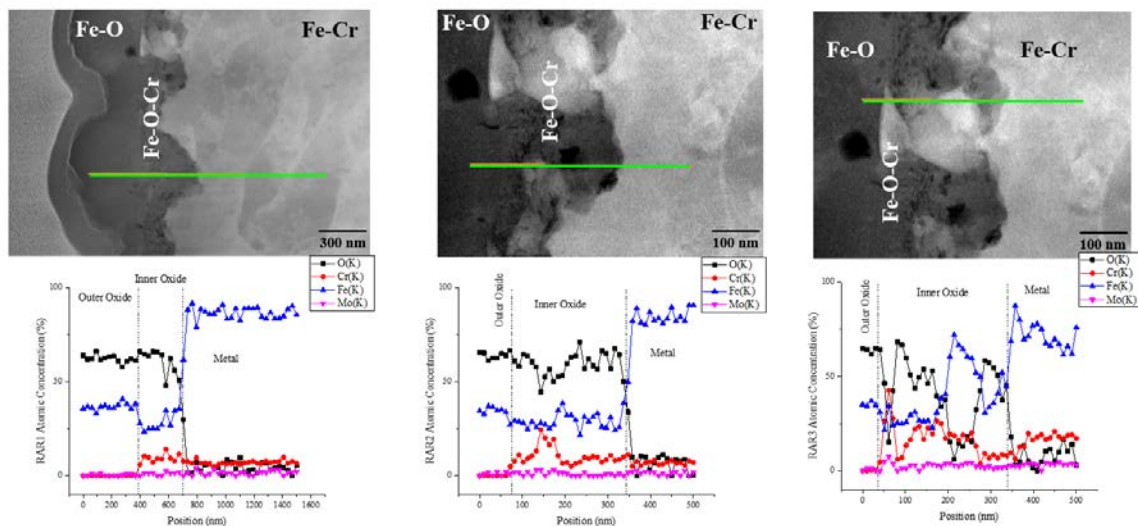


Figure C10: TOP: STEM bright field images of RAR region of the T91 sample in the Hydrogen saturated water (the thin arrow shows the length of the EDX line scan and the direction is from left to right) BOTTOM: STEM EDX line scan results across the different layers of T91 sample in the Hydrogen saturated water (Outer, Inner Oxide layer and the T91 metal).

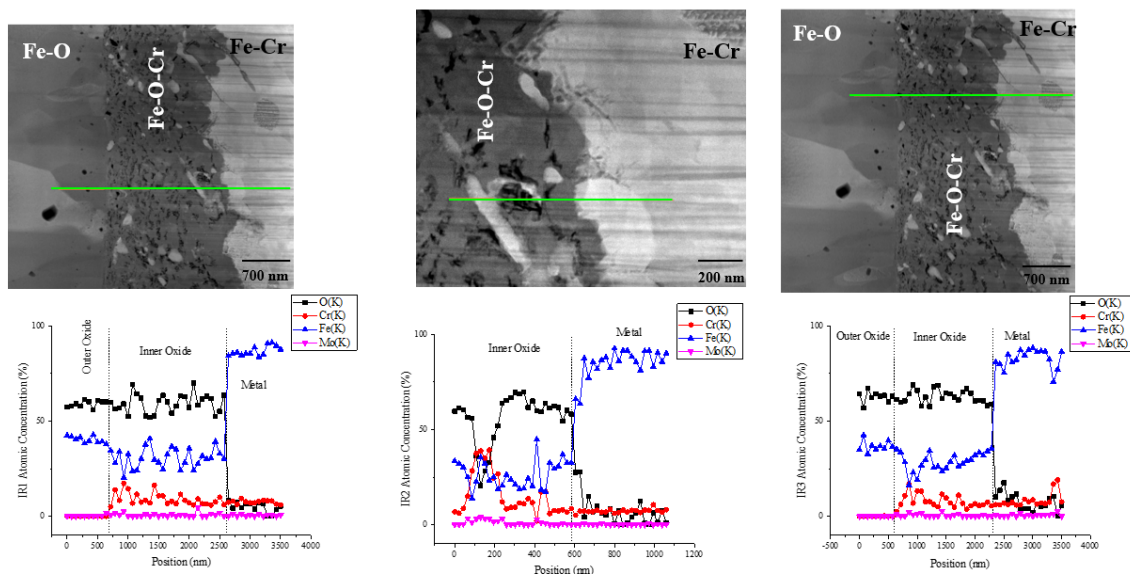


Figure C11: TOP: STEM bright field images of IR region of the T91 sample in the Hydrogen saturated water (the thin arrow shows the length of the EDX line scan and the direction is from left to right) BOTTOM: STEM EDX line scan results across the different layers of T91 sample in the Hydrogen saturated water (Outer, Inner Oxide layer and the T91 metal).

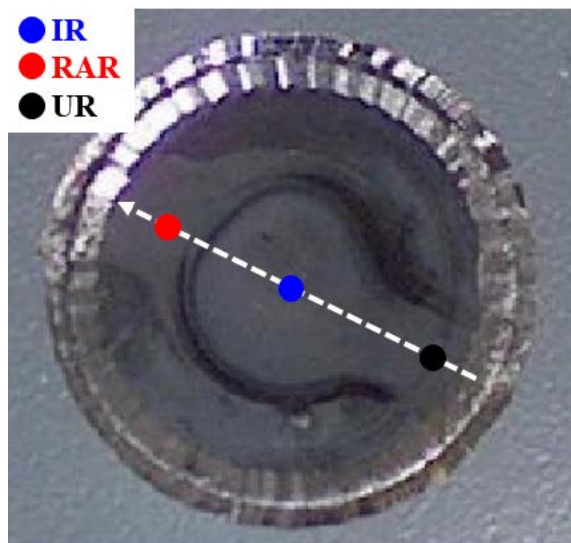
Raman Spectroscopy – Oxide Phase

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated sample. Spectra were recorded using a Micro-Raman Spectrometer (NRS-5100,

Jasco). The spectra were collected using a 532 nm wavelength green laser, at a typical laser power of 50 mW, during a total of 600s of exposure time.

Three regions on the irradiated sample were measured using Raman spectroscopy, irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR). Five individual spectra were also taken in each region for data consistency check.

Raman spectra of the UR, RAR and IR region of the T91 sample in the H_2 saturated water are presented in Figure C12. The majority of the peaks collected from the outer oxide layer in the RAR and IR regions were identified as Fe_2O_3 while the UR region spectrum featured only two peaks, both identified as Fe_3O_4 . This suggests that Fe_2O_3 forms on the surface of Fe_3O_4 .



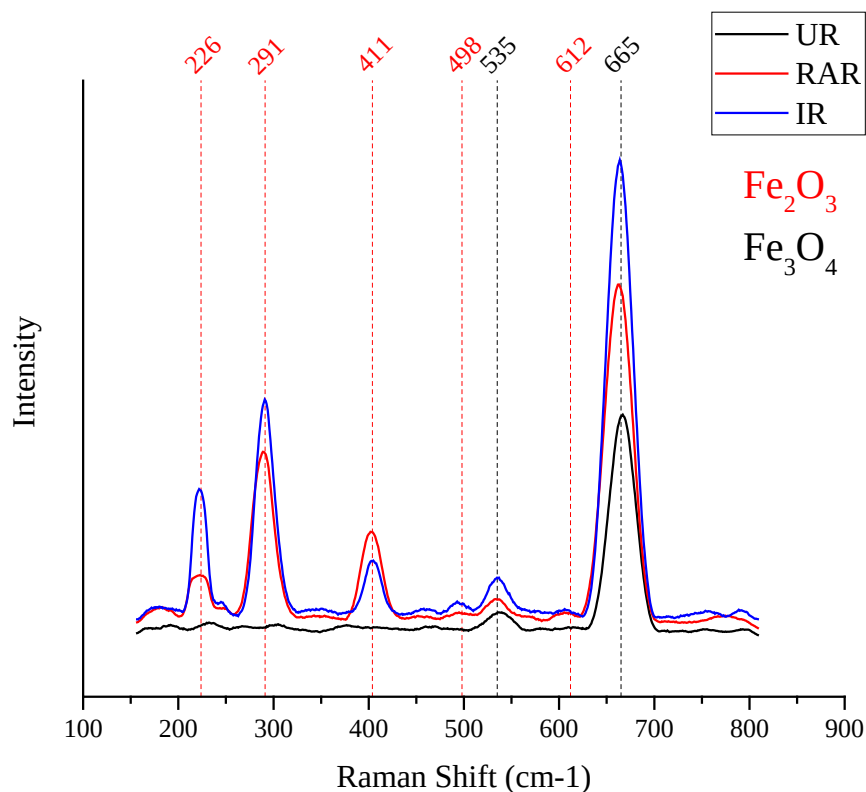


Figure C12: Post-Irradiation Raman spectra collected from 24-hour electron-beam T91 sample in Hydrogen saturated water. Representation of the three different regions (IR, RAR and UR). TOP: Photo of T91 sample with representation of locations on the sample where Raman spectrum was taken; BOTTOM: Raman spectra.

C4. Post Irradiation Characterization of T91 O₂ sample

Water loop data for T91 NWC 24 hr e-beam irradiated sample in 2 ppm Oxygen-saturated water is shown in the Figure C13 below. In this experiment, the outlet conductivity dropped from 0.40 to 0.32 $\mu\text{S}/\text{cm}$ during the course of the experiment compared to the unchanged inlet conductivity at 0.08 $\mu\text{S}/\text{cm}$. This indicates that as the sample surface developed a layer of oxide, the amount of dissolved metal that goes into solution decreases.

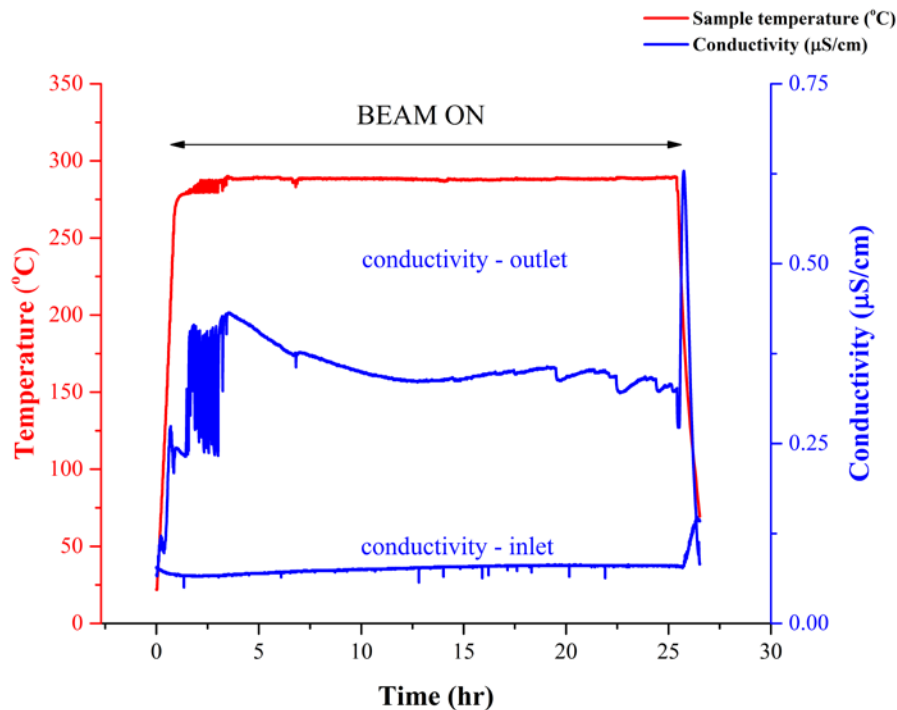


Figure C13: Water loop data of 24 hr electron irradiation of T91 NWC in 288°C 2 ppm O₂ water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

Optical microscopy and SEM Imaging – Oxide Morphology

Post-irradiation optical image of T91 NWC is shown in Figure C14. The irradiated area of the sample is presented by the red dotted circle with diameter of about 1 mm for better visualization, considering the irradiated region does not have a well-defined shape. It is clear from the image that the sample surface throughout all regions was discolored after 24 hours of e-beam exposure showing interference colors. The IR region of T91 NWC sample is characterized by a very dark green and grey color surrounded by dark maroon color.

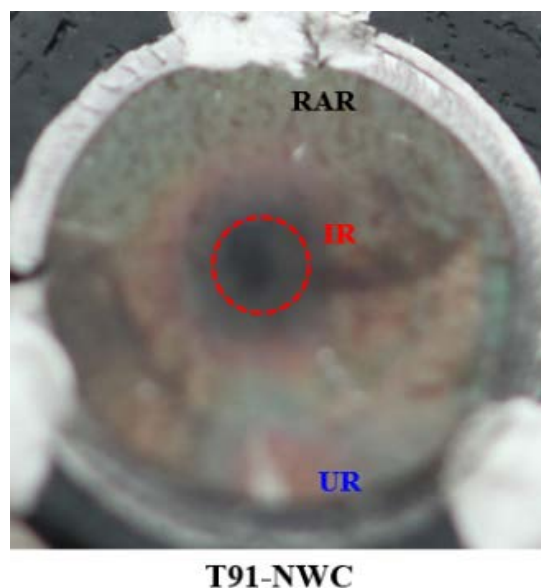


Figure C14: Post-irradiation optical image of T91 NWC 24-hour electron-beam irradiated samples in Oxygen-saturated water. Representation of the three different regions (UR, IR and RAR).

The high magnification SEM images in following figures represent the precipitated oxide particles of the three different regions in all three NWC samples.

The oxide particles in T91 NWC sample can be seen in Figure C15. Oxide morphologies in the UR and RAR regions are very similar. In both regions an irregular shaped oxide was observed with particle size larger than 3-4 μm . In the IR region oxide particles were mostly faceted with a size of $\sim 1 \mu\text{m}$ as indicated in Figure C15.

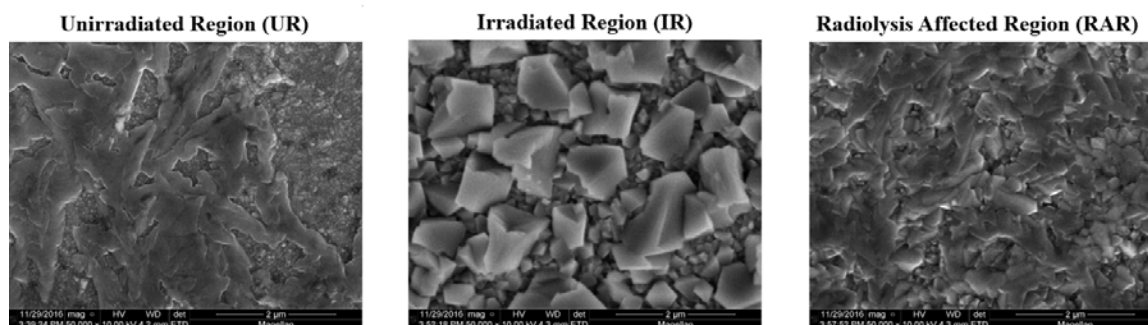


Figure C15: Post-irradiation SEM images of 24-hour electron-beam irradiated T91 NWC sample. Representation of the three different regions (UR, IR, RAR).

TEM Imaging and EDX Line scans – Oxide Thickness

Illustration of the different regions (UR, IR and RAR) via TEM imaging is demonstrated in Figure C16 for 24-hour electron-beam irradiated T91 NWC sample. As seen from the TEM images in Figure C16, the irradiated region of the T91 NWC sample features a thick

outer oxide or precipitation layer. In all three samples, the boundaries between the inner and outer oxide are not clearly visible. Also, there is a significantly larger oxide thickness in the IR region or T91 NWC sample (about 431 ± 157 nm) which is mostly due to the large precipitation layer.

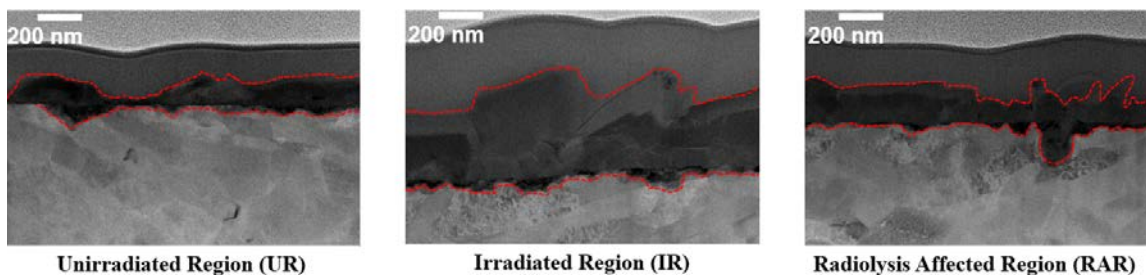


Figure C16: Post-Irradiation TEM images of 24-hour electron-beam T91 NWC sample in Oxygen-saturated water. Representation of the three different regions (UR, IR and RAR). The red dotted lines represent the oxide layer in the regions of interest.

EDX line scans were performed on the 24-hour electron-beam irradiated T91 NWC sample in Oxygen-saturated water to reveal elemental distribution information about the sample. Multiple EDX line scans were completed on each TEM sample and some are shown in the Figures C17, C18 and C19 for the UR, IR and RAR regions, respectively. The EDX line scans of this sample are very similar. Most of them show an outer oxide, inner oxide and metal region, and some of them show a platinum region. The outer oxide layer in the three regions of interest as the line scans suggest contains about 50-60% atomic concentration of Oxygen, about 30% atomic concentration of iron as well as about 10-30% atomic concentration of Nickel content. The inner oxide region is very similar in sense of Oxygen and iron content, however, the Nickel content has significantly dropped or it is non-existent. The inner oxide also features Chromium enrichment as it is a constituent of the original metal. The metal region of the UR sample features a metal-oxide transition region where the Oxygen content starts to decrease. This can be seen in TEM lamellas in which the sample is significantly thin and there is a region where grains overlap. In regards to the metal region of the IR and RAR regions, the EDX line scan shows the highest content of Iron (about 90-100%) with some Chromium enrichment as they are constituents of the original metal.

EDX of T91-NWC Unirradiated Region (UR)

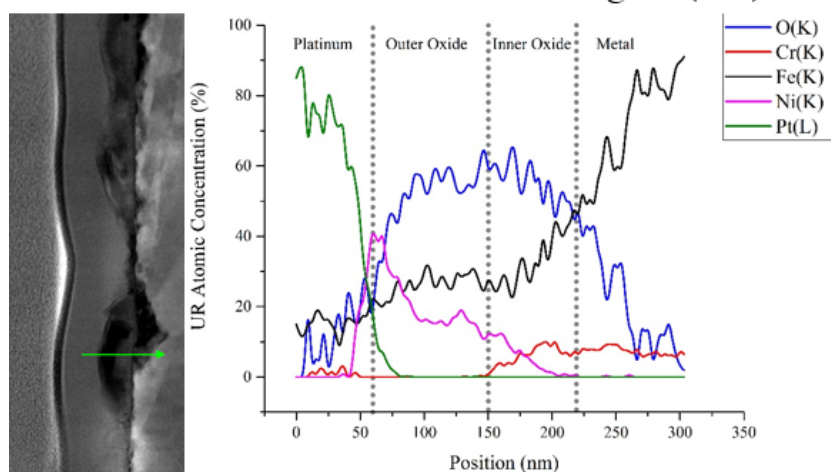


Figure C17: Left: STEM bright field image of UR region of the 24-hour electron-beam irradiated T91 NWC sample (the thin arrow shows the length of the EDX line scan and its direction). Right: STEM EDX UR line scan results, atomic concentration vs. position, representation of oxide and metal region of scan.

EDX of T91-NWC Irradiated Region (IR)

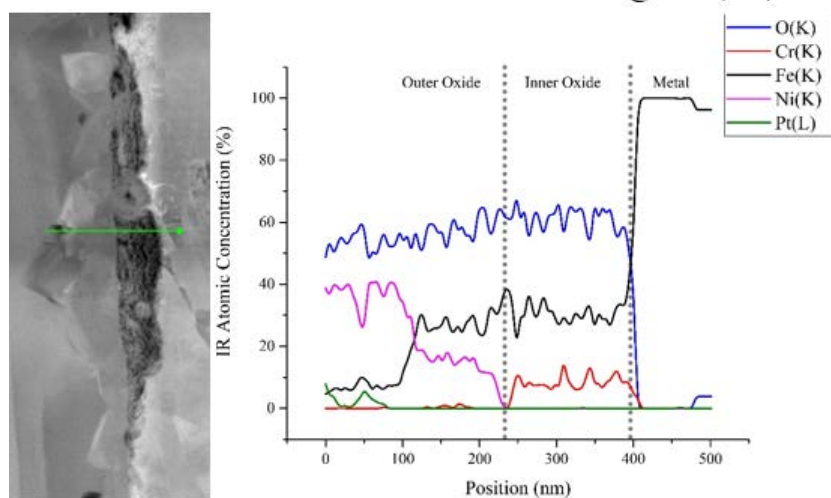


Figure C18: Left: STEM bright field image of IR region of the 24-hour electron-beam irradiated T91 NWC sample (the thin arrow shows the length of the EDX line scan and its direction). Right: STEM EDX IR line scan results, atomic concentration vs. position, representation of oxide and metal region of scan.

EDX of T91-NWC Radiolysis Affected Region (RAR)

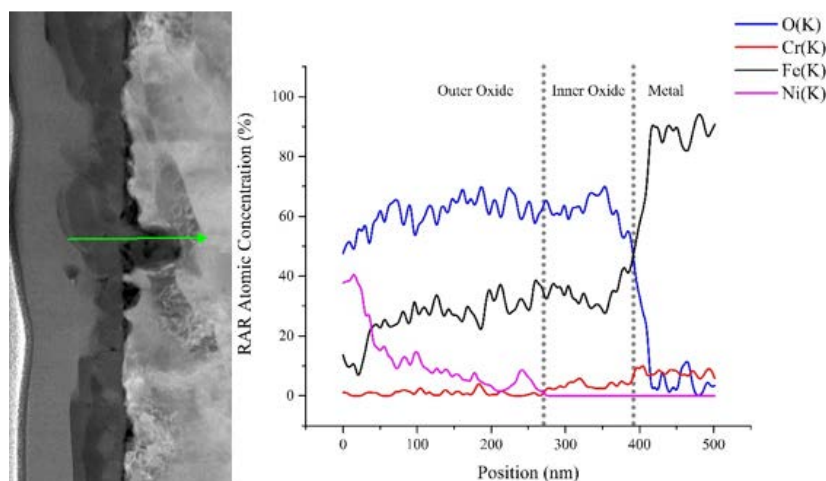


Figure C19: Left: STEM bright field image of RAR region of the 24-hour electron-beam irradiated T91 NWC sample (the thin arrow shows the length of the EDX line scan and its direction). Right: STEM EDX UR line scan results, atomic concentration vs. position, representation of oxide and metal region of scan.

Raman Spectroscopy – Oxide Phase

The post-irradiation Raman spectra for T91 NWC are shown in Figure C20. The black line represents the irradiated region, the maroon line represents the radiolysis affected region and the dark turquoise line represents the unirradiated region. The Raman peaks related to NiCr_2O_4 are present in all the regions of the sample which confirms the presence of Nickel in the EDX line scans. In addition to that, there might be presence of FeCr_2O_4 and Cr_2O_3 considering some of the peaks lay in between NiCr_2O_4 (blue dotted lines) and FeCr_2O_4 (pink dotted lines) or NiCr_2O_4 (blue dotted lines) and Cr_2O_3 (green dotted lines). Also, the radiolysis affected region of the T91 NWC samples suggests possible presence of $\alpha\text{-Fe}_2\text{O}_3$ again, based on some peaks being positioned in between NiCr_2O_4 (blue dotted lines) and $\alpha\text{-Fe}_2\text{O}_3$ (red dotted lines).

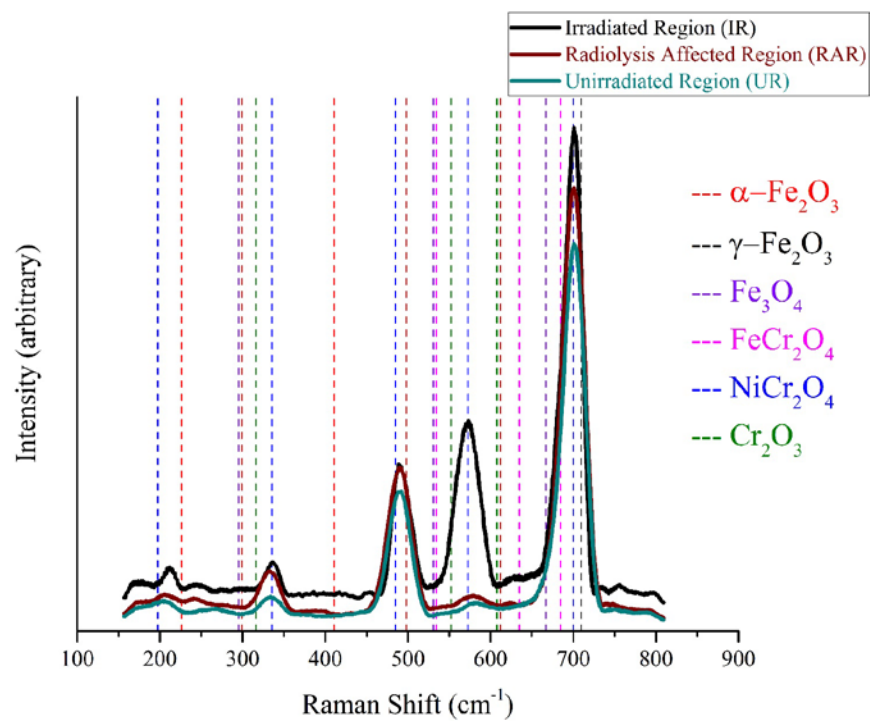


Figure C20: Post-Irradiation Raman spectra collected from the 24-hour electron-beam irradiated T91 NWC sample in Oxygen-saturated water. Representation of the three different regions (IR, RAR and UR) and associated Raman peaks.

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

June 2016 Milestone report for MA956 ODS Alloy

Four MA956 steel sample irradiations were completed to assess the corrosion behavior of this steel under reactor-like conditions. In this experiment the thin samples actually serve as the interface between the accelerator vacuum system on one side, and water at high pressure and temperature on the other. The samples irradiated at the University of Michigan used high energy protons while at University of Notre Dame an electron beam was used. The protons have energy of ca. 1.7MeV as they pass through the oxide into the water, and electrons have energy of ca. 1.5MeV. The protons have much higher momentum, and so (like high energy neutrons) are capable of causing significant atomic displacement damage in the oxide layer. They also move much more slowly than the relativistic electrons, so their LET (linear energy transfer) is ca. 200x larger than the electrons. To compensate and give nearly the same average energy dose to the sample and water near the surface, the electron beam flux (amps/cm²) is adjusted to be ca. 100x greater than the proton beam. Electrons do essentially no displacement damage to the solid.

Detailed analysis of the several MA956 samples is shown below in sections A-C. A summary of oxide thickness generated in the 24 hour irradiated samples is presented in Figure 1. The plot shows comparison between three different regions of interest: unirradiated region upstream of the radiation (UR), the directly irradiated region (IR), and a radiolysis affected region (RAR) downstream of the sample. Samples were irradiated at 320°C (HWC) and 288°C (NWC). The e-beam irradiated sample at 288°C proved to be badly contaminated by graphite packing material from a pressure seal, and so is omitted from consideration, though the corrosion was qualitatively similar to the proton beam result. In general, we find no very large difference in the corrosion properties between irradiated and unirradiated zones, beyond those to be expected from typical stainless steels under these extreme conditions of irradiation. We conclude that MA956 steel is a viable candidate material for nuclear fuel cladding.

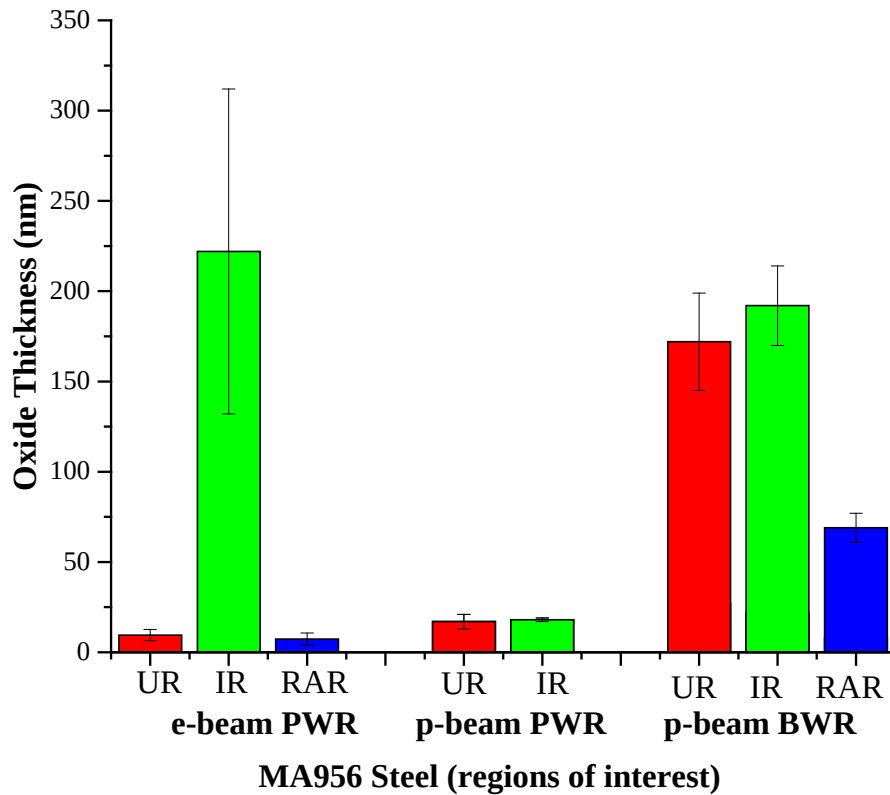


Figure 1: MA956 Oxide thickness comparison between ND and UM 24 hour irradiated samples.

A. MA956 Base Metal Characterization

The bulk material was obtained from Special Metals, and chemical composition is listed in Table A1.

Table A1. Chemical composition of as-received MA956, supplied by Special Metals.

Heat	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
NA	0.1	0.3	0.02	-	-	0.15	0.5	20	-
	Al	Nb	Zr	V	Ti	N	Y	Fe	
	4	-	-	-	0.4	-	0.5	Bal.	

EDS element analysis was carried out on a FEI NOVA SEM/FIB with EDAX detector. EDS spectrum is shown in Fig. A1. Atomic and weight percentage of each alloy element was shown in Table A2. The concentration of major alloying elements were consistent with the specification received from Special Metal.

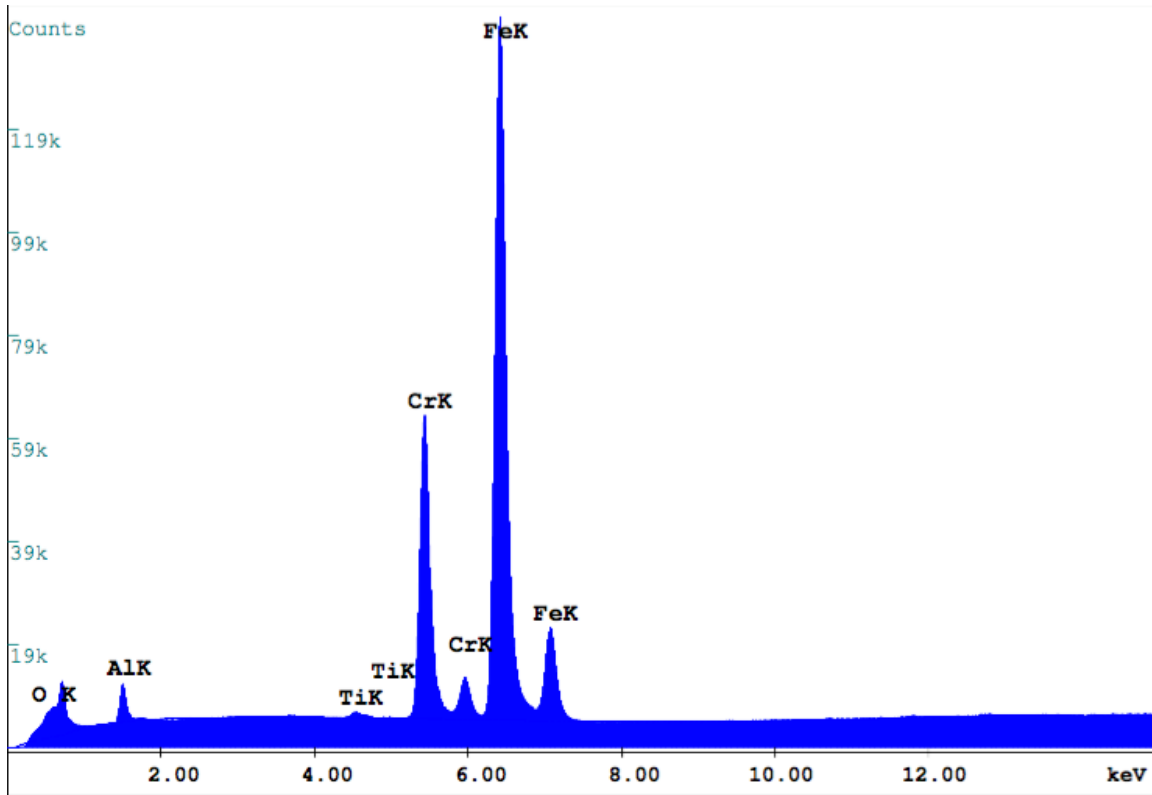


Figure A1. EDS spectrum of as-received MA956.

Table A2. Alloy element analysis by EDS.

Element	Wt %	At%
Fe	76	72
Cr	19	20
Al	3.69	7.24

Optical image of the polished and etched sample cross-section are shown in Figure A2. The horizontal direction is the rolling direction, and samples parallel to the rolling direction were prepared and used in this study.



Figure A2: Optical image of a cross-sectional view of the bulk material.

TEM analysis was performed using a JEOL 2100F STEM on twin-jet polished samples. The sample showed a typical OSD ferritic steel microstructure with large number of Y_2O_3 particles evenly distributed within the grains, as shown in Figure A3. The average particle density was calculated as 1.7×10^{10} particles/cm². Average grain size was about 300 ~500 μm.

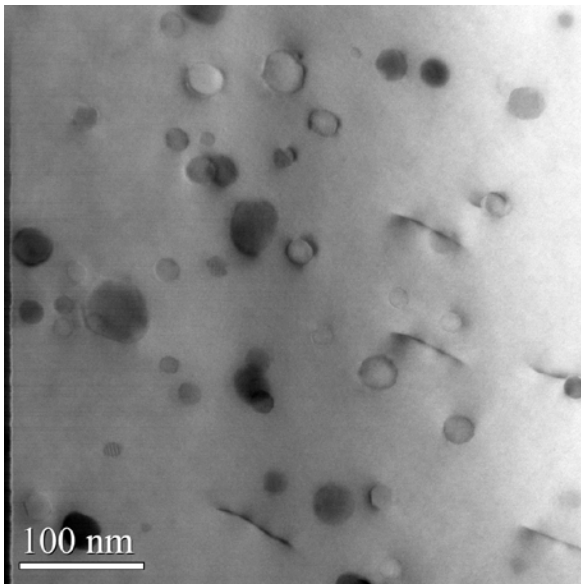


Figure A3. TEM dark-field images of MA956 base metal.

B. Proton Irradiation Experiments (U. Michigan)

B1. Summary

Proton irradiations of MA956 were completed in PWR primary water (PWR-PW), and in BWR normal water chemistry (BWR-NWC) at 320°C and 288°C, respectively. A 5.4 MeV proton beam at 2 μ A/cm² current density was used for these irradiations. The sample thickness was 80 microns, and the energy of the protons as they cross the oxide layer and enter the water is 1.7MeV. The LET in water is 5.6 x 10⁻¹¹ J/cm/e⁻. The dose rate to the water directly at the interface is 500kJ/kg/s. Various regions of the irradiated sample were analyzed using SEM and Raman Spectroscopy and characterizations of the oxide microstructure were carried out on the TEM.

Table B1: List of irradiation experiments completed for MA956.

Sample ID	Proton energy (MeV)	Temp (°C)	Water chemistry	Water dose rate (kGy/s)	Damage rate (dpa/s)	Duration (hr)
MA956-PW-24IR	5.4	320	PWR-PW (3 ppm H ₂)	500kGy/s	2.2 x10 ⁻⁷	24
MA956-NWC-24IR	5.4	288	BWR-NWC (2 ppm O ₂)	500kGy/s	2.2 x10 ⁻⁷	24

B2. Proton Irradiation Experimental conditions

Two MA956 samples were irradiated for 24 hr under the experimental conditions listed in Table B1. Water loop data and beamline data are shown in Figures B1 and B2 for PWR-PW condition and Figures B3 and B4 for BWR-NWC condition.

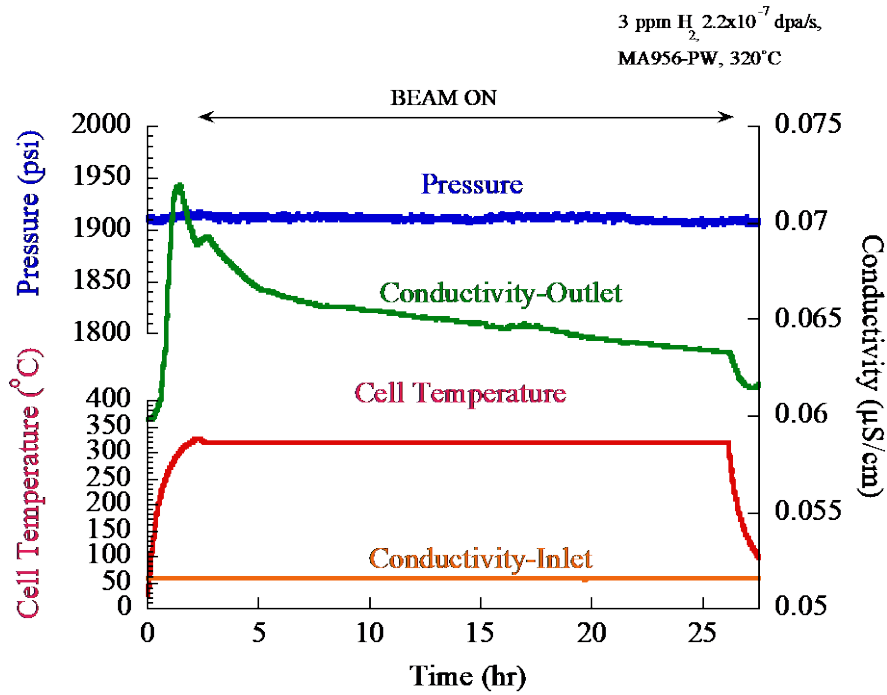


Figure B1: Water loop data of 24 hr proton irradiation of MA956 in 320°C 3 ppm H₂ water at a damage rate of 2.2x10⁻⁷ dpa/s.

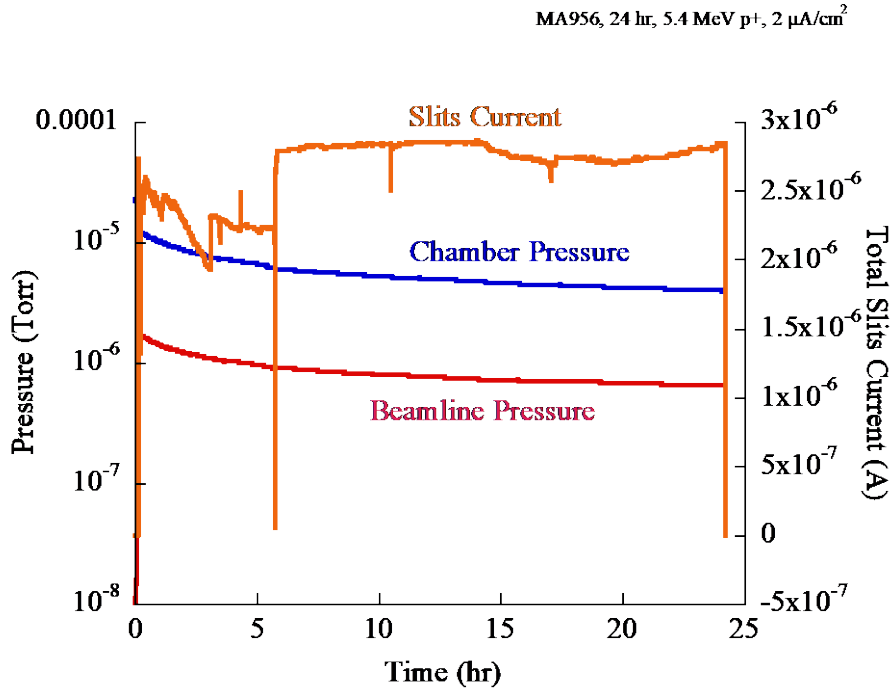


Figure B2: Beam current and pressure in the beamline and target chamber for the MA956 proton irradiation experiment in PWR-PW condition.

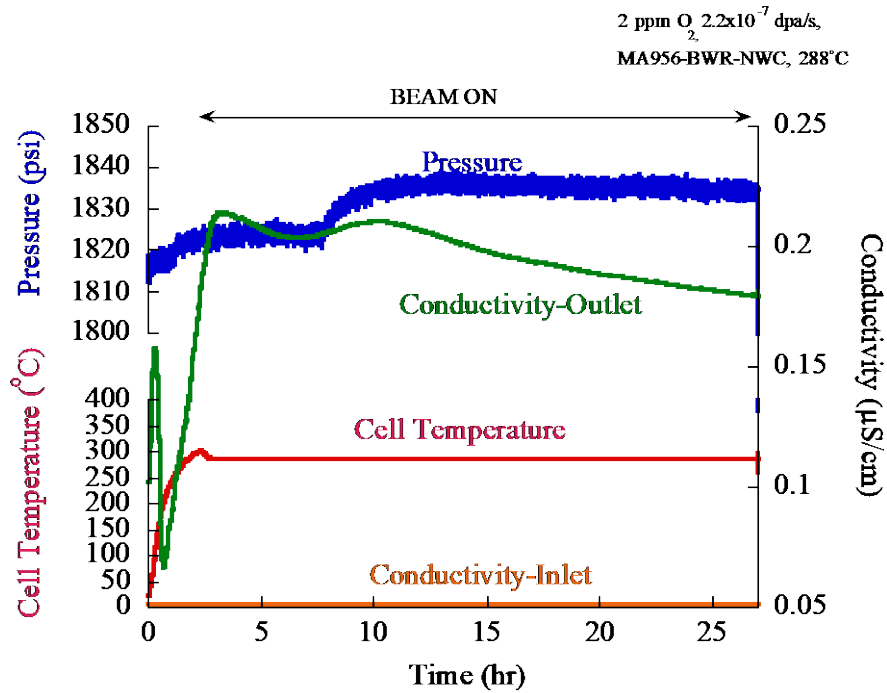


Figure B3: Water loop data of 24 hr proton irradiation of MA956 in 288°C 2 ppm O₂ water at a damage rate of 2.2×10^{-7} dpa/s.

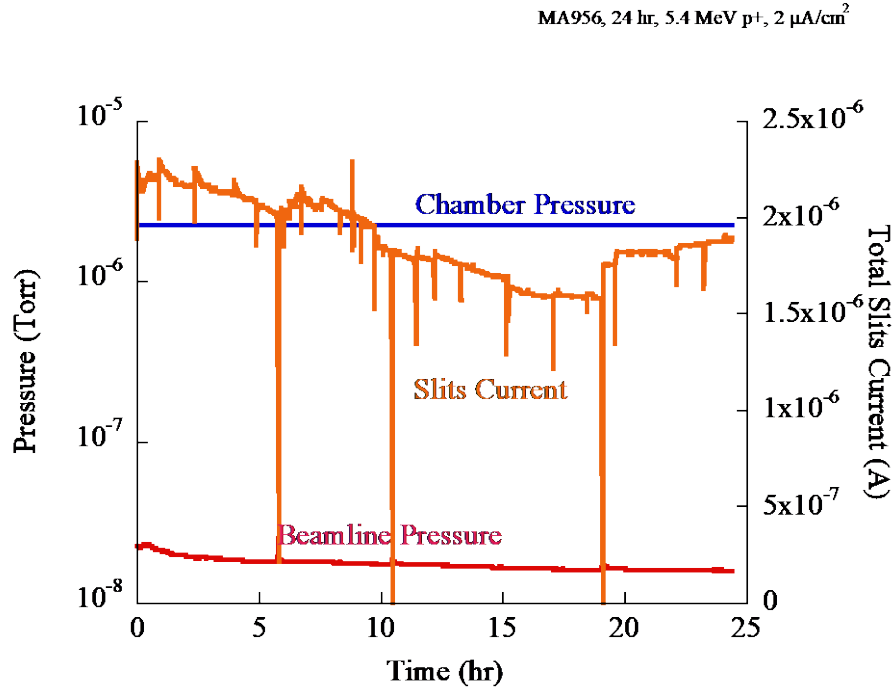


Figure B4: Beam current and pressure in the beamline and target chamber for the MA956 proton irradiation experiment in BWR-NWC condition.

B3. Post Irradiation Characterization

Three distinctive regions of the sample surface were characterized, namely the Irradiated Region (IR), Radiolysis Affected Region (RAR) and the Unirradiated Region (UR).

Optical Images

Sample MA956-PW-24IR remained as shiny as the polished surface in the UR region, as indicated in Figure B5, whereas the IR region has a matte gray appearance. Around the IR region, a noticeable rim of darker oxide was observed, most likely to be the RAR region, however, a distinctive flow region was not observed on this sample.

Sample MA956-NWC-24IR was discolored and showed interference colors, shown in Figure B5. The crescent shaped UR region was observed at the lower part of the sample. An IR region with dark blue appearance was connected with a distinctive fan shaped flow region (i.e. RAR region) covers the upper part of the sample, making it easy to identify the sample orientation.

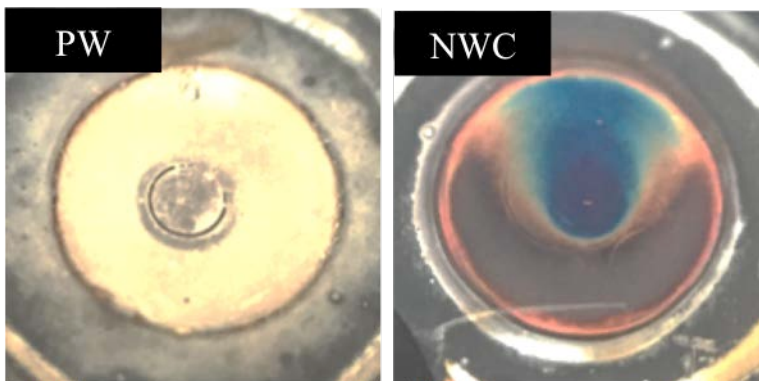


Figure B5: Optical images of irradiated samples MA956-PW-24IR and MA956-NWC-24IR.

Surface Oxide Morphology Analysis

Sample MA956-PW-24IR has a matte gray appearance after 24 hr exposure in primary water condition; an SEM image with circles outlining each region is shown in Figure B6. Oxide morphologies in UR and RAR regions were similar. In both regions an regular shaped outer oxide was observed with particle size of ~ 500 nm. In the IR region oxide particles were less faceted with a size of ~ 250 nm as indicated in Figure B7. Outer oxide particle density was significantly higher in the IR region compared with RAR and UR region.

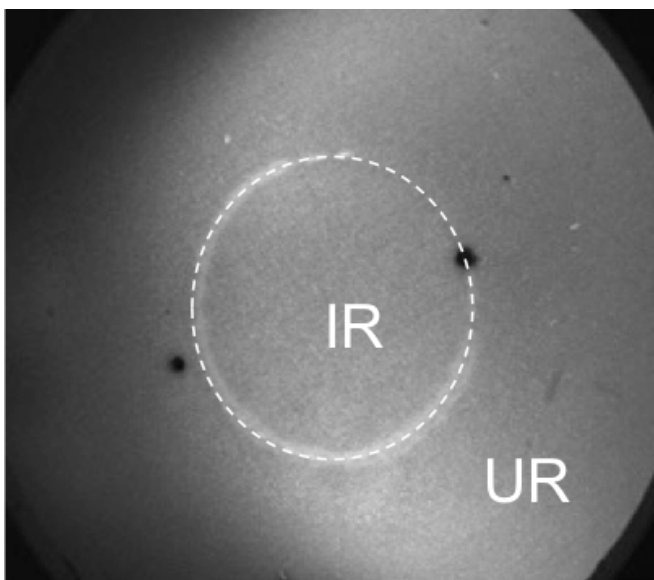


Figure B6: SEM image of sample MA956-PW-24IR. The irradiated region (IR) and unirradiated region (UR) are indicated by the dotted line.

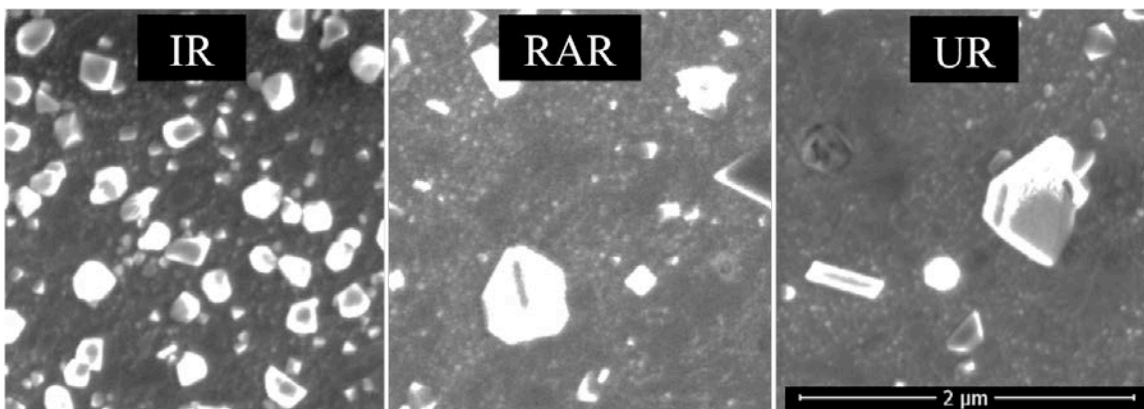


Figure B7: High magnification SEM images of the three regions observed on sample MA956-PW-24IR.

Sample MA956-NWC-24IR was discolored after 24 hr of exposure in BWR-NWC water chemistry. In Figure B8, the IR and RAR regions can still be observed on the surface of the sample. However, the high magnification SEM images shown in Figure B9 indicated that there was no significant difference in terms of oxide particle size (50-100 nm) and morphology. Oxide particles in the UR region has large aspect ratio compared to the oxides found in the RAR and IR regions. The particle size in the UR region is $\sim 1\text{-}2\text{ }\mu\text{m}$.

FIB lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared and TEM analysis was carried out on these TEM lamellas.

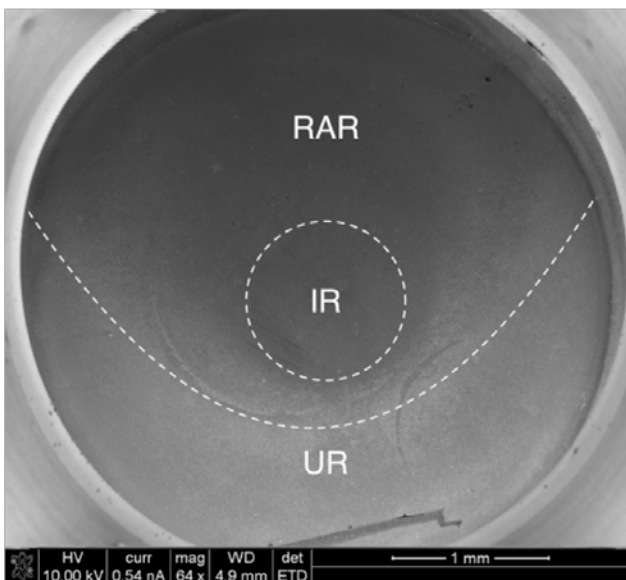


Figure B8: SEM image of sample MA956-NWC-24IR. The irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR) are indicated by the dotted line.

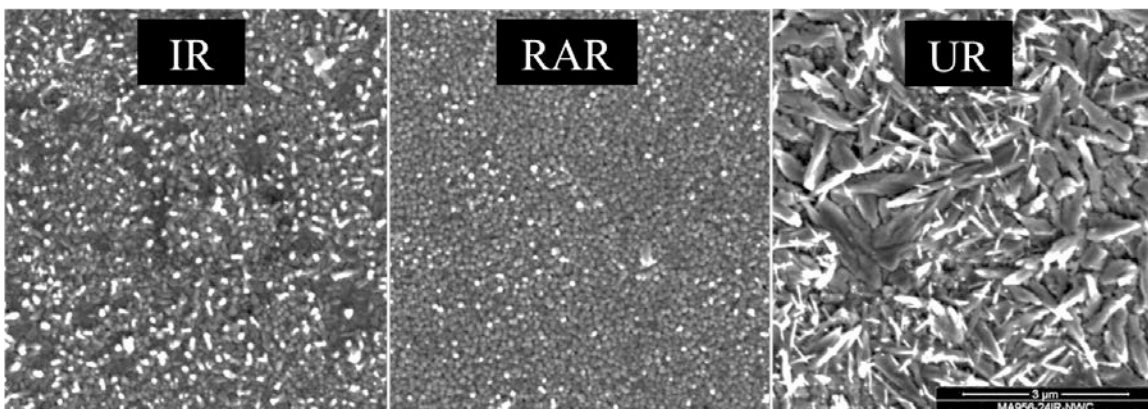


Figure B9: High magnification SEM image of the three regions observed on sample MA956-NWC-24IR.

Oxide Phase Analysis with Raman Spectroscopy

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated samples. Spectra were recorded using a Renishaw inVia microscope with a RenCam CCD detector. The spectra were collected using a 633 nm wavelength red laser, at a typical laser power of 50 mW, during a total of 500 s of acquisition time.

All three regions (IR, RAR and UR) on the irradiated samples were measured using Raman spectroscopy. Three individual spectra were also taken in each region for data consistency check.

For **sample MA956-PW-24IR**, the Raman peaks related to $\alpha\text{-Fe}_2\text{O}_3$ were observed in the IR region as shown in Figure B10. This observation indicated that when the sample surface was in contact with the radiolyzed water, the corrosion potential must be high enough for the formation of hematite. The cause of hematite formation could be the presence of short- and long-lived radical species and hydrogen peroxide. The short-lived radiolysis products (e.g. OH radicals) cannot escape the IR region, however, the product species H_2O_2 can be carried away from the IR region into the RAR region by convection flow of the heated water. This was the primary reason of the region formed around IR region, where oxidizing species could have migrated $\sim 100\ \mu\text{m}$ away from the IR region, but hematite formation was not observed in the area where convection flow of the heated water took place. This indicated that H_2O_2 was not directly affecting the oxide species in the RAR region. The UR and RAR regions showed a typical Raman spectrum of magnetite (Fe_3O_4). In primary water chemistry (PWC), the only stable iron oxide is magnetite which was observed in the UR and RAR region only. However, the $665\ \text{cm}^{-1}$ peak which was related to Fe_3O_4 was observed in all regions, indicating that the inner layer may also consist of magnetite phase, or a spinel phase which was deficient in Cr content, e.g. $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$. Further compositional analysis of the inner oxide layer is required to confirm identity of the inner oxide. In the IR region, the oxide consisted of a spinel $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$ inner layer and a Fe_2O_3 outer layer. Possible dissolution of Cr^{3+} could have occurred in the inner layer and substitution of Cr with Fe would result in an oxide that it is close to Fe_3O_4 , which could be the reason for the presence of $665\ \text{cm}^{-1}$ Fe_3O_4 peak.

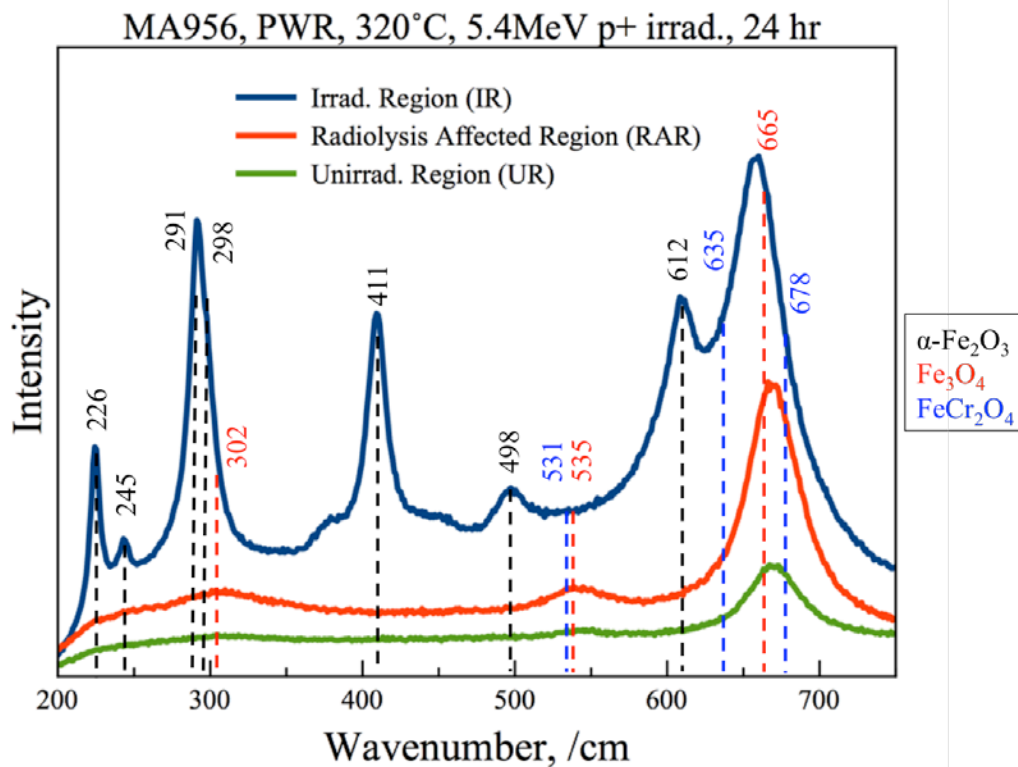


Figure B10: Raman spectra collected from IR, RAR and UR region on the 24 hr irradiated MA956 sample in primary water condition.

For **MA956-NWC-24IR**, the Raman peaks related to Fe_2O_3 are more intense in the IR and RAR region as shown in Figure B11. This indicates that oxide in those regions maybe thicker compared with the UR region. Also some of the peaks cannot be fitted by a single peak of Fe_2O_3 or Fe_3O_4 , which suggests both oxide phases maybe present in the spectra. However, in BWR-NWC water chemistry, Fe_2O_3 is still the dominant oxide, with possible Fe substituting Cr in FeCr_2O_4 . A weak shoulder peak at 635 cm^{-1} for FeCr_2O_4 could be the evidence for the Cr dissolution mechanism.

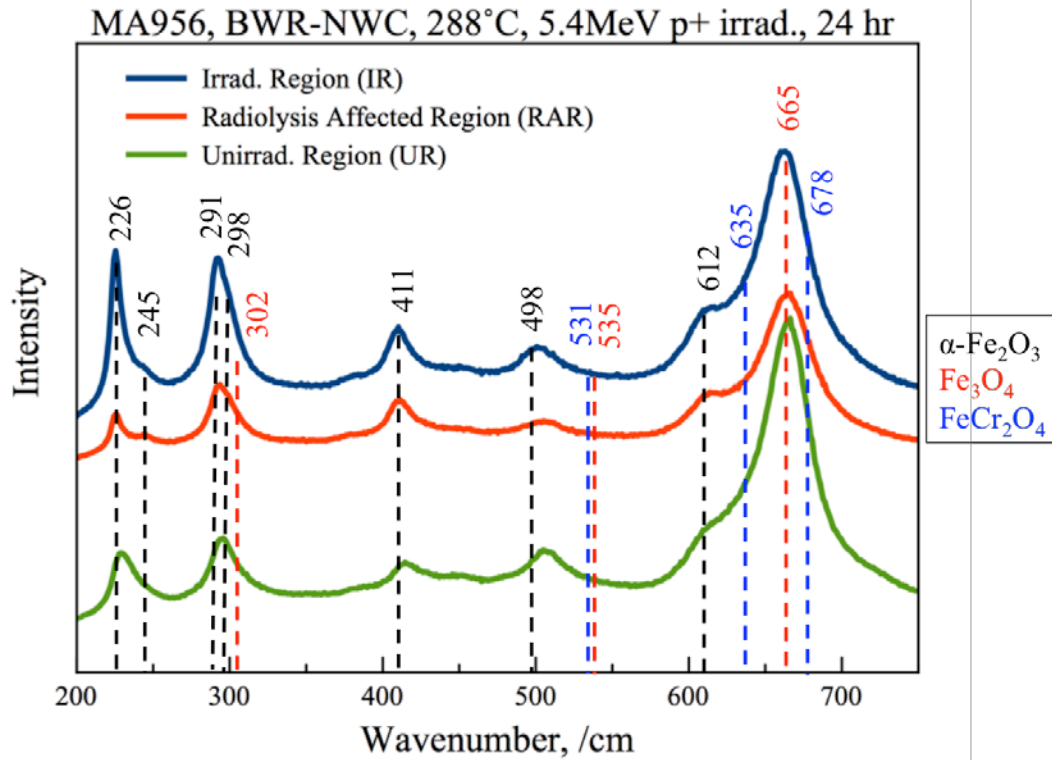


Figure B11: Raman spectra collected from irradiated region, unirradiated regions and the radiolysis affected region on the 24 hr irradiated MA956 sample in BWR-NWC water condition.

Oxide Morphology with TEM

TEM lamellas from IR and UR regions were prepared using FIB, and a JEOL 3100R05 TEM/STEM was used for TEM analysis.

The high angle annular dark field (HAADF) images were collected for oxide thickness analysis. Under such imaging conditions, the oxide would have a dark contrast compared to metal substrate or platinum protective coating.

On sample **MA956-PW-24IR**, as shown in Figure B12, the oxide inner layer appeared to be extremely thin. Although there were some outer oxide particles found on the surface of the sample, however, these TEM lamellas did not capture any of those particles. Average total oxide thickness, individual inner and outer layer thickness were listed in Table B2.

For **MA956-NWC-24IR**, the HAADF STEM images shown in Figure B13, had indicated that the oxide layers were much thicker compared with the hydrogenated (and higher temperature) condition. The interface of inner and outer oxide layer became indistinguishable under NWC condition, indicating possible inner oxide dissolution had occurred.

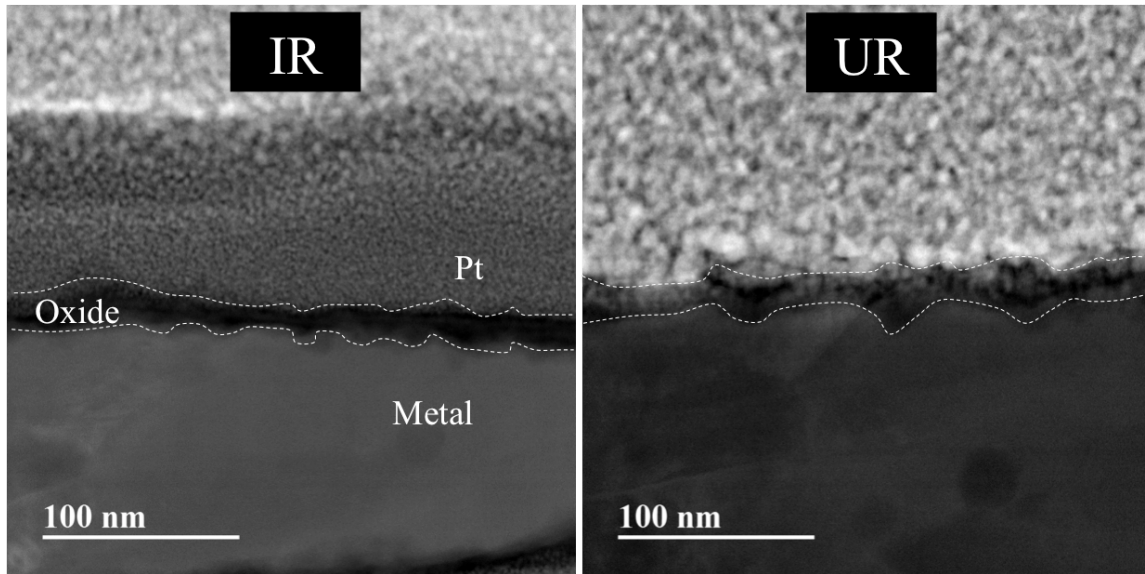


Figure B12: High Angle Annular Dark Field STEM (HAADF-STEM) images of the FIB lamellas taken from the irradiated sample MA956-PW-24IR.

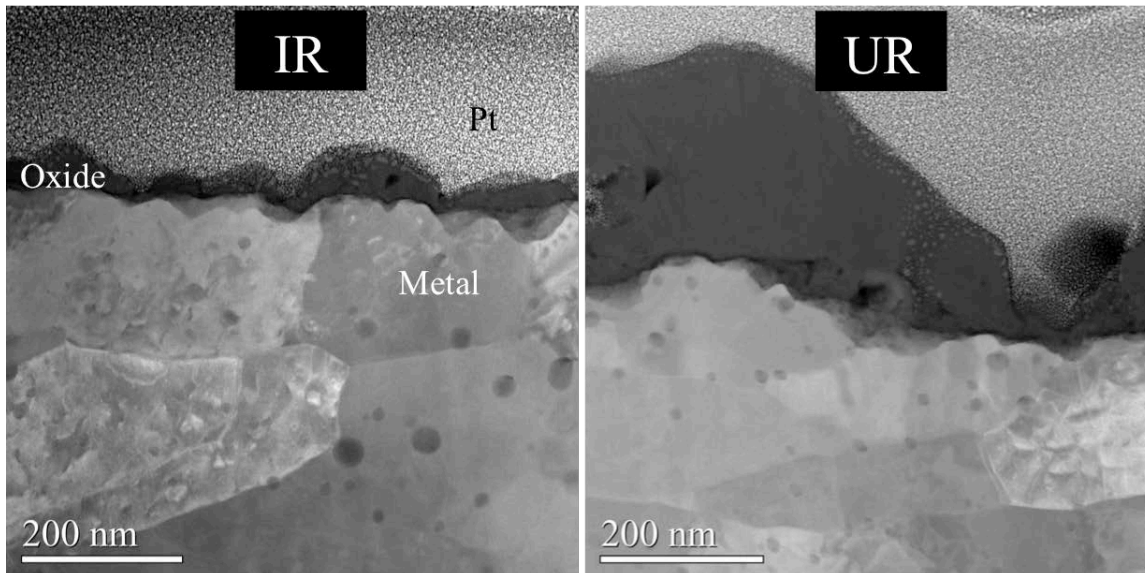


Figure B13: HAADF-STEM images of the FIB lamellas taken from the irradiated sample MA956-NWC-24IR.

Table B2: Oxide thickness observed on samples irradiated in both PW and NWC conditions.

Sample	Region	Total Oxide (μm)
MA956-PW-24IR	IR	0.008 ± 0.001
	UR	0.017 ± 0.004
MA956-NWC-24IR	IR	0.192 ± 0.022
	RAR	0.069 ± 0.008
	UR	0.172 ± 0.027

Oxide Composition Analysis with EDS

Energy Dispersive x-ray Spectroscopy (EDS) was used to determine the oxide compositions. The EDS spectra were collected on JEOL 2010F STEM with EDAX detector.

For hydrogenated water conditions in **sample MA956-PW-24IR**, EDS results of IR and UR region are shown in Figure B14. The IR region oxide composition was consistent with Fe_2O_3 , which is 40 at% Fe and 60 at% O for the outer oxide, the thin inner oxide was not directly observed with EDS. EDS result from the UR region had confirmed that the outer oxide was Fe_3O_4 (theoretical values for Fe_3O_4 is 43 at% Fe and 57 at% O), and the thin UR region inner oxide was also not observed.

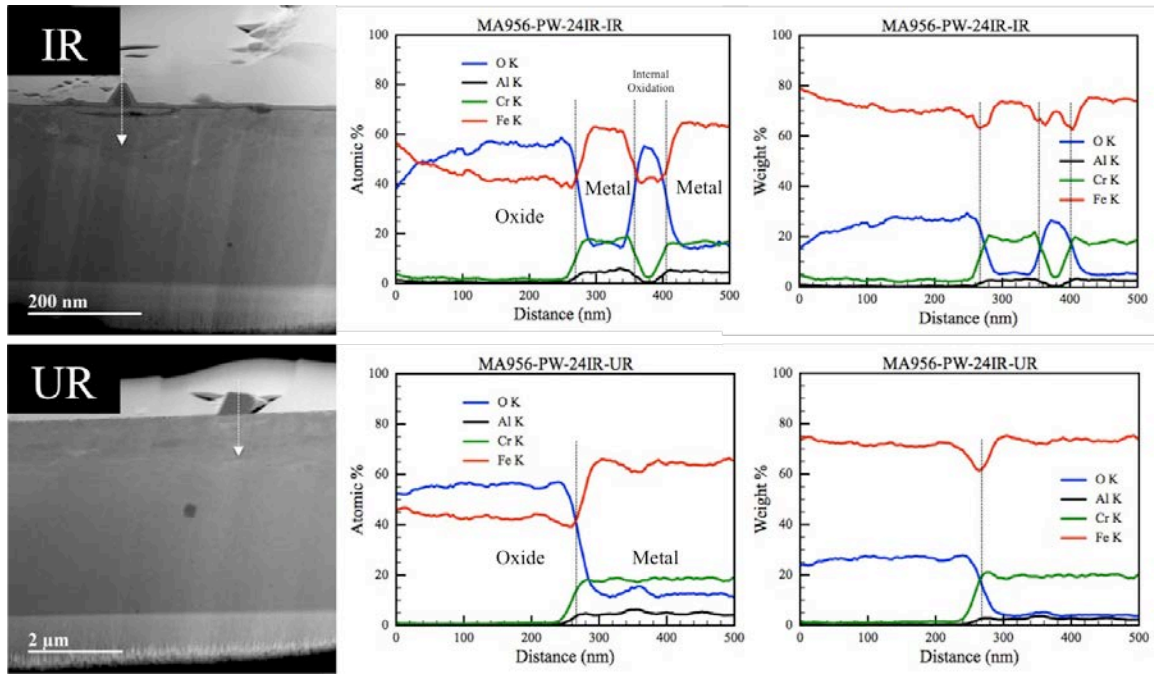


Figure B14: EDS line scans of oxide regions (IR and UR) formed on sample MA956-PW-24IR.

For the NWC condition of **sample MA956-NWC-24IR**, EDS results of IR and UR region are shown in Figure B15. In the IR regions, the outer oxide particle showed a Fe-Cr spinel composition, however, the apparent Fe concentration was too high in the outer oxide (almost 65 at% Fe) and oxygen concentration being extremely low for the spinel phase. The low oxygen concentration would likely to be caused by a software issue that mis-fitting the Cr-La peak (0.573 keV) to the O-K α peak (0.525 keV) at the lower end of the spectrum,

resulting a mis-quantification of the atomic percentage of each element. In the UR region, the outer oxide consisted of a Fe rich Fe-Cr spinel phase, since the PB ratio of spinel oxide is about 2, the Cr concentration in the oxide would be half of the Cr concentration in the metal.

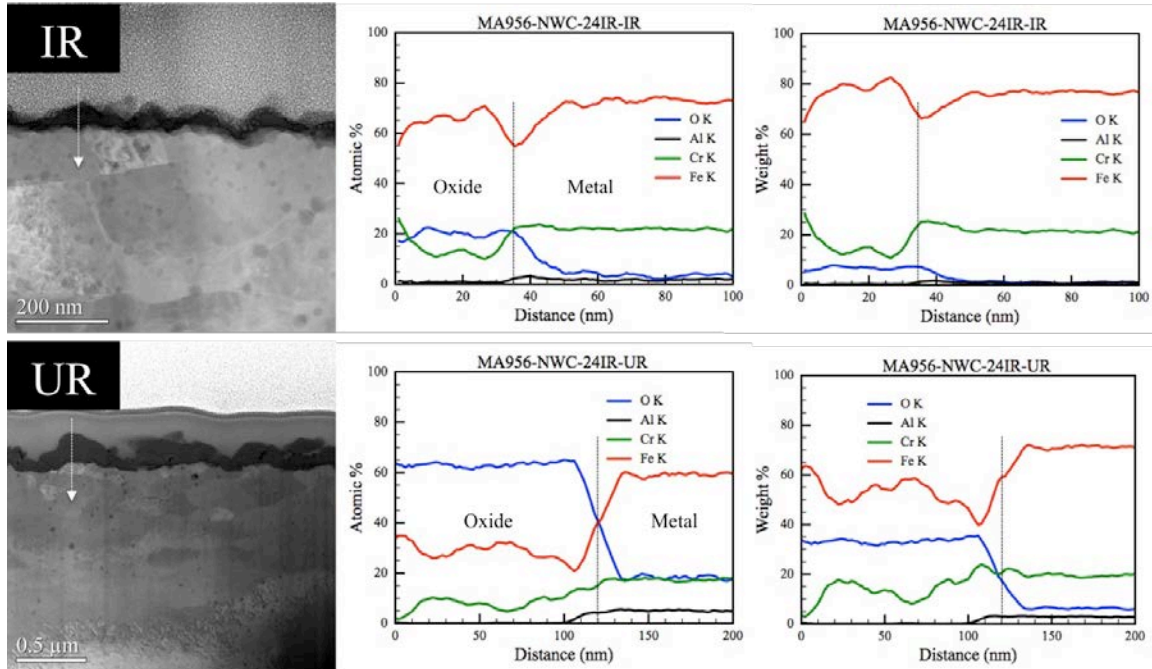


Figure B15: EDS line scans of oxide regions (IR and UR) formed on sample MA956-NWC-24IR.

Proton Post Irradiation Characterization Summary

The oxide species found on irradiated samples under different conditions were confirmed using Raman and the findings were summarized in Table B3.

Table B3: Summary of the oxide species found on MA956 in PW and NWC conditions under proton irradiation.

Samples	Regions	Outer Oxide/Inner Oxide	
		NWC 288°C, 2 ppm O ₂	PW 320°C, 3 ppm H ₂
MA956	IR	$\alpha\text{-Fe}_2\text{O}_3$ /Fe(Cr, Fe) ₂ O ₄	$\alpha\text{-Fe}_2\text{O}_3$ /Fe(Cr, Fe) ₂ O ₄
	RAR		Fe_3O_4 /Fe(Cr, Fe) ₂ O ₄
	UR		

C. Electron Irradiation Experiments (ND)

C1. Summary

Electron irradiations of MA956 were completed (samples ID and conditions are listed in Table C1) in PWR primary water (PWR-PW), and in Argon and Oxygen-saturated water chemistry at 320°C and 288°C, respectively. A 2.5 MeV electron beam at 120 $\mu\text{A}/\text{cm}^2$ current density was used for these irradiations. Given ~ 250 micron sample thickness, energy of electrons as they cross the oxide layer and enter the water is ca. 1.5 MeV, so that they are still relativistic, and have LET of 1.9×10^6 eV/cm/e-. Dose rate to the water at the surface is ca. 170 kGy/s. Post-irradiation characterization of various regions of the irradiated samples was completed by means of Raman spectroscopy, SEM, TEM imaging and EDX line scans.

Table C1: List of irradiation experiments completed for MA956

Sample ID	e- Energy (MeV)	Temp (°C)	Water chemistry	current density (mA/cm ²)	Water dose rate (kGy/s)	Duration (hr)
MA956- 320H2-24IR	2.5	320	3 ppm H ₂	120	170	24
MA956- 288Ar-24IR	2.5	288	Ar Saturation	120	170	24
MA956- NWC	2.5	288	2 ppm O ₂	120	170	24

C2. Post Irradiation Characterization of MA956 sample

a. Optical Microscopy and SEM Imaging – Oxide Morphology

All MA956 steel samples (e-beam irradiated) were analyzed via microscopy. All samples were slightly discolored after 24 hr of e-beam exposure. The sample irradiated in Argon-saturated water condition was found to be contaminated with an over-layer of carbon. It was subsequently confirmed that this came from the graphite packing material used to seal the sapphire window above the sample. The cell has been modified to avoid this in the future and additional experiments are going to be performed to analyze BWR conditions. Consequently this section of the post-irradiation characterization report focuses entirely on the MA956 H₂-saturated sample at PWR conditions. Section C3 emphasizes the post-irradiation characterization of MA956 NWC at BWR conditions.

Under the optical microscopy, three distinctive regions can be identified on the sample surface, Irradiated Region (IR), Radiolysis Affected Region (RAR) and Unirradiated Region (UR), shown in Figure C1 (left) for the MA956-H₂-sat sample. The irradiated area of the sample was defined as a circular-shaped area with diameter of about 1 mm as seen in the SEM micrograph in Figure C1 (right). The sample's irradiated region was discolored after 24 hr of e-beam exposure, observed as a darker circular region.

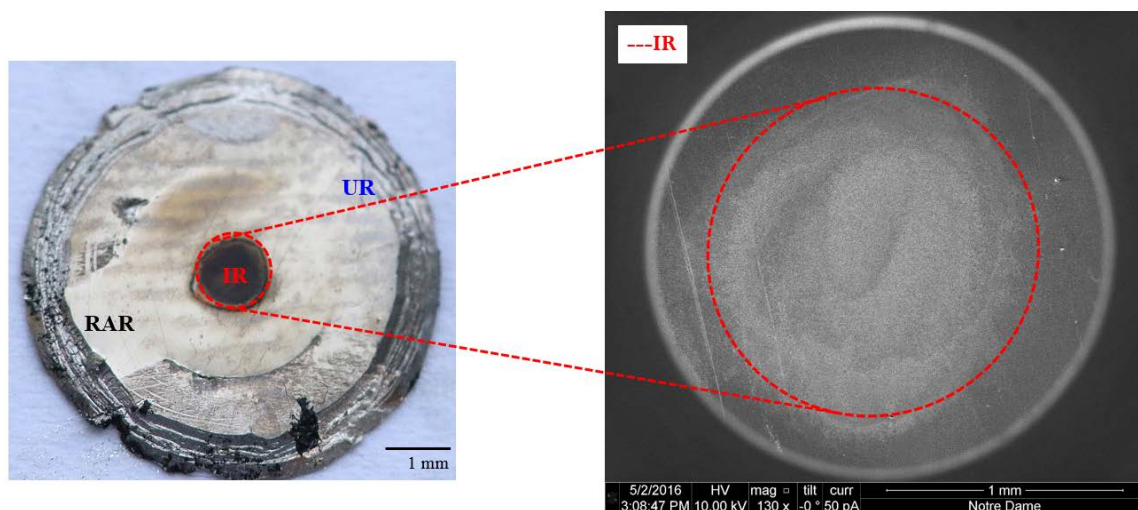


Figure C1: Post-irradiation optical image (left) and SEM micrograph (right) of 24-hour electron-beam irradiated MA956 sample in Hydrogen-saturated water. Representation of unirradiated region (UR), irradiated region (IR) and radiolysis affected region (RAR).

The high magnification SEM images in Figure C2 represent the oxide particles of the three different regions (UR, IR and RAR) in the MA956 Hydrogen-saturated sample. The particles in the UR and RAR region look very similar, however, the oxide particles size in the RAR region seem slightly larger. In comparison to both UR and RAR region, the IR region particles are much larger in size, well defined in shape and densely packed. The plot presented in Figure C3 compare the oxide particle size between the different regions of interest in MA956 Hydrogen-saturated sample.

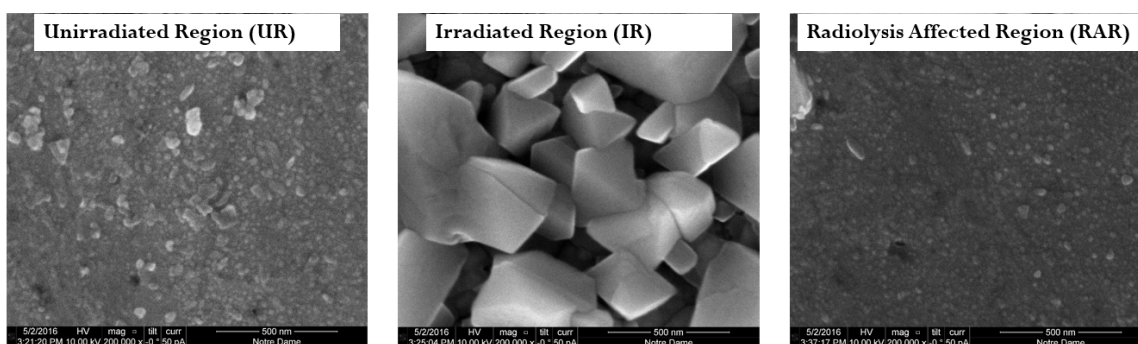


Figure C2: Post-Irradiation SEM images of 24-hour electron-beam MA956 sample in Hydrogen-saturated water. Representation of the three different regions, UR, IR and RAR.

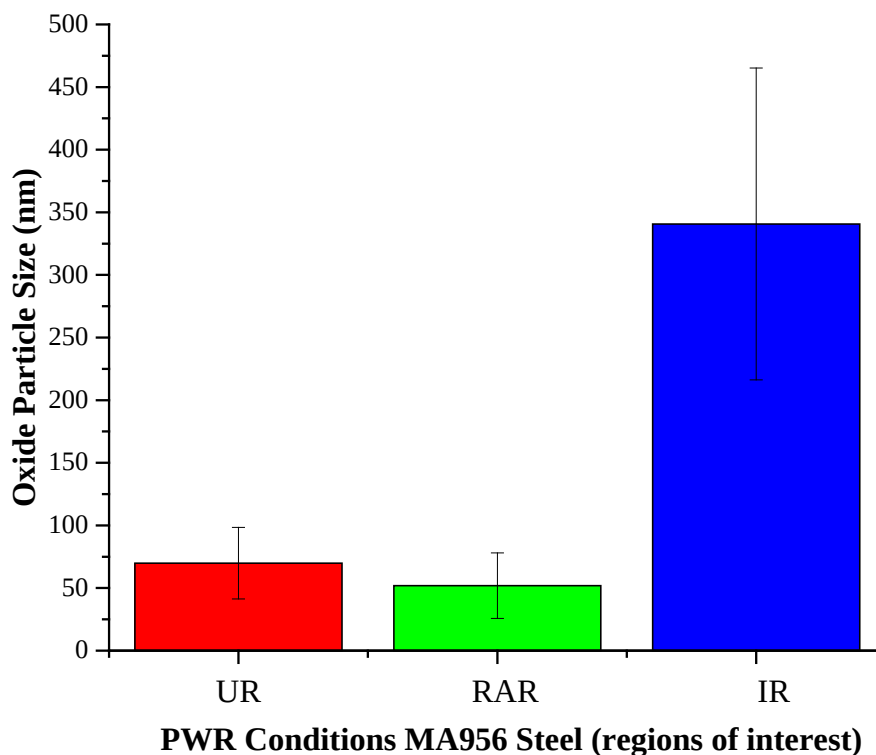


Figure C3: Oxide particle size comparison of the MA956 sample in the Hydrogen-saturated water. The plot represents the average oxide particle size over the three different regions (UR, RAR and IR). The error bars indicate the 90% confidence limit associated with the measurements.

b. TEM Imaging and EDX Line scans – Oxide Thickness

Focused ion beam (FIB) lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared for transmission electron microscope (TEM) analysis of the oxide layer thickness and morphology. The FIB lift-outs were prepared using the FEI-HELIOS dual beam FIB and the samples were further investigated via high magnification TEM images and EDX linescans, performed with the Titan TEM (FEI Titan 80/30 TEM) that is equipped with an energy-dispersive X-ray system by which line profiles can be measured; both instruments are located at the Notre Dame Integrated Imaging Facility.

Illustration of the different regions (UR, IR and RAR) via TEM imaging is demonstrated in Figure C4 for MA956 Hydrogen-saturated sample.

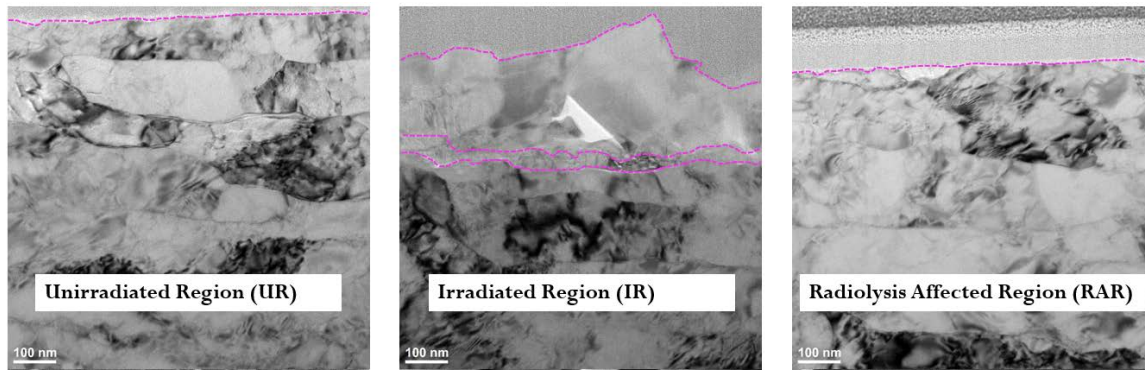


Figure C4: Post-Irradiation TEM images of 24-hour electron-beam MA956 sample in Hydrogen-saturated water. Representation of the three different regions (UR, IR and RAR).

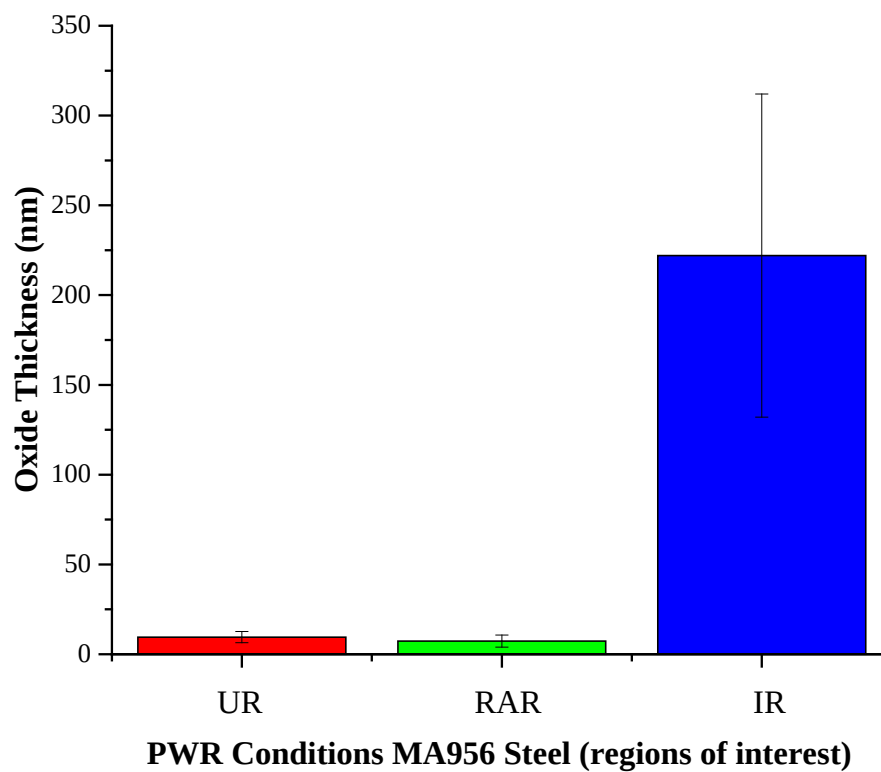


Figure C5: Oxide thickness comparison of the MA956 sample in the Hydrogen-saturated water. The plot represents the average oxide thickness over the three different regions (UR, RAR and IR). The error bars indicate the 90% confidence limit associated with the measurements.

The plot presented in Figure C5 compares the oxide thickness between the different regions of interest in MA956 Hydrogen-saturated sample. As seen in the plot, there is a very small oxide thickness in the UR (about $9\pm 3\text{nm}$) and the RAR (about $7\pm 4\text{ nm}$). In comparison to the UR and RAR, the IR region of MA956 sample features a larger oxide thickness (about $222\pm 90\text{ nm}$) which is mostly due to the precipitation oxide layer that is absent in the other regions.

EDX line scans were performed to reveal elemental distribution information about the sample. Multiple EDX line scans were completed on each TEM sample and are shown in the Figures C6, C7 and C8. In addition to that, Table C2 represents the chemical content and concentration the different regions of interest.

The EDX line scan of the UR region of the MA956 sample in the Hydrogen-saturated water is presented in Figure C6. It was confirmed that the sample does not contain any precipitation oxide layer as the line scan suggests (about 70-80% atomic concentration of Iron). It is apparent that this type of steel is Chromium-rich (about 20% atomic concentration of Chromium). There is also an indication of possible iron oxides throughout the metal, not necessarily a result of radiolysis considering the oxides are present in the unirradiated metal region.

The EDX line scan of the IR region of the MA956 sample in the Hydrogen-saturated water is presented in Figure C7. The EDX line scan shows the iron oxide precipitation layer which consists of mostly hematite. In regards to the MA956 metal region, the EDX line scan shows the highest content of Iron with Chromium enrichment and small amounts of Aluminum as they are constituents of the original metal. Similarly to the UR region there is presence of oxides through the metal region.

The EDX line scan of the RAR region of the MA956 sample in the Hydrogen-saturated water is presented in Figure C8. The EDX line scan is very similar to the line scan of the UR region. There is absence of precipitation oxide layer. The difference between the UR and RAR region is that, as suggested by the line scans, the RAR region contains slightly less Iron than the IR resulting in more iron oxides through the metal region.

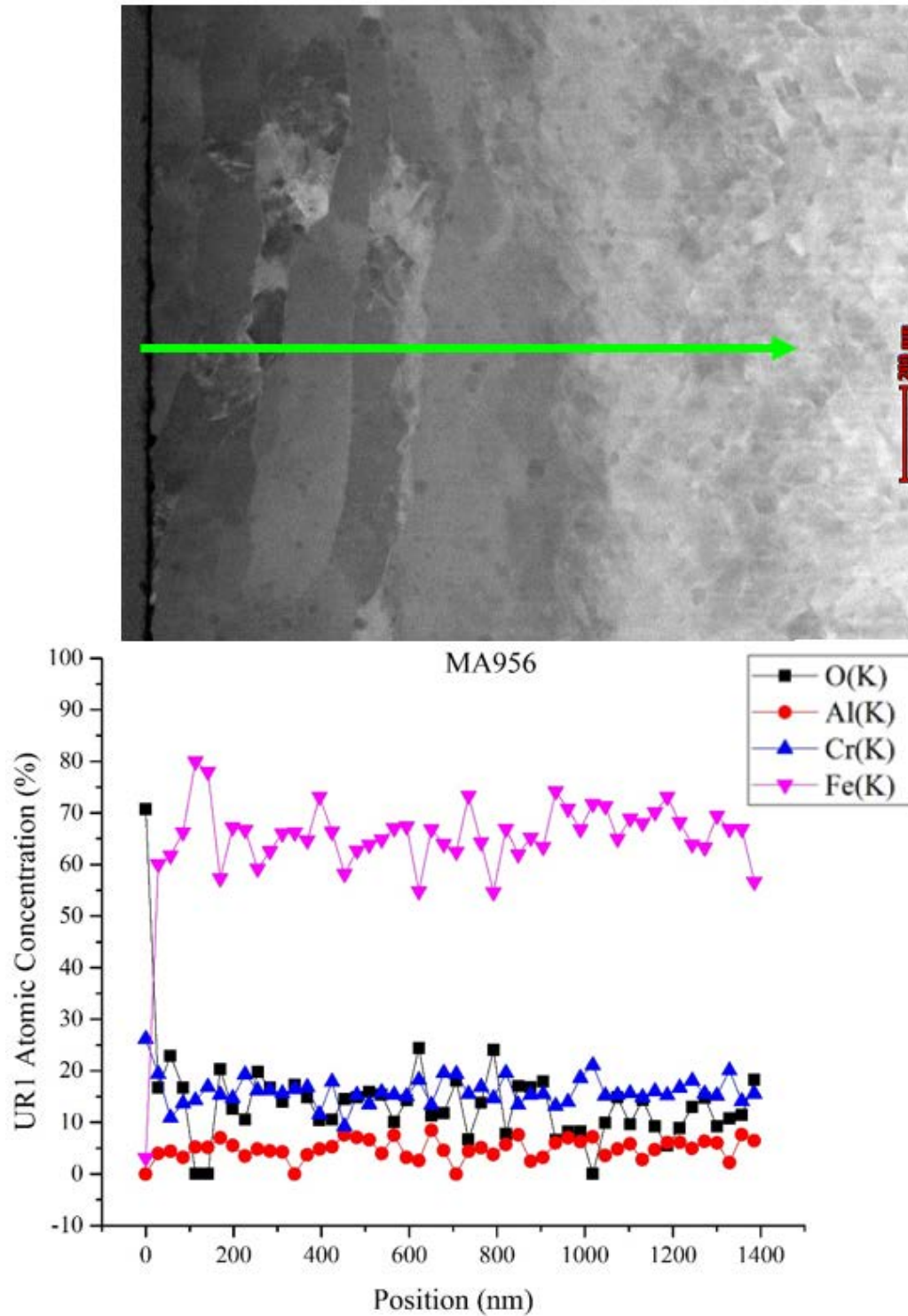


Figure C6: TOP: STEM bright field image of UR region of the MA956 sample in the Hydrogen-saturated water (the thin arrow shows the length of the EDX line scan and the direction is from left to right) BOTTOM: STEM EDX line scan results, atomic concentration vs. position.

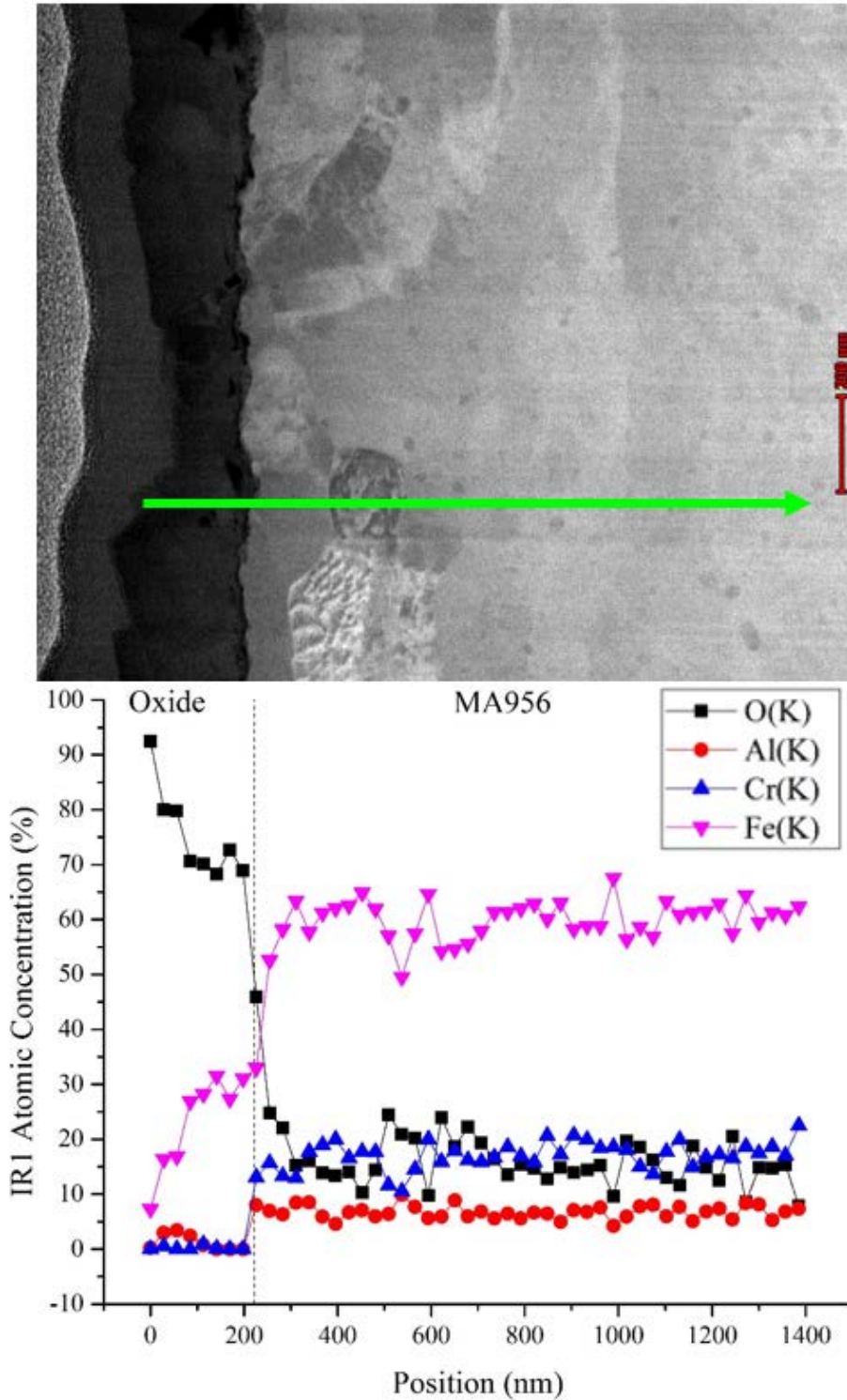


Figure C7: TOP: STEM bright field image of IR region of the MA956 sample in the Hydrogen-saturated water (the thin arrow shows the length of the EDX line scan and the direction is from left to right) BOTTOM: STEM EDX line scan results, atomic concentration vs. position.

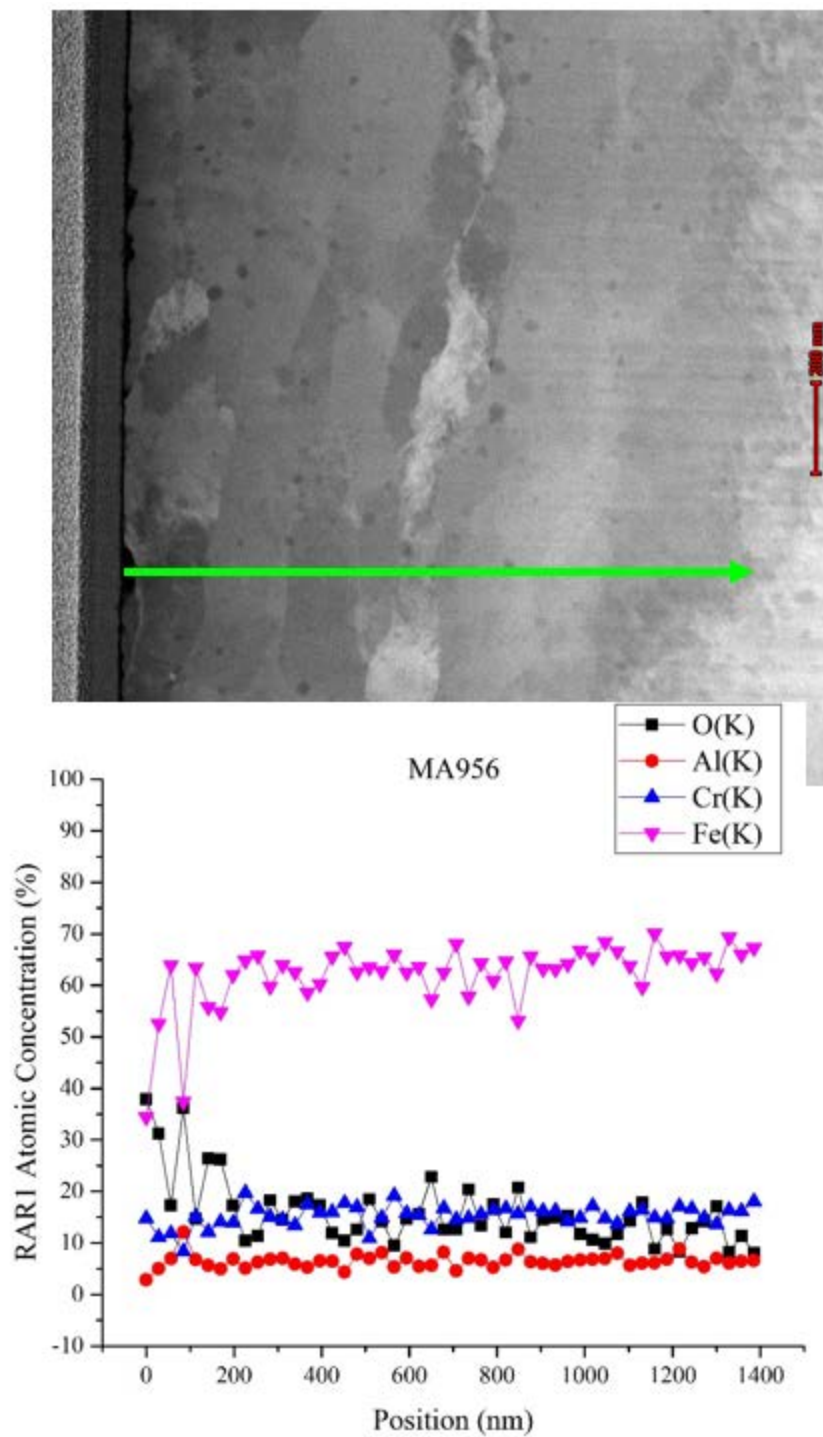


Figure C8: TOP: STEM bright field image of RAR region of the MA956 sample in the Hydrogen-saturated water (the thin arrow shows the length of the EDX line scan and the direction is from left to right) BOTTOM: STEM EDX line scan results, atomic concentration vs. position.

Table C2: Average chemical content quantified from EDX line scans of the MA956.

Region	O(K)	Al(K)	Cr(K)	Fe(K)	Y(K)
Atomic %					
UR	14.44	4.86	16.03	64.31	0.34
IR	26.20	5.86	14.32	53.31	0.30
RAR	15.77	6.46	15.27	62.10	0.19
Weight %					
UR	4.43	2.70	17.60	74.58	0.68
IR	12.41	3.51	15.96	67.52	0.59
RAR	6.24	3.73	17.06	72.55	0.40

c. Raman Spectroscopy – Oxide Phase

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated sample. Spectra were recorded using a Micro-Raman Spectrometer (NRS-5100, Jasco). The spectra were collected using a 532 nm wavelength green laser, at a typical laser power of 50 mW, during a total of 600s of exposure time.

Three regions on the irradiated sample were measured using Raman spectroscopy, irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR). Five individual spectra were also taken in each region for data consistency check.

Raman spectra of the UR, RAR and IR region of the MA956 sample in the Hydrogen-saturated water are presented in Figure C9. Raman analysis in the IR region showed that the corrosion products are mainly composed of a mixture of oxides (maghemite, hematite, magnetite). It is assumed the corrosion is due to the thicker precipitation oxide layer. The formation of hematite is associated with a high corrosion potential which is absent in the RAR and UR region, however, a presence of maghemite peak is noticed. Maghemite is thermodynamically unstable with respect to hematite and it forms through low-temperature oxidation of spinels containing iron(II) such as magnetite. It is also considered to be an iron(II) deficient magnetite. Maghemite has the same crystalline structure like magnetite. Main distinct features of maghemite are the presence of vacancies in Fe position with symmetry reduction. Regardless of the mechanism used to form maghemite, it appears that the presence of water under conditions of limited O₂ supply is necessary for its formation. The presence of maghemite peaks in the RAR and UR regions show presence of corrosion that are due to radiolysis of water on the surface. Though, there is no evident oxide layer on the surface, rather the oxidation is present in the material, most probably due to the vacancies in Fe positions present in the material. This result is observed in the EDX linescans of the RAR and UR regions.

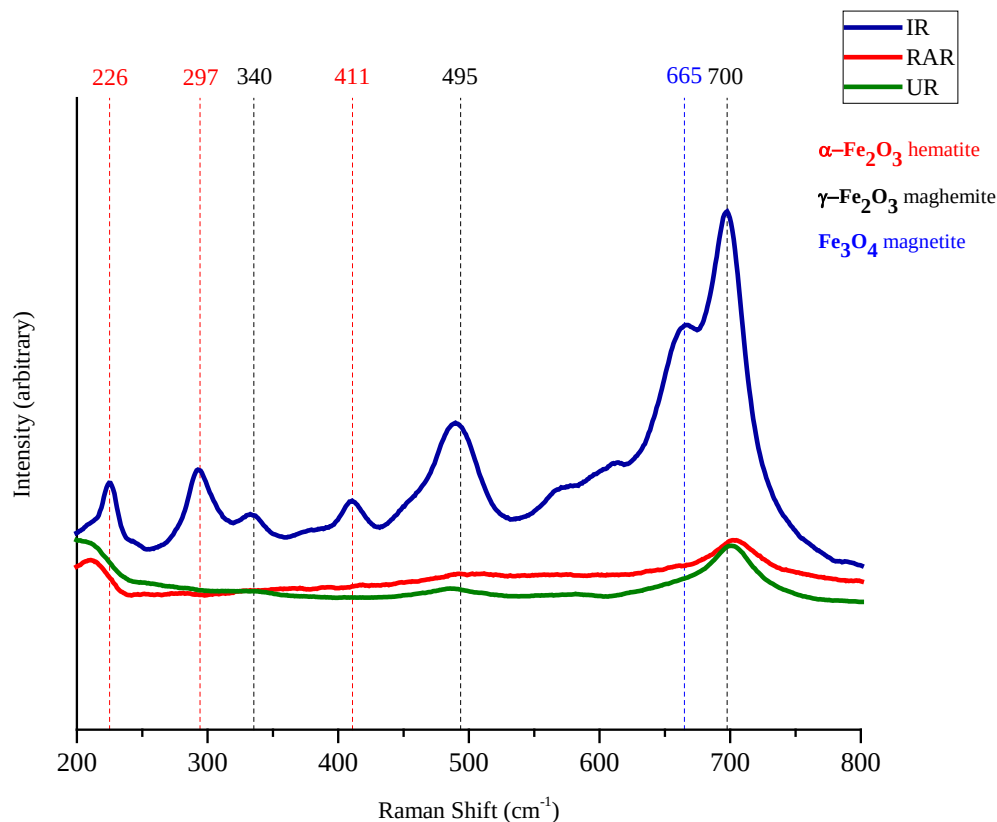


Figure C9: Post-Irradiation Raman spectra collected from 24-hour electron-beam MA956 sample in Hydrogen-saturated water. Representation of the three different regions (IR, RAR and UR).

C3. Post Irradiation Characterization of MA956 NWC sample

a. Optical Microscopy and SEM Imaging – Oxide Morphology

Under the optical microscopy, three distinctive regions can be identified on the sample surface, Irradiated Region (IR), Radiolysis Affected Region (RAR) and Unirradiated Region (UR), shown in Figure C10 for the MA956 NWC sample. The irradiated area of the sample was defined as a circular-shaped area with diameter of about 1 mm. The sample's irradiated region was discolored after 24 hr of e-beam exposure, observed as a darker middle region.

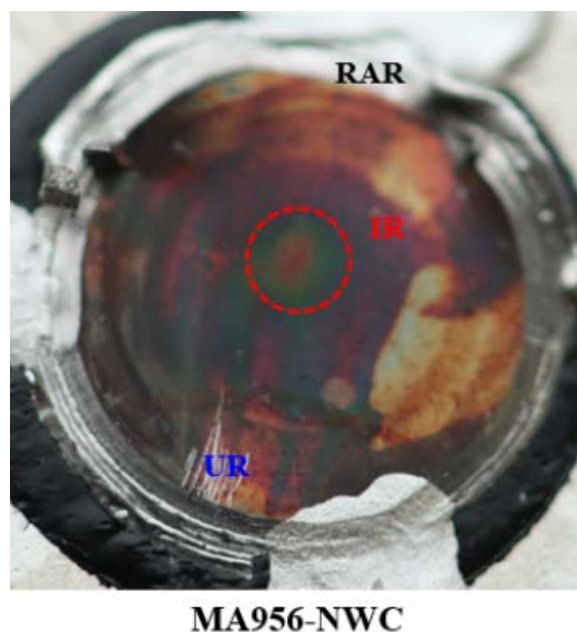


Figure C10: Post-irradiation optical image of MA956 NWC 24-hour electron-beam irradiated samples in Oxygen-saturated water. Representation of the three different regions (UR, IR and RAR).

The high magnification SEM images in Figure C11 represent the oxide particles of the three different regions (UR, IR and RAR) in the MA956 Oxygen-saturated sample. Even though the sample is fairly discolored and the difference regions can be observed in the optical image, the high mag SEM images indicate that there was no significant difference in terms of oxide particle size ($\sim 300\text{-}500\text{ nm}$) and morphology.

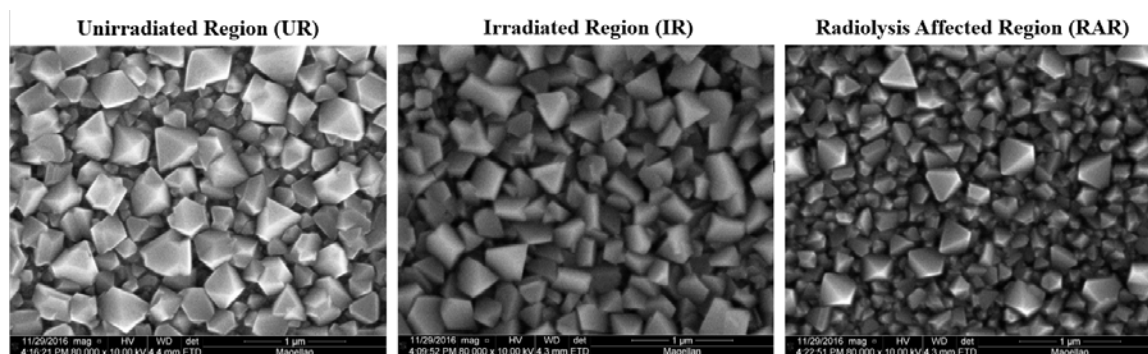


Figure C11: Post-irradiation SEM images of 24-hour electron-beam irradiated MA956 NWC sample. Representation of the three different regions (UR, IR, RAR).

b. TEM Imaging and EDX Line scans – Oxide Thickness

Focused ion beam (FIB) lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared for transmission electron microscope (TEM) analysis of the oxide layer thickness and morphology. The FIB lift-outs were prepared using the FEI-HELIOS dual beam FIB and the samples were further investigated via high magnification TEM images and EDX linescans, performed with the Titan TEM (FEI Titan 80/30 TEM) that is equipped with an energy-dispersive X-ray system by which line profiles can be measured; both instruments are located at the Notre Dame Integrated Imaging Facility.

Illustration of the different regions (UR, IR and RAR) via TEM imaging is demonstrated in Figure C12 for MA956 Oxygen-saturated sample. If comparing all samples there is not a significant difference between all analyzed regions of interest.

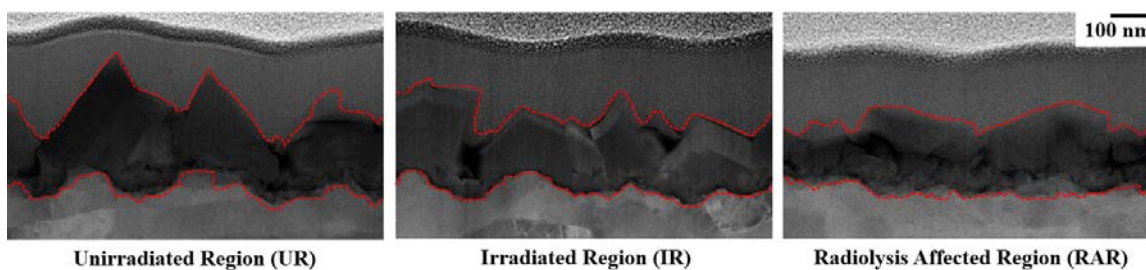


Figure C12: Post-Irradiation TEM images of 24-hour electron-beam MA956 NWC sample in Oxygen-saturated water. Representation of the three different regions (UR, IR and RAR). The red dotted lines represent the oxide layer in the regions of interest.

EDX line scans were performed to reveal elemental distribution information about the sample. EDX line scans were performed on the 24-hour electron-beam irradiated MA956 NWC sample in Oxygen-saturated water to reveal elemental distribution information about the sample. Multiple EDX line scans were completed on each TEM sample and some are shown in the Figures C13, C14 and C15 for the UR, IR and RAR regions, respectively.

The EDX line scan of the UR region of the MA956 NWC sample in the oxygenated water is presented in Figure C13. The oxide layer as the line scan suggests contains about 40-50% atomic concentration of Oxygen, about 30-40% atomic concentration of iron as well as about 10-20% atomic concentration of Nickel content. In regards to the MA956 metal region, the EDX line scan shows the highest content of Iron with Chromium and some Aluminum enrichment as they are constituents of the original metal.

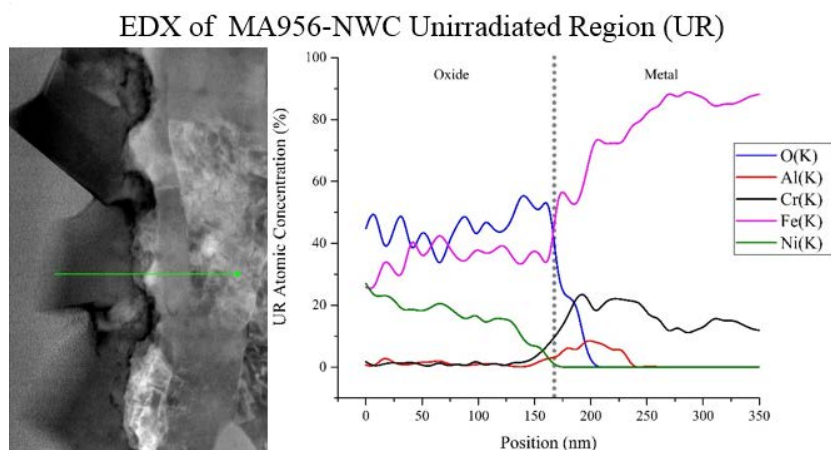


Figure C13: Left: STEM bright field image of UR region of the 24-hour electron-beam irradiated MA956 NWC sample (the thin arrow shows the length of the EDX line scan and its direction). Right: STEM EDX UR line scan results, atomic concentration vs. position, representation of oxide and metal region of scan.

The EDX line scan of the IR region of the MA956 NWC sample in the oxygenated water is presented in Figure C14. The oxide layer of this region is very similar to the oxide layer of the UR region as the line scan suggests contains about 50% atomic concentration of Oxygen, about 20-40% atomic concentration of iron as well as about 10-30% atomic concentration of Nickel content. In regards to the MA956 metal region, the EDX line scan shows the highest content of Iron (about 80%) with Chromium and Aluminum enrichment as they are constituents of the original metal.

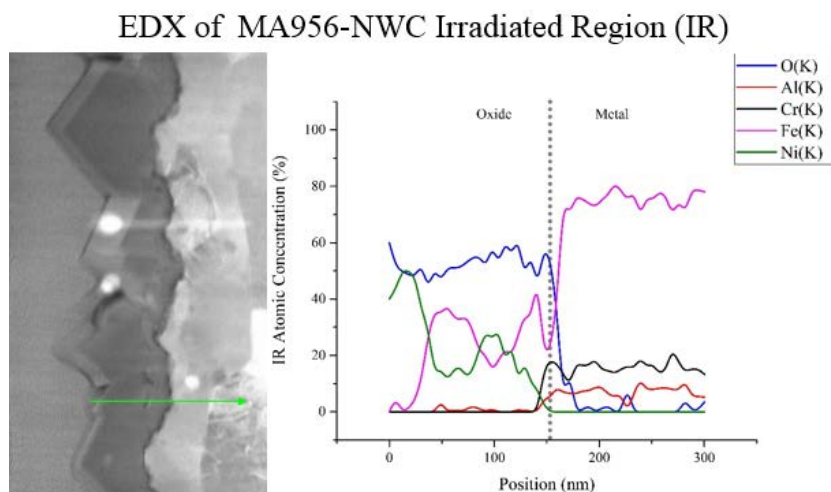


Figure C14: Left: STEM bright field image of IR region of the 24-hour electron-beam irradiated MA956 NWC sample (the thin arrow shows the length of the EDX line scan and its direction). Right: STEM EDX IR line scan results, atomic concentration vs. position, representation of oxide and metal region of scan.

The EDX line scan of the RAR region of the MA956 NWC sample in the oxygenated water is presented in Figure C15. The TEM sample of the RAR region includes a platinum layer as seen in the plot. Past this layer, the oxide layer of this region as suggested by the line scan contains 60% atomic concentration of Oxygen, about 30% atomic concentration of iron as well as about 20% atomic concentration of Nickel content.

EDX of MA956-NWC Radiolysis Affected Region (RAR)

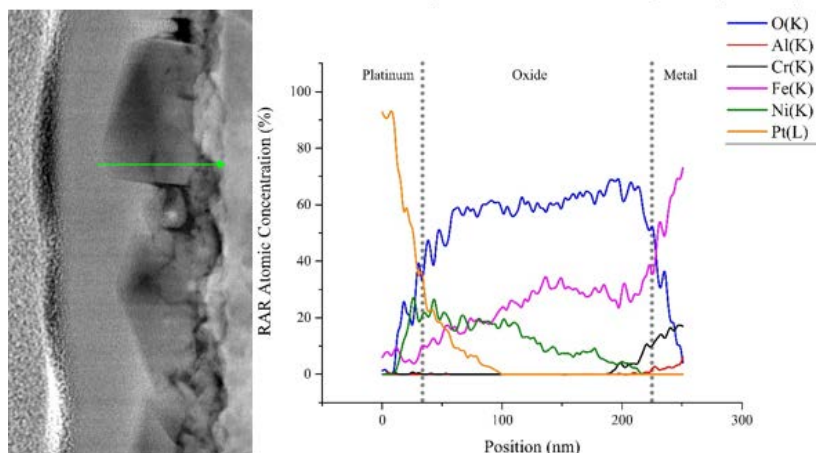


Figure C15: Left: STEM bright field image of RAR region of the 24-hour electron-beam irradiated MA956 NWC sample (the thin arrow shows the length of the EDX line scan and its direction). Right: STEM EDX UR line scan results, atomic concentration vs. position, representation of oxide and metal region of scan.

c. Raman Spectroscopy – Oxide Phase

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated sample. Spectra were recorded using a Micro-Raman Spectrometer (NRS-5100, Jasco). The spectra were collected using a 532 nm wavelength green laser, at a typical laser power of 50 mW, during a total of 600s of exposure time.

Three regions on the irradiated sample were measured using Raman spectroscopy, irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR). Five individual spectra were also taken in each region for data consistency check.

Raman spectra of the UR, RAR and IR region of the MA956 sample in the Oxygen-saturated water are presented in Figure C16. The black line represents the irradiated region, the maroon line represents the radiolysis affected region and the dark turquoise line represents the unirradiated region. The Raman peaks related to NiCr_2O_4 are present in all the regions in all NWC samples which confirms the presence of Nickel in the EDX line scans. In addition to that, there might be presence of FeCr_2O_4 and Cr_2O_3 considering some of the peaks lay in between NiCr_2O_4 (blue dotted lines) and FeCr_2O_4 (pink dotted lines) or NiCr_2O_4 (blue dotted lines) and Cr_2O_3 (green dotted lines). Also, the radiolysis affected region in all NWC samples suggests possible presence of $\alpha\text{-Fe}_2\text{O}_3$ again, based on some peaks being positioned in between NiCr_2O_4 (blue dotted lines) and $\alpha\text{-Fe}_2\text{O}_3$ (red dotted lines).

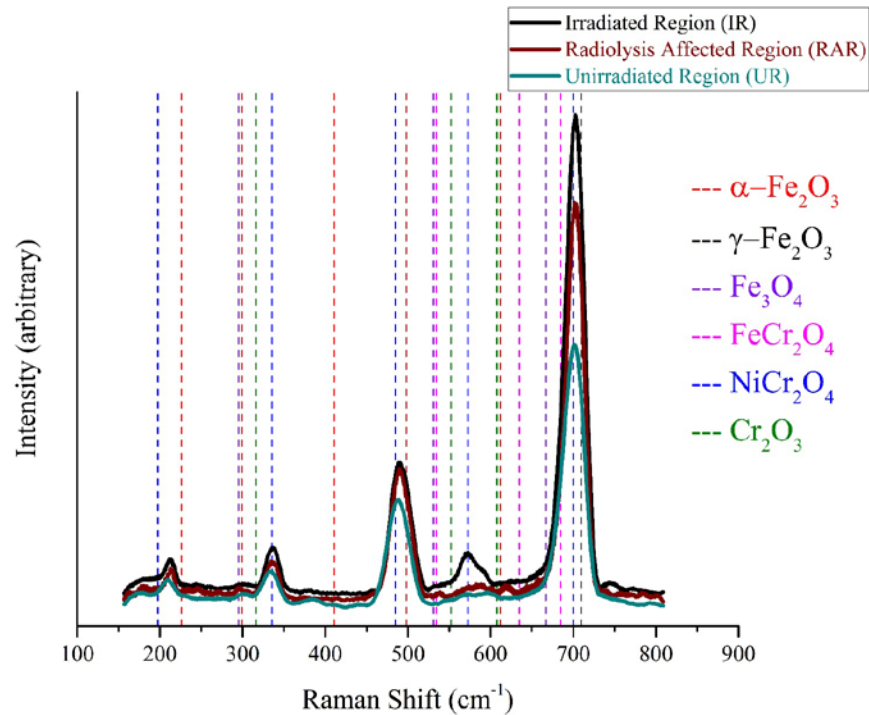


Figure C16: Post-Irradiation Raman spectra collected from the 24-hour electron-beam irradiated MA956 NWC sample in Oxygen-saturated water. Representation of the three different regions (IR, RAR and UR) and associated Raman peaks.

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

December 2016 Milestone report for T54Y2 Alloy

Four T54Y2 steel sample irradiations were completed to assess the corrosion behavior of this steel under reactor-like conditions. In this experiment the thin samples actually serve as the interface between the accelerator vacuum system on one side, and water at high pressure and temperature on the other. The samples irradiated at the University of Michigan used high energy protons while at University of Notre Dame an electron beam was used. The protons have energy of ca. 1.7MeV as they pass through the oxide into the water, and electrons have energy of ca. 1.5MeV. The protons have much higher momentum, and so (like high energy neutrons) are capable of causing significant atomic displacement damage in the oxide layer. They also move much more slowly than the relativistic electrons, so their LET (linear energy transfer) is ca. 200x larger than the electrons. To compensate and give nearly the same average energy dose to the sample and water near the surface, the electron beam flux (amps/cm²) is adjusted to be ca. 100x greater than the proton beam. Electrons do essentially no displacement damage to the solid.

Detailed analysis of the several T54Y2 samples is shown below in sections A-C. A summary of oxide thickness generated in the 24 hour irradiated samples is presented in Figure 1. The plot shows comparison between three different regions of interest: unirradiated region upstream of the radiation (UR), the directly irradiated region (IR), and a radiolysis affected region (RAR) downstream of the sample. Samples were irradiated at 320°C with 3ppm hydrogen (HW), and 288°C with 2 ppm oxygen (NWC).

We conclude that T54Y2 steel is a viable candidate cladding material as the corrosion is not dramatically enhanced in the direct radiation zones compared to the unirradiated zones. Its performance is reasonably similar to other candidate steels under these conditions of extreme radiation in either hydrogenated or oxygenated water.

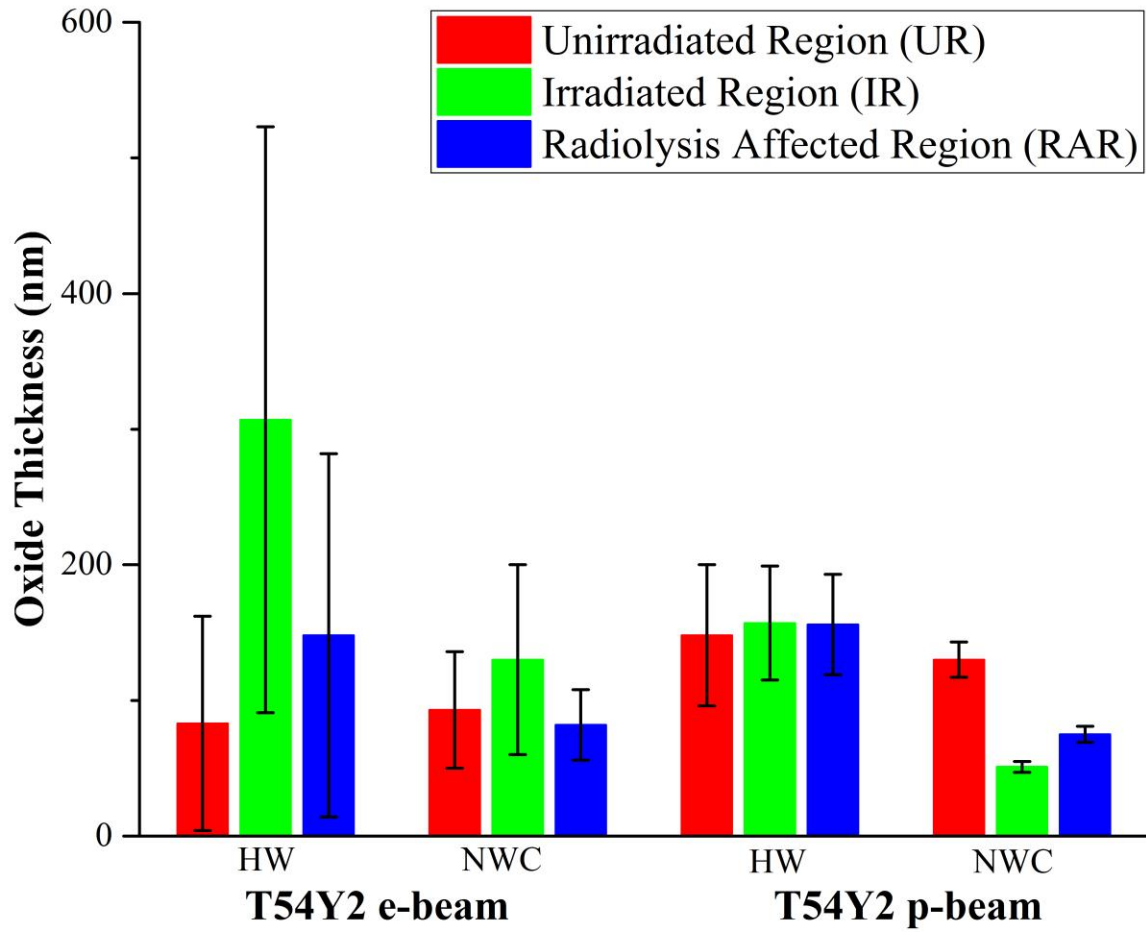


Figure 1: T54Y2 Oxide thickness comparison between ND e-beam and UM p-beam 24 hour irradiated samples. Water chemistry was either 320°C with 3ppm H₂ (HW), or 288°C with 2ppm O₂ (NWC).

A. T54Y2 Base Metal Characterization

The material was cast by a vacuum induction melting from pure element feedstock homogenized at 1200°C, hot-extruded at 1050°C, and then stress-relief annealed at 700°C.

The bulk material was obtained from ORNL, and chemical composition is listed in Table A1.

Table A1. Chemical composition of as-received T54Y2, supplied by ORNL.

Heat	C	O	P	S	Si	B	Ni	Cr	Mo
NA	0.002	0.0011	<0.002	0.0003	0.02	0.001	-	15.06	-
	Al	Nb	Zr	V	Ti	N	Y	Fe	
	3.93	-	-	-	-	0.001	0.12	Bal.	

EDS element analysis was carried out on a FEI NOVA SEM/FIB with EDAX detector. EDS spectrum is shown in Fig. A1. Atomic and weight percentage of each alloy element was shown in Table A2. The concentration of major alloying elements was consistent with the specification received from ORNL.

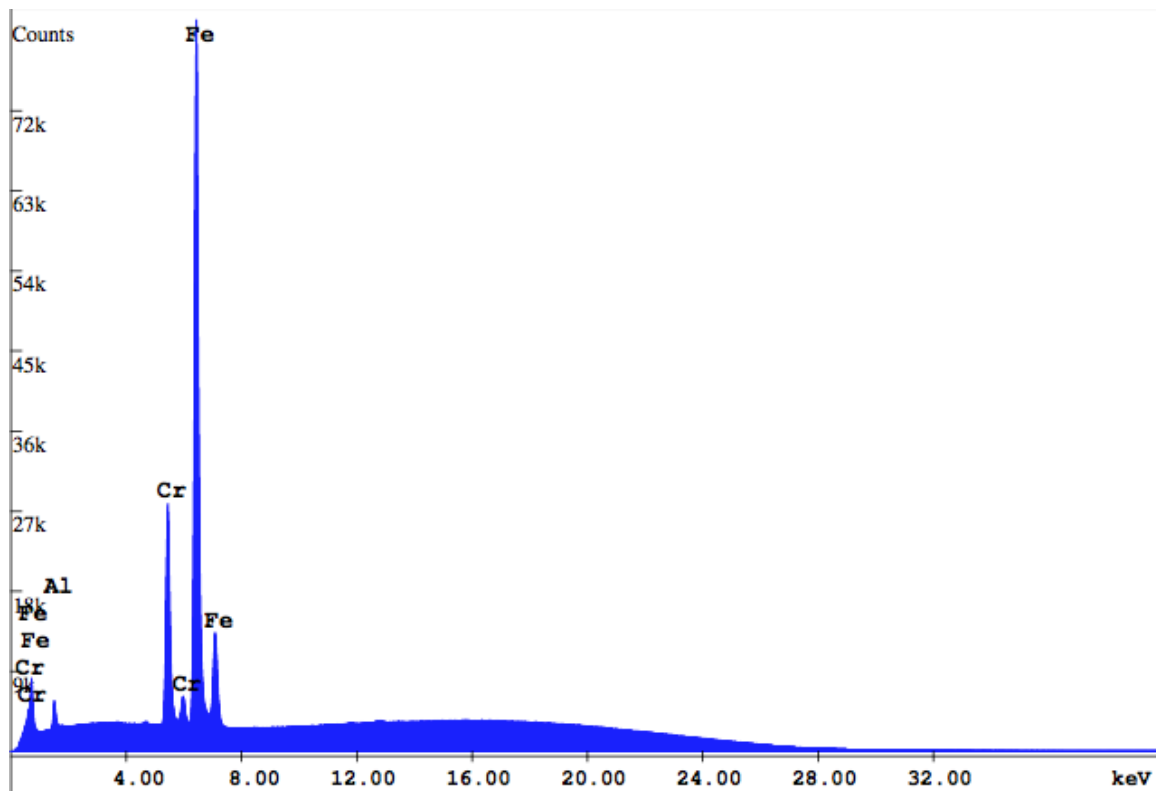


Figure A1. EDS spectrum of as-received T54Y2.

Table A2. Alloy element analysis by EDS.

Element	Wt %	At%
Fe	81.84	78.44
Cr	15.17	15.62
Al	3.00	5.95

Optical images of the polished and etched sample cross-section are shown in Figure A2. The image was taken in the plane perpendicular to the extrusion direction, and equiaxed grain structure was observed in both the extrusion axis and transverse direction. The sample showed typical ferritic steel microstructure with a large number of intermetallic precipitates containing either yttrium or aluminum evenly distributed within the grains. The average particle density and grain size were calculated as 6.7×10^4 particles/cm² and 53 μ m, respectively.

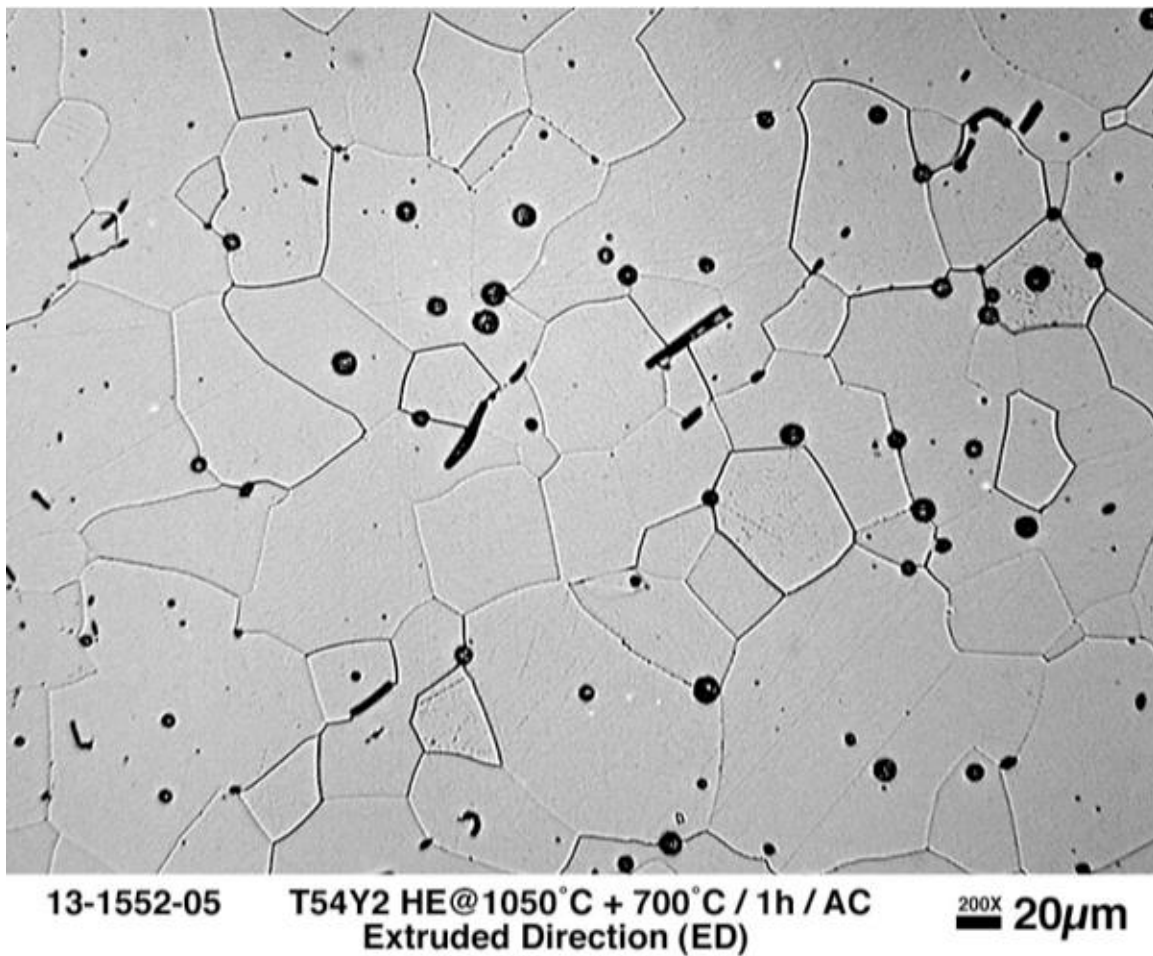
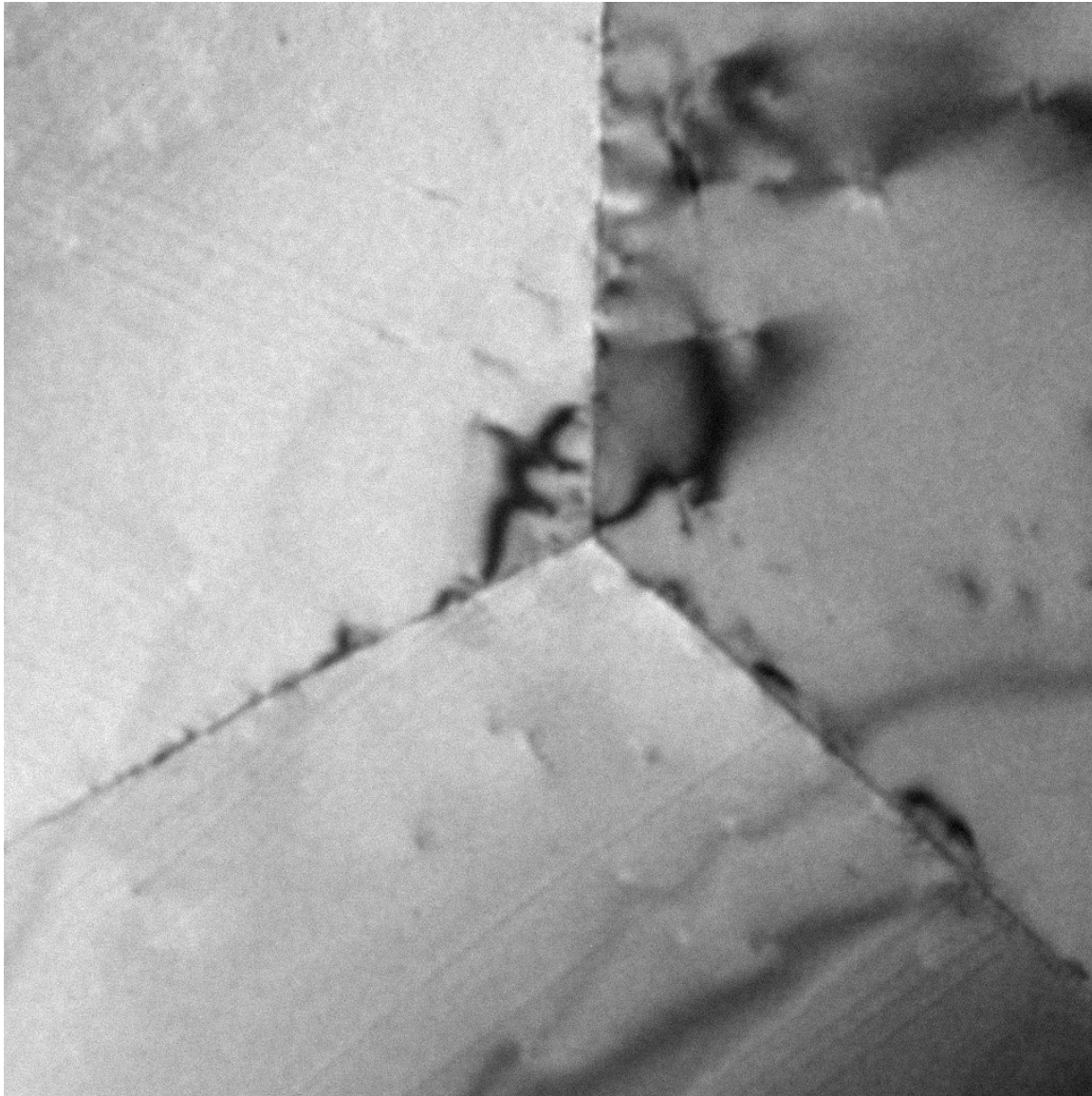


Figure A2: Optical image of a cross-sectional view of the bulk material.

TEM analysis was performed using a JEOL 3011 TEM on twin-jet polished TEM discs. Very clear grain boundaries are shown in Figure A3, and no other visible precipitates (except Y and Al containing precipitate) were observed within the grains or at the grain boundaries.



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TEM Mode: Imaging

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Figure A3. TEM Bright-field images of T54Y2 base metal at a triple grain boundary junction.

B. Proton Irradiation Experiments (U. Michigan)

B1. Summary

Proton irradiations of T54Y2 were completed in PWR hydrogenated water (PWR-HW), and in BWR normal water chemistry (BWR-NWC) at 320°C and 288°C, respectively. A 5.4 MeV proton beam at 2 μ A/cm² current density was used for these irradiations. The sample thickness was 80 microns, and the energy of the protons as they cross the oxide layer and enter the water is 1.7MeV. The LET in water is 5.6 x 10⁻¹¹ J/cm/e⁻. The dose rate to the water directly at the interface is 500kJ/kg/s. Various regions of the irradiated sample were analyzed using SEM and Raman Spectroscopy and characterizations of the oxide microstructure were carried out on the TEM.

Table B1: List of irradiation experiments completed for T54Y2.

Sample ID	Proton energy (MeV)	Temp (°C)	Water chemistry	Water dose rate (kGy/s)	Damage rate (dpa/s)	Duration (hr)
T54Y2-HW-24IR	5.4	320	PWR-HW (3 ppm H ₂)	500kGy/s	2.2 x10 ⁻⁷	24
T54Y2-NWC-24IR	5.4	288	BWR-NWC (2 ppm O ₂)	500kGy/s	2.2 x10 ⁻⁷	24

B2. Proton Irradiation Experimental conditions

Two T54Y2 samples were irradiated for 24 hr under the experimental conditions listed in Table B1. Water loop data and beamline data are shown in Figures B1 and B2 for PWR-HW condition and Figures B3 and B4 for BWR-NWC condition.

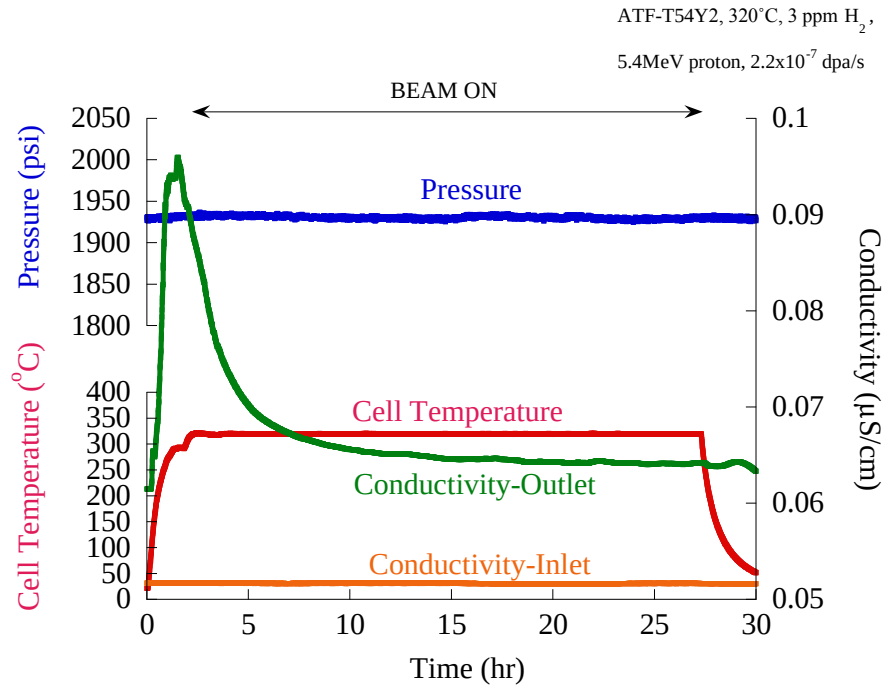


Figure B1: Water loop data of 24 hr proton irradiation of T54Y2 in 320°C 3 ppm H₂ water at a damage rate of 2.2x10⁻⁷ dpa/s.

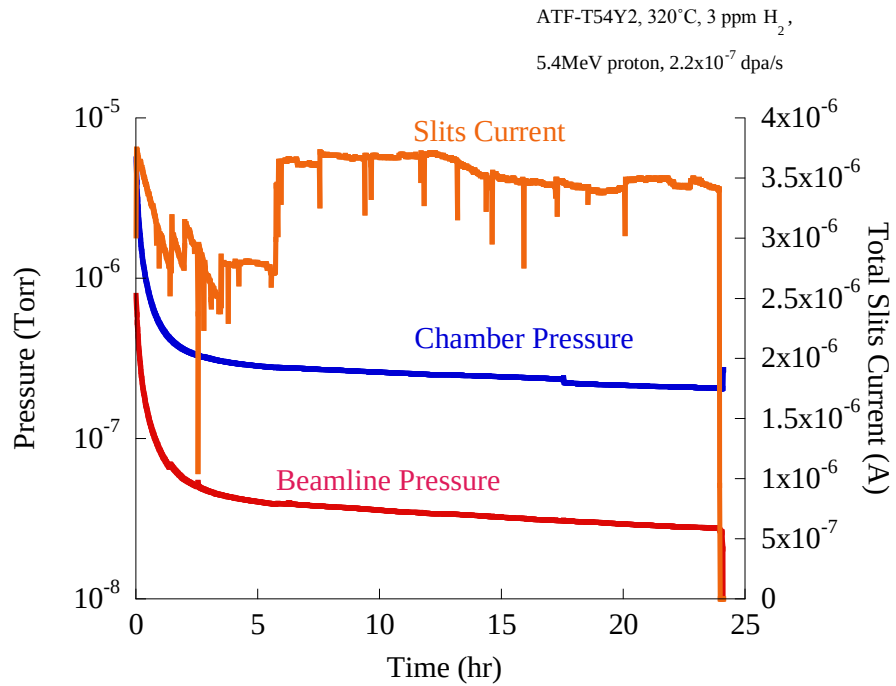


Figure B2: Beam current and pressure in the beamline and target chamber for the T54Y2 proton irradiation experiment in PWR-HW condition.

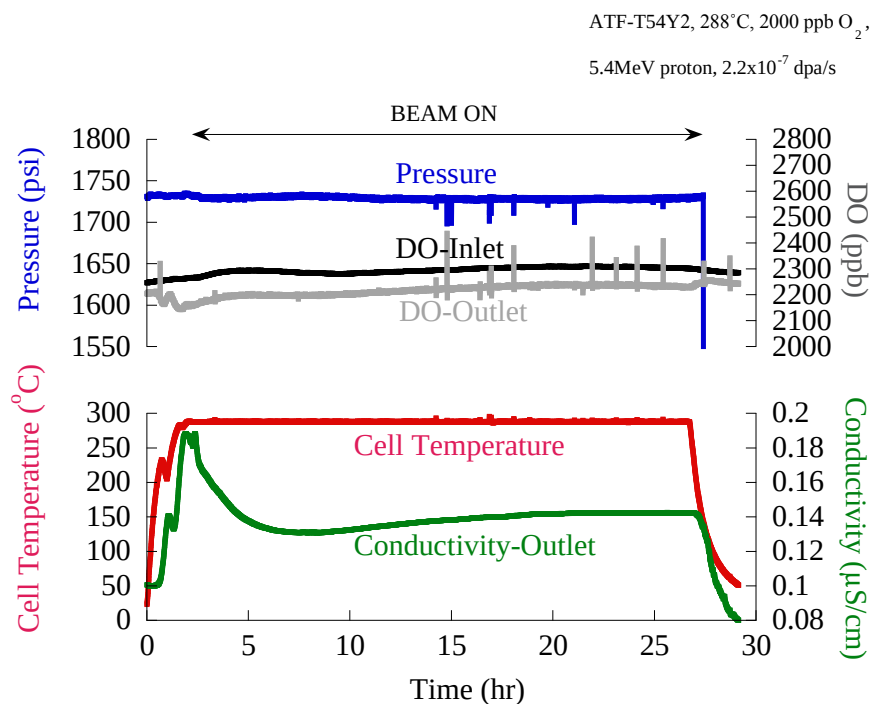


Figure B3: Water loop data of 24 hr proton irradiation of T54Y2 in 288°C 2 ppm O₂ water at a damage rate of 2.2x10⁻⁷ dpa/s.

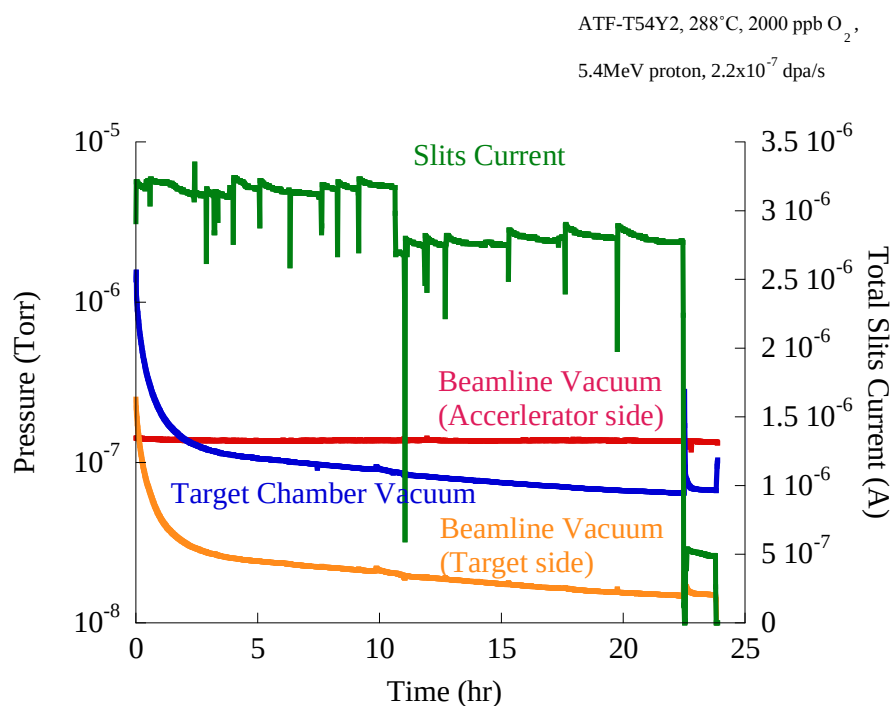


Figure B4: Beam current and pressure in the beamline and target chamber for the T54Y2 proton irradiation experiment in BWR-NWC condition.

B3. Post Irradiation Characterization

Three distinctive regions of the sample surface were characterized, namely the Irradiated Region (IR), Radiolysis Affected Region (RAR) and the Unirradiated Region (UR).

Optical Images

Sample T54Y2-HW-24IR remained as shiny as the polished surface in the UR region, as indicated in Figure B5, whereas the IR region has a matte gray appearance. Around the IR region, a noticeable rim of darker oxide was observed, most likely to be the RAR area, however, a distinctive flow region was not found in this sample.

Sample T54Y2-NWC-24IR was discolored and showed interference colors, shown in Figure B5. The crescent shaped UR region was observed at the lower part of the sample. An IR region with dark blue appearance was connected with a unique fan-shaped flow region (i.e. RAR region) covers the upper part of the sample, making it easy to identify the sample orientation.

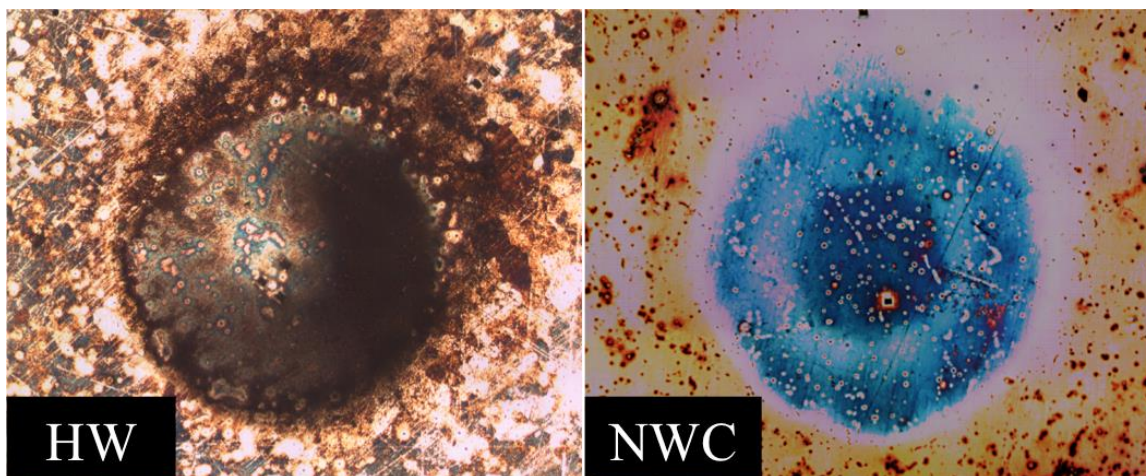


Figure B5: Optical images of irradiated samples T54Y2-HW-24IR and T54Y2-NWC-24IR.

Surface Oxide Morphology Analysis

Sample T54Y2-HW-24IR has a matte gray appearance after 24 hr exposure in primary water condition; a SEM image with circles outlining each region is shown in Figure B6. Oxide morphologies in UR and RAR regions were similar. Outer surface particles in the UR region are more faceted compared with the one in the RAR region. In both regions, a regular shaped outer oxide was observed with the particle size of $\sim 1 \mu\text{m}$. In the IR region, oxide particles were less faceted with a size of $\sim 250 \text{ nm}$ as indicated in Figure B7. Outer oxide particle density was significantly higher in the IR region compared with RAR and UR region.

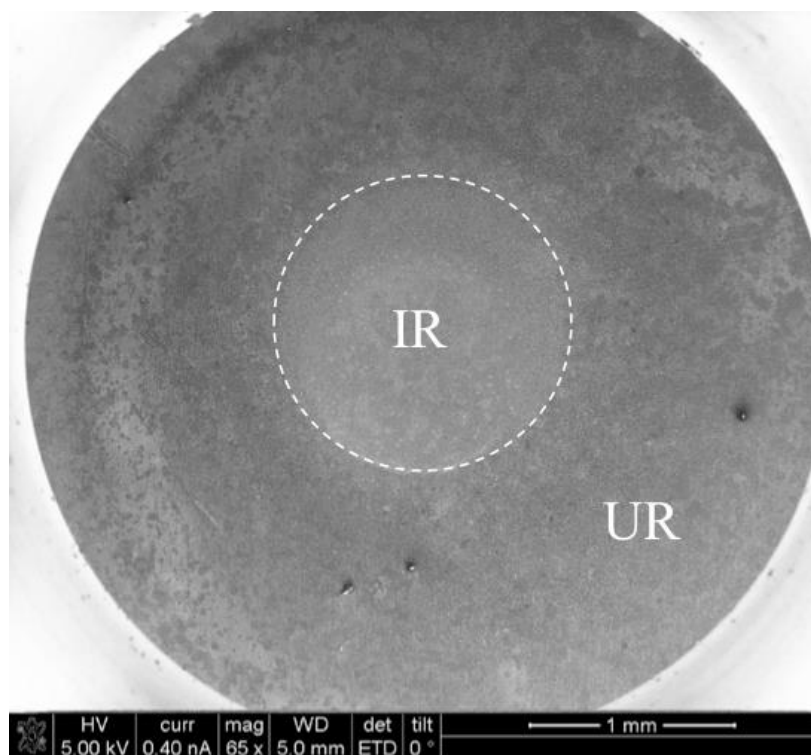


Figure B6: SEM image of sample T54Y2-HW-24IR. The irradiated region (IR) and unirradiated region (UR) are indicated by the dotted line.

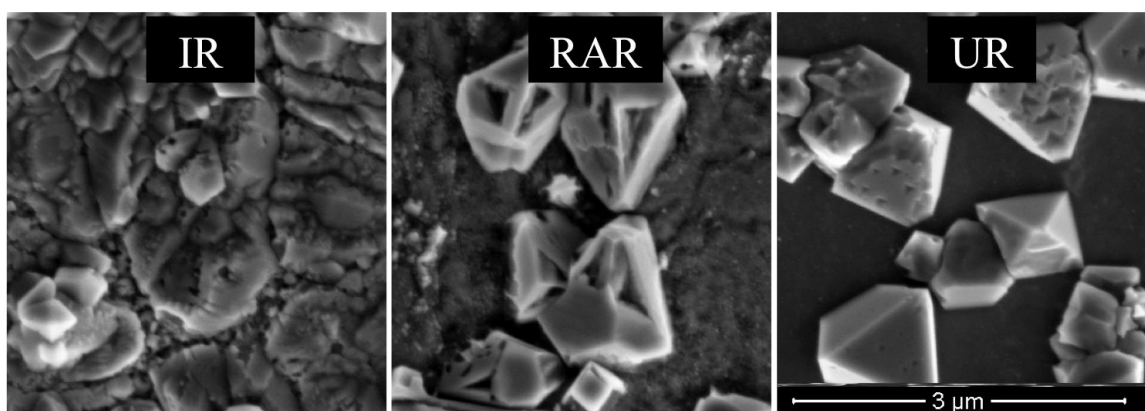


Figure B7: High magnification SEM images of the three regions observed on sample T54Y2-HW-24IR.

Sample T54Y2-NWC-24IR was discolored after 24 hr of exposure in BWR-NWC water chemistry. In Figure B8, the IR and RAR regions can still be observed on the surface of the sample. However, the high magnification SEM images shown in Figure B9 indicated that there was no significant difference regarding oxide particle size (50-200 nm) and morphology in the IR and RAR regions. Oxide particles in the UR region have large aspect ratio compared to the oxides found in the RAR and IR regions. The particle size in the UR region is ~ 200 -400 nm.

FIB lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared, and TEM analysis was carried out on these TEM lamellas.

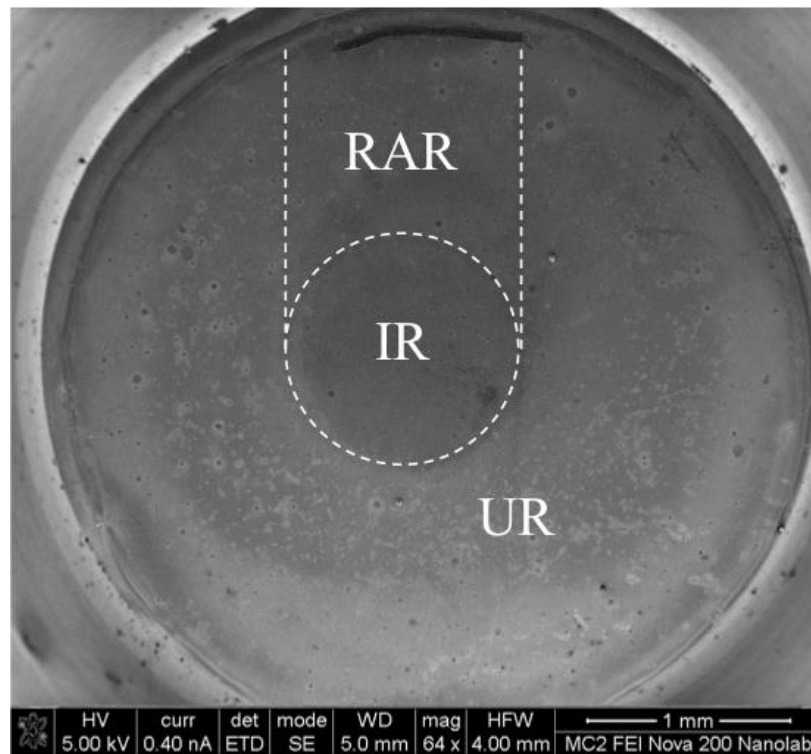


Figure B8: SEM image of sample T54Y2-NWC-24IR. The irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR) are indicated by the dotted line.

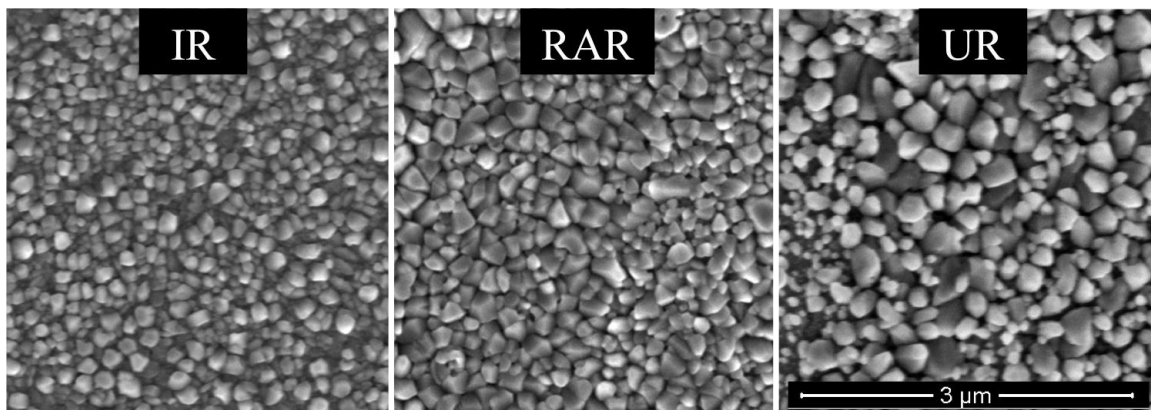


Figure B9: High magnification SEM image of the three regions observed on sample T54Y2-NWC-24IR.

Oxide Phase Analysis with Raman Spectroscopy

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated samples. Spectra were recorded using a Renishaw inVia microscope with a RenCam CCD detector. The spectra were collected using a 633 nm wavelength red laser, at a typical laser power of 50 mW, during a total of 500 s of acquisition time.

All three regions (IR, RAR and UR) on the irradiated samples were measured using Raman spectroscopy. Three individual spectra were taken in each region for data consistency check.

For **sample T54Y2-HW-24IR**, the Raman peaks related to α -Fe₂O₃ were observed in the IR region as shown in Figure B10. This observation indicated that when the sample surface was in contact with the directly irradiated water, the corrosion potential must be high enough for the formation of hematite. The cause of hematite formation could be the presence of short- and long-lived radical species and hydrogen peroxide. The short-lived radiolysis products (e.g. OH[•] radicals) cannot escape the IR region. However, the product species H₂O₂ can be carried away from the IR region into the RAR region by convection flow of the heated water, and give rise to hematite formation there. However, only some of the areas exposed to convective flow experienced the formation of hematite. In areas where hematite signal was found dominating the Raman spectra (RAR-brighter region), more intermetallic particles were found embedded in the metal substrate. Outer particles formed on the surface of the sample in close proximity to the embedded precipitates have a pseudo-cubic morphology (Fig. B11), indicating it could be α -Fe₂O₃ in nature [1]. Other areas in the RAR region missing the embedded precipitates showed Raman response of a magnetite structure. The outer oxide particles have an octahedral morphology in these regions, which is unique to magnetite [2].

Because the electronegativity of Al and Y is much lower than Fe, electrochemically the Al or Y containing precipitate of this steel acts as an anode, and FeCrAl matrix acts as a cathode. The Al,Y precipitates will be preferentially oxidized. The oxidation is due to the H₂O₂ produced in the water by the very high dose rate irradiation (direct production of O₂ is prohibited by the H₂ overpressure). According to the iron Pourbaix diagram, by increasing local pH value and redox potential, the Fe³⁺ will be preferentially precipitated, resulting in the formation of Fe₂O₃. This Fe₂O₃ oxide indicates that the local water environment around these embedded precipitates plays a critical role in formation of outer precipitates in the RAR region.

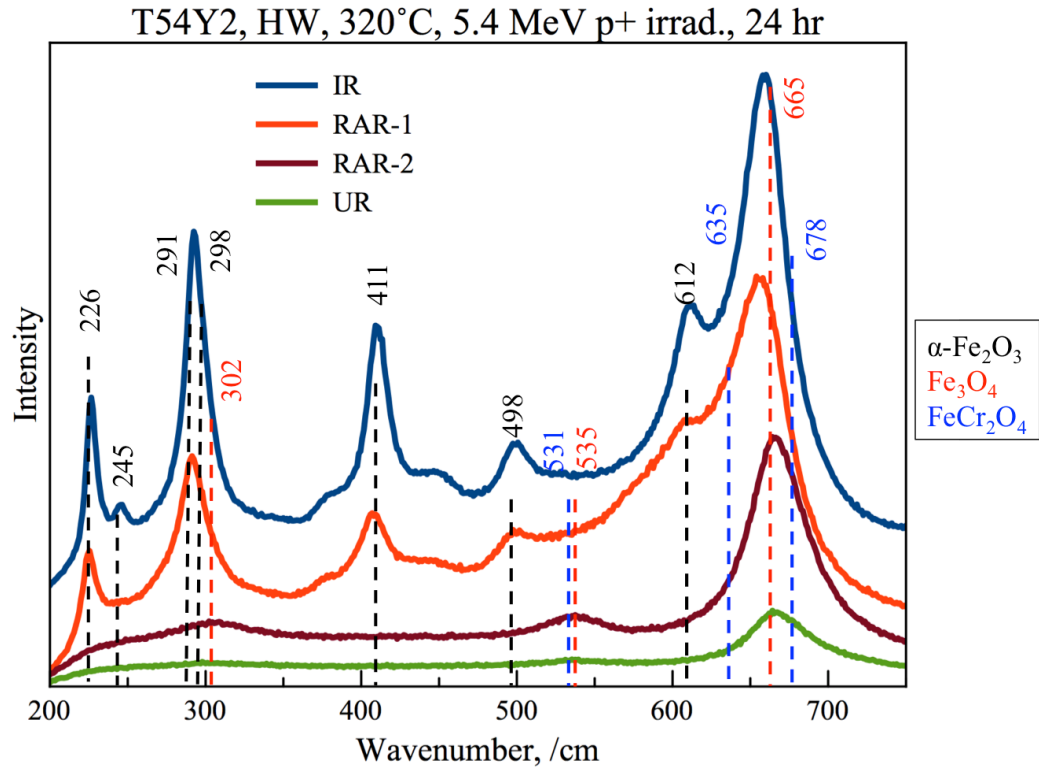


Figure B10: Raman spectra collected from IR, RAR and UR region on the 24 hr irradiated T54Y2 sample in primary water condition.

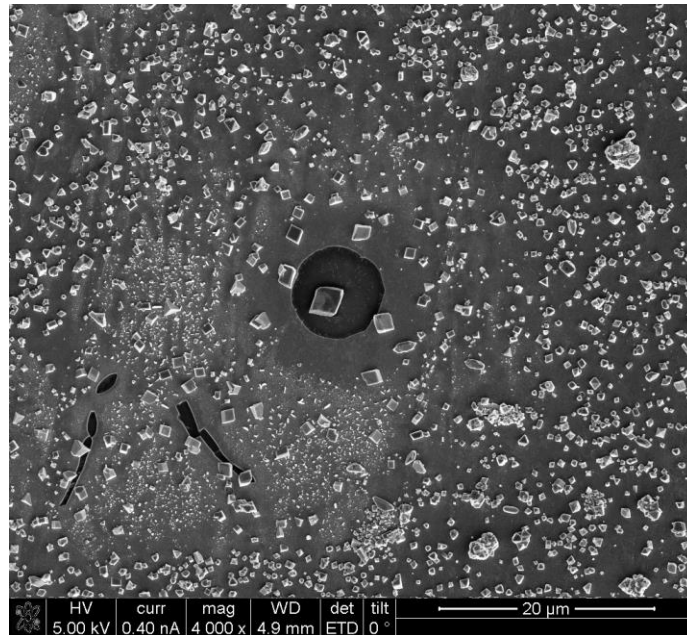


Figure B11: High magnification SEM image of the RAR region with embedded precipitates observed on sample T54Y2-NWC-24IR.

The UR regions showed a typical Raman spectrum of magnetite (Fe_3O_4). However, the 665 cm^{-1} peak which was related to magnetite was observed in all regions, indicating that the inner layer may also consist of magnetite phase or a spinel phase which was deficient in Cr content, e.g. $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$. Although, the spinel phase will cause a slight shift in the Raman peak positions, from 665 to a lower wavenumber, e.g. the 635 cm^{-1} for FeCr_2O_4 . Further compositional analysis of the inner oxide layer is required to confirm the identity of the inner oxide. In the IR region, the oxide consisted of a spinel $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$ inner layer and a Fe_2O_3 outer layer.

For **T54Y2-NWC-24IR**, the Raman peaks related to Fe_2O_3 are present in all the regions as shown in Figure B12. Also, some of the peaks cannot be fitted by a single peak of Fe_2O_3 , spinel or Fe_3O_4 , which suggests multiple oxide phases may be present in the spectra. However, in BWR-NWC water chemistry, Fe_2O_3 is still the dominant oxide, with possible Fe substituting Cr in FeCr_2O_4 .

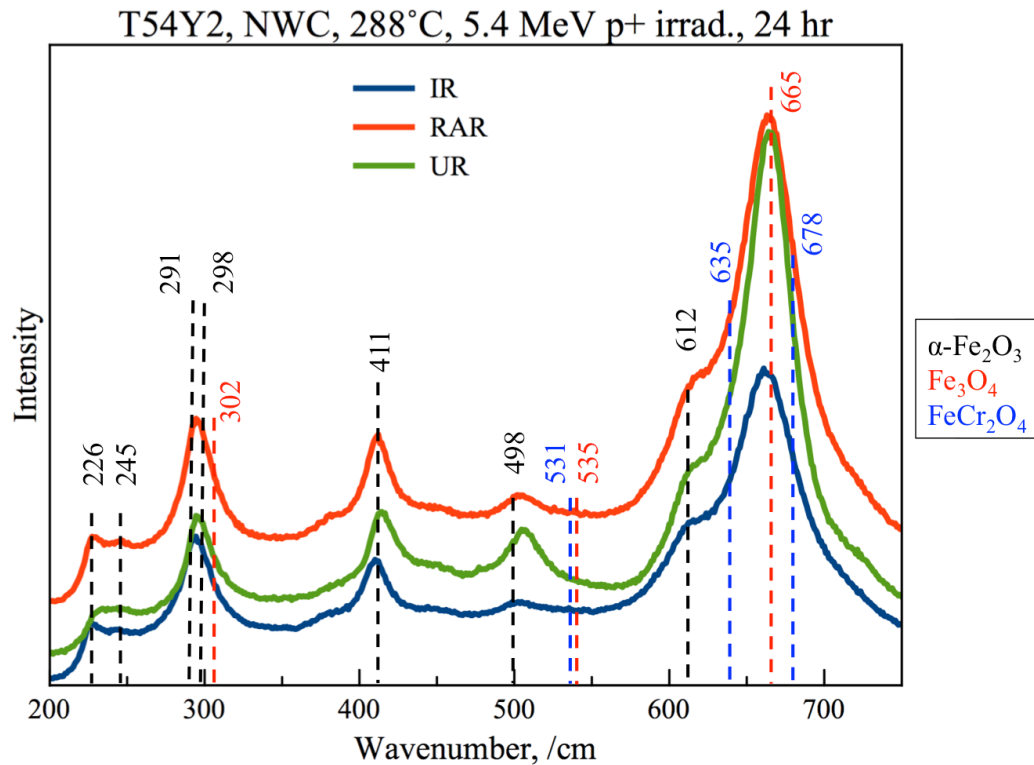


Figure B12: Raman spectra collected from irradiated region, unirradiated regions and the radiolysis affected region on the 24 hr irradiated T54Y2 sample in BWR-NWC water condition.

Oxide Morphology with TEM

TEM lamellas from IR and UR regions were prepared using FIB, and a JEOL 3100R05 TEM/STEM was used for TEM analysis.

The high angle annular dark field (HAADF) images were collected for oxide thickness analysis. Under such imaging conditions, the oxide would have a dark contrast compared to a light-colored metal substrate or platinum protective coating.

On sample **T54Y2-HW-24IR**, as shown in Figure B13, the inner oxide layer appeared to be very thin. Some outer oxide particles were found on the surface of the sample; however, due to the TEM lamella size, no outer particles were captured in the liftout from the RAR region. Although original metal surface was oxidized, the flat shape of the interface can still be observed in the UR and RAR regions. Oxide layer in the IR region has an undulated appearance, and the original sample surface cannot be observed. Average total oxide thickness for different regions was listed in Table B2.

For **T54Y2-NWC-24IR**, the HAADF STEM images shown in Figure B14, had indicated that the oxide layers were much thinner compared with the hydrogenated (and higher temperature) condition. The interface of inner and outer oxide layer became indistinguishable under NWC condition, indicating possible inner oxide dissolution had occurred. Large undulation of the metal/oxide interface was also observed. This was caused by heterogeneous inner oxide growth rate. At locations where outer oxide particle coverage is relatively thick, the inner oxide would appear to be thin, and vice versa.

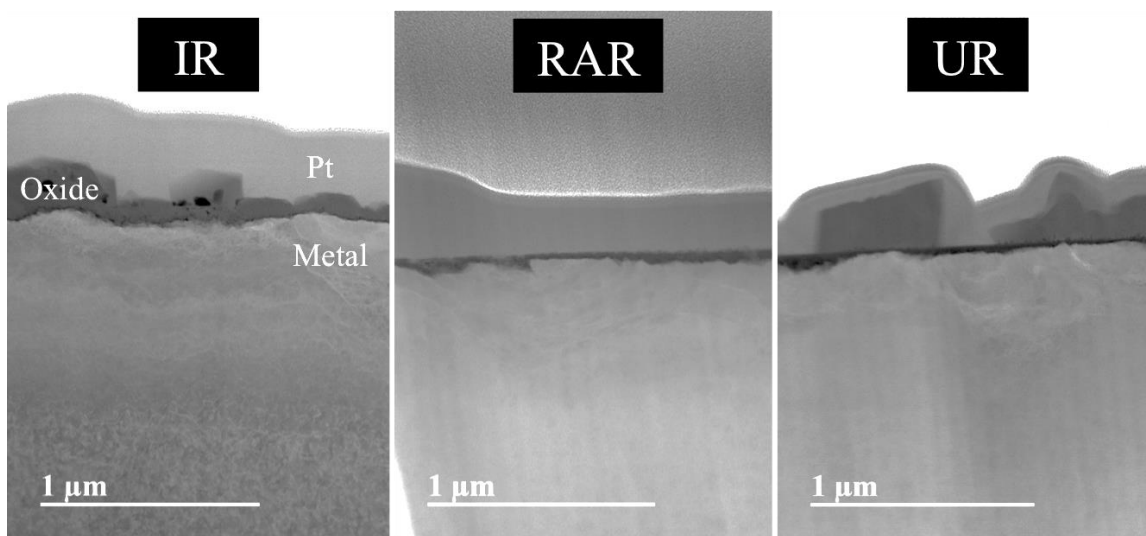


Figure B13: High Angle Annular Dark Field STEM (HAADF-STEM) images of the FIB lamellas taken from the irradiated sample T54Y2-HW-24IR.

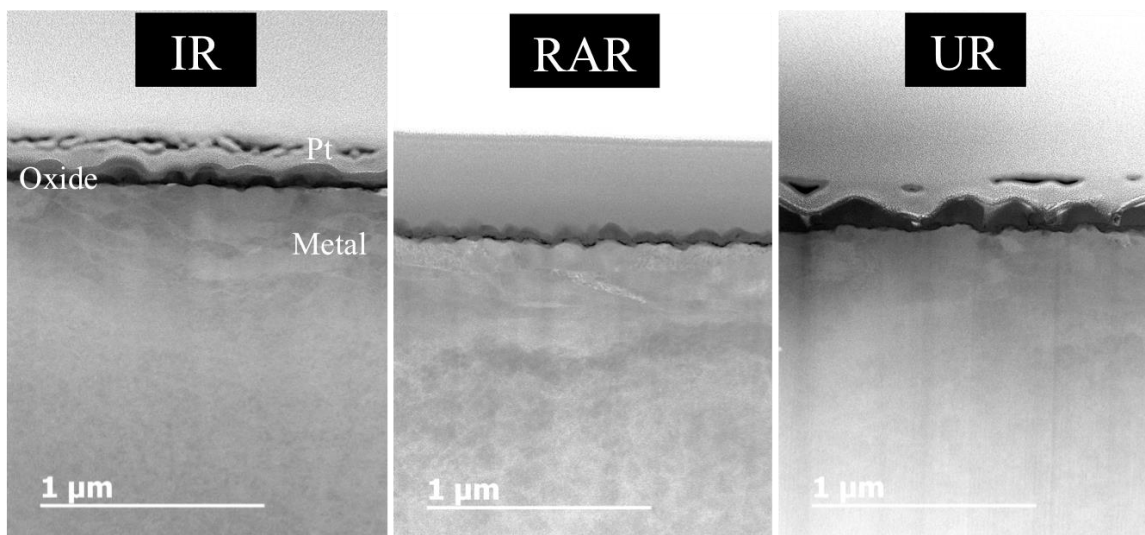


Figure B14: HAADF-STEM images of the FIB lamellas taken from the irradiated sample T54Y2-NWC-24IR.

Table B2: Oxide thickness observed on samples irradiated in both HW and NWC conditions.

Sample	Region	Total Oxide (nm)
T54Y2-HW-24IR	IR	157 ± 42
	RAR	156 ± 37
	UR	148 ± 52
T54Y2-NWC-24IR	IR	51 ± 4
	RAR	75 ± 6
	UR	130 ± 13

Oxide Composition Analysis with EDS

Energy Dispersive x-ray Spectroscopy (EDS) was used to determine the oxide compositions. The EDS spectra were collected on JEOL 2010F STEM with EDAX detector.

For **sample T54Y2-HW-24IR**, EDS results of IR and UR region are shown in Figure B15 and B16. The IR region oxide composition was consistent with Fe_2O_3 , which is 40 at% Fe and 60 at% O for the outer oxide (line-scan A). The thin inner oxide was not too different from the outer oxide (line-scan B). EDS result from the UR region had confirmed that the outer oxide was Fe_3O_4 (line-scan A) with theoretical values for Fe_3O_4 of 43 at% Fe and 57 at% O.

The inner oxide of UR region consists of a spinel phase; its composition slightly deviates from FeCr_2O_4 (line-scan A). Some aluminum was also present in this inner layer (line-scan B), however, its oxidation state and which oxide constituent it belongs to was unknown.

The RAR region has a mixture of outer particles; the presence of both hematite and magnetite were suggested by its Raman response in Fig. B10. EDS line-scans (Figure B17) become insensitive to these two oxides with similar atomic and weight percentage for each constituent elements (line-scan A). The inner oxide in the RAR region also showed some similarity when compared with UR region inner oxide (line-scan B).

Direct irradiation has a direct impact on the chromium content of the inner oxides. Without irradiation, a spinel phase was observed in the inner oxide; with irradiation, the inner oxide became similar to hematite, however, a trace amount of chromium can still be found, indicating some chrome-containing oxide is still present.

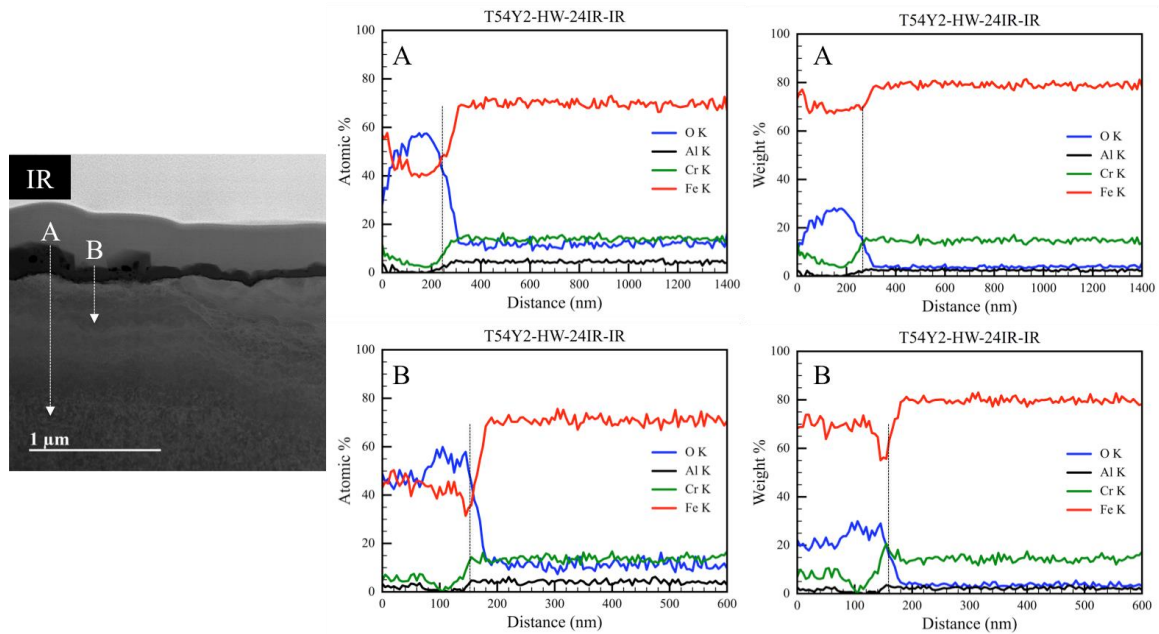


Figure B15: EDS line scans of oxide regions (IR) formed on sample T54Y2-HW-24IR.

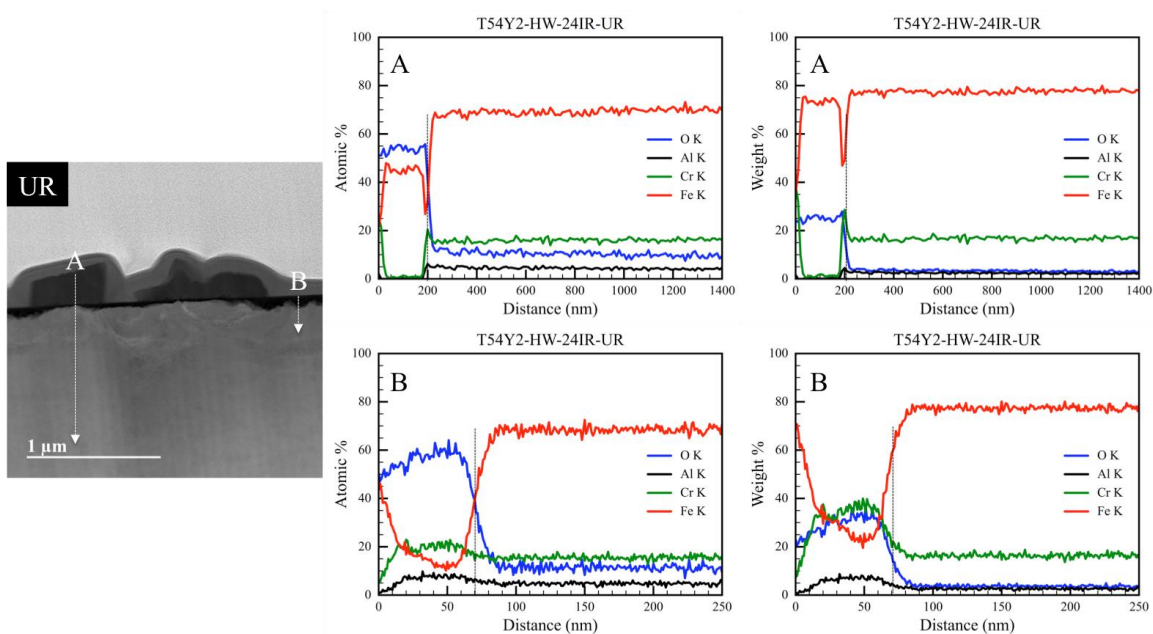


Figure B16: EDS line scans of oxide regions (UR) formed on sample T54Y2-HW-24IR.

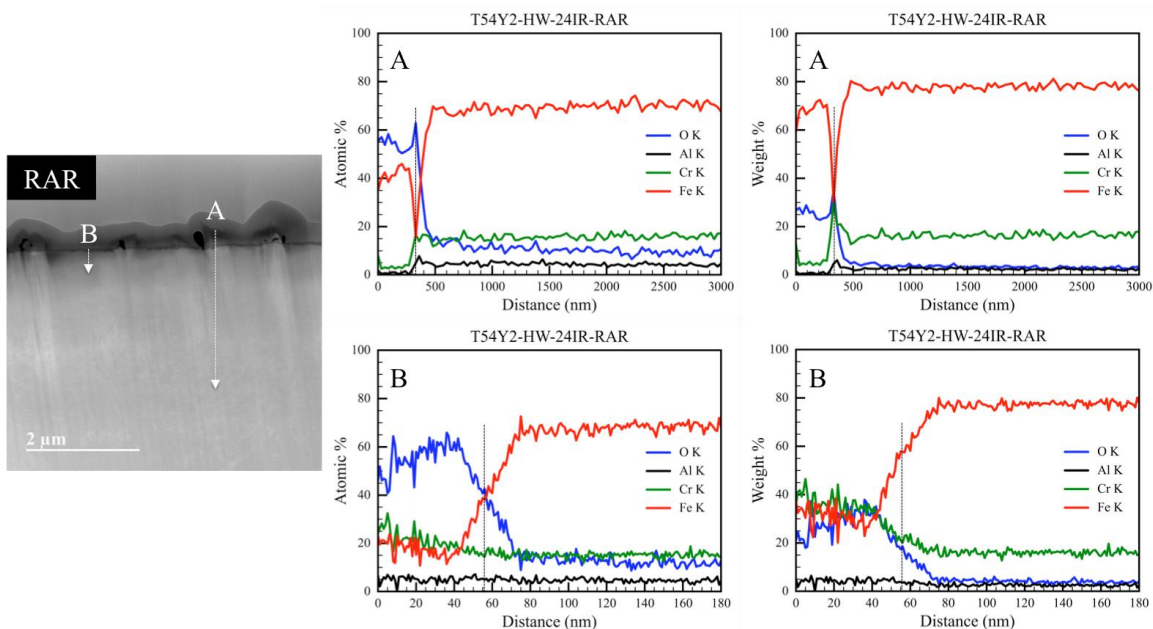


Figure B17: EDS line scans of oxide regions (RAR) formed on sample T54Y2-HW-24IR.

For the NWC condition of **sample T54Y2-NWC-24IR**, EDS results of IR and UR region are shown in Figure B18 and B19. In the IR regions, the outer oxide particle showed a hematite composition; the inner layer was very thin and its composition became difficult for the EDS to resolve. In the UR region, the outer oxide consisted of a Fe-rich Fe-Cr spinel

phase; no aluminum was found. In the RAR region (Fig. B20), hematite phase was observed which is consistent with the Raman results for this region.

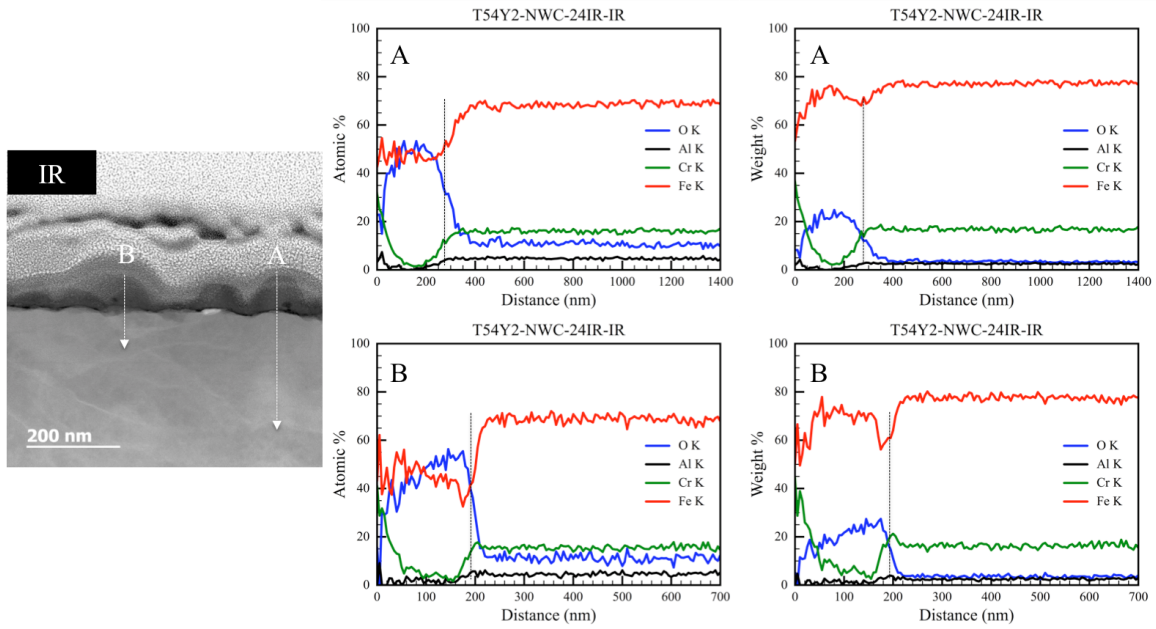


Figure B18: EDS line scans of oxide regions (IR) formed on sample T54Y2-NWC-24IR.

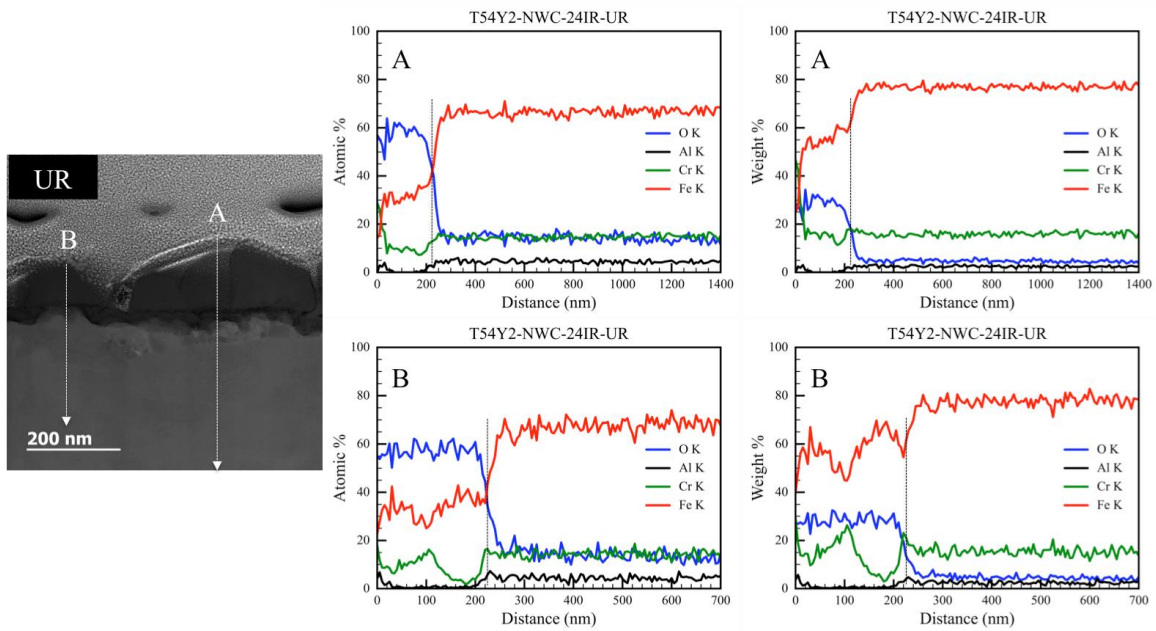


Figure B19: EDS line scans of oxide regions (UR) formed on sample T54Y2-NWC-24IR.

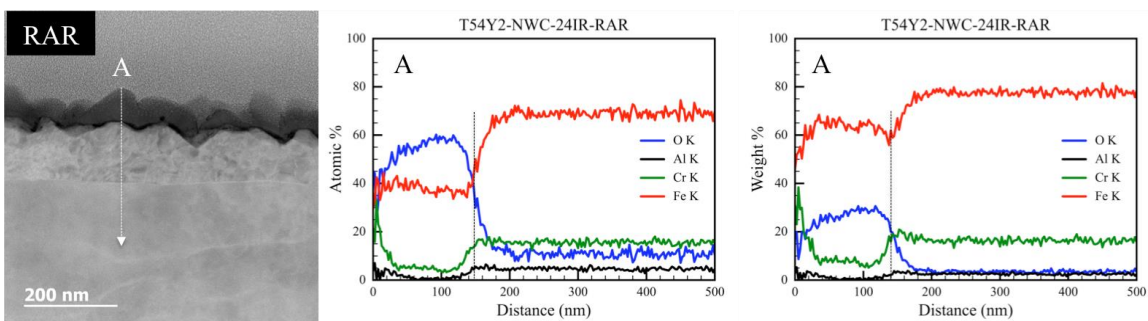


Figure B20: EDS line scans of oxide regions (RAR) formed on sample T54Y2-NWC-24IR.

Proton Post Irradiation Characterization Summary

The oxide species found on irradiated samples under different conditions were confirmed using Raman and the findings were summarized in Table B3.

Table B3: Summary of the oxide species found on T54Y2 in HW and NWC conditions under proton irradiation.

Samples	Regions	Outer Oxide/Inner Oxide	
		NWC 288°C, 2 ppm O ₂	HW 320°C, 3 ppm H ₂
T54Y2	IR	$\alpha\text{-Fe}_2\text{O}_3$ /Fe(Cr, Fe) ₂ O ₄	$\alpha\text{-Fe}_2\text{O}_3$ /Fe(Cr, Fe) ₂ O ₄
	RAR		Fe_3O_4 /Fe(Cr, Fe) ₂ O ₄
	UR		

References:

[1] J. Ouyang, et al., Supersaturation-controlled shape evolution of $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals and their facet-dependent catalytic and sensing properties, ACS, Appl. Mater. Interfaces 2014, Vol. 6, pp. 12505-12514.

[2] L. Chen, et al., Shape-evolution and growth mechanism of Fe_3O_4 polyhedrons, Advances in Materials Science and Engineering, Vol. 2015, Article ID 763124.

C. Electron Irradiation Experiments (U. of Notre Dame)

C1. Summary

Electron irradiations of T54Y2 were completed (samples ID and conditions are listed in Table C1) in PWR conditions – 3 ppm hydrogenated water (HW) at 320°C , and in BWR conditions – normal water chemistry (NWC) at 288°C. A 2.5 MeV electron beam at 120 $\mu\text{A}/\text{cm}^2$ current density was used for these irradiations. Given the ~250 micron sample thickness, energy of electrons as they cross the oxide layer and enter the water is ca. 1.5 MeV, so that they are still relativistic, and have LET of 1.9×10^6 eV/cm/e-. Dose rate to the water at the surface is ca. 170 kGy/s. Post-irradiation characterization of various regions of the irradiated samples was completed by means of SEM, TEM imaging and EDX line scans and Raman spectroscopy.

Table C1: List of irradiation experiments completed for T54Y2

Sample ID	e- Energy (MeV)	Temp (°C)	Water chemistry	current density ($\mu\text{A}/\text{cm}^2$)	Water dose rate (kGy/s)	Duration (hr)
T54Y2-HW	2.5	320	3 ppm H ₂	120	170	24
T54Y2-NWC	2.5	288	2 ppm O ₂	120	170	24

Water loop data for the 24 hr e-beam irradiated T54Y2 HW and NWC experiments are shown in Figures C1 and C2, respectively. In the T54Y2 HW experiment, note that the outlet conductivity dropped from 3.5 to 1.5 $\mu\text{S}/\text{cm}$ during the course of the experiment compared to the unchanged inlet conductivity at 0.09 $\mu\text{S}/\text{cm}$. In the T54Y2 NWC experiment, the outlet conductivity dropped from 0.67 to 0.45 $\mu\text{S}/\text{cm}$ during the course of the experiment compared to the unchanged inlet conductivity at 0.08 $\mu\text{S}/\text{cm}$. This indicates that as the sample surface developed a layer of oxide, the amount of dissolved metal that goes into solution decreases.

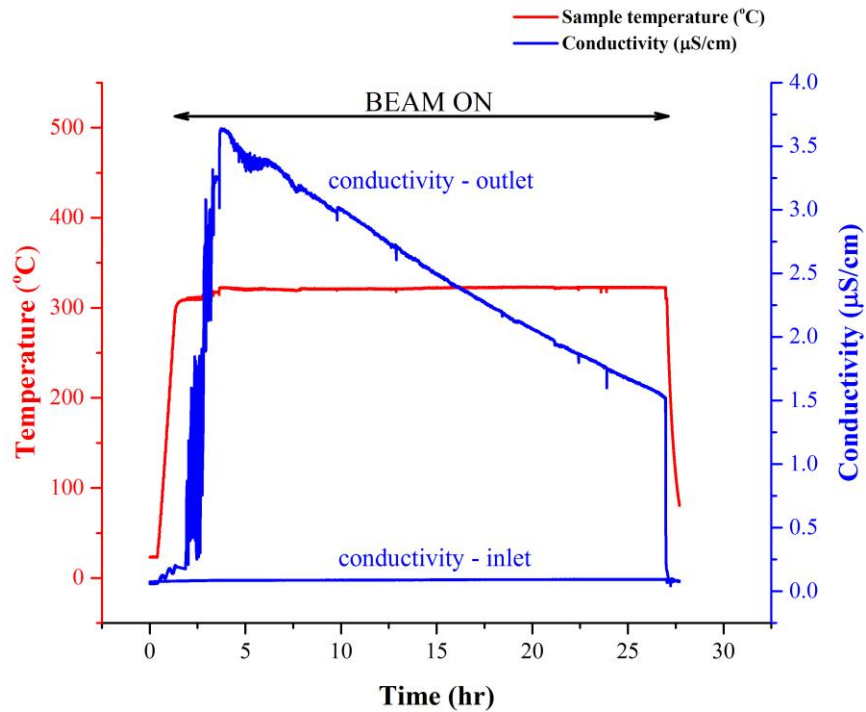


Figure C1: Water loop data of 24 hr electron irradiation of T54Y2 HW in 320°C 3 ppm H_2 water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

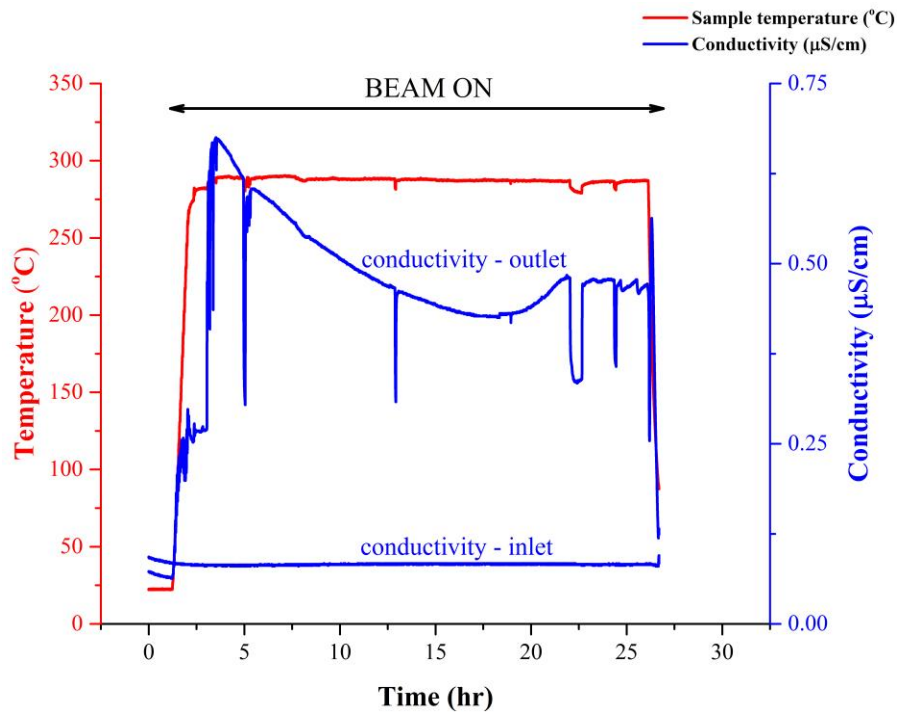


Figure C2: Water loop data of 24 hr electron irradiation of T54Y2 NWC in 288°C 2 ppm O_2 water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

C2. Post Irradiation Characterization of T54Y2 samples

a. Optical Microscopy and SEM Imaging – Oxide Morphology

Both T54Y2 steel samples (e-beam irradiated) were analyzed via microscopy. Both samples were discolored after 24 hr of e-beam exposure. Under the optical microscopy, three distinctive regions can be identified on the sample surface, Irradiated Region (IR), Radiolysis Affected Region (RAR) and Unirradiated Region (UR), shown in Figure C3 (left) for the T54Y2 HW sample and Figure C3 (right) for the T54Y2 NWC sample. The sample's irradiated region was discolored after 24 hr of e-beam exposure, observed as a darker circular region in the HW case and a golden region in the NWC case without a clearly defined shape of the irradiated region.

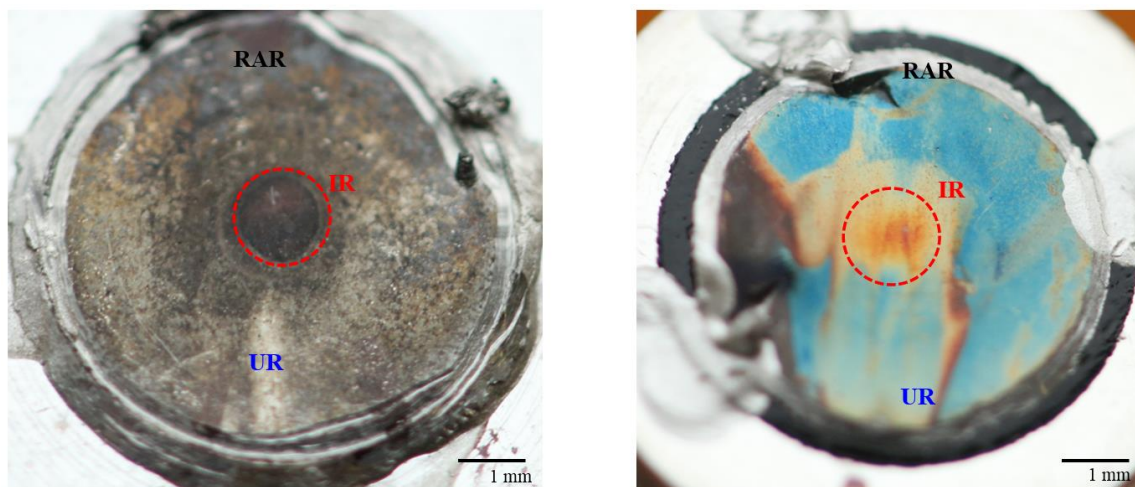


Figure C3: Post-irradiation optical image of 24-hour electron-beam irradiated T54Y2 sample in HW (left) and NWC (right). Representation of unirradiated region (UR), irradiated region (IR) and radiolysis affected region (RAR).

The high magnification SEM images in Figure C4 represent the oxide particles of the three different regions (UR, IR and RAR) in the T54Y2 Oxygen-saturated sample (top three images) and Hydrogen-saturated sample (bottom three images). There are similarities in the population density of the particles when comparing the regions of the different irradiating conditions; the IR region features the most densely populated particles, then the RAR region and the UR region. In both cases, the RAR region features particles of mixed nature from both IR and UR region. The IR region in the NWC case features very small particles if compared to the particles in the IR region of the HW case. Also, the particles in the IR region in both conditions seem to grow in different direction, forming something similar to a “zig-zag” pattern. This cannot be seen clearly in Figure C4; therefore, supporting SEM images at lower magnification can be seen in Figure C5.

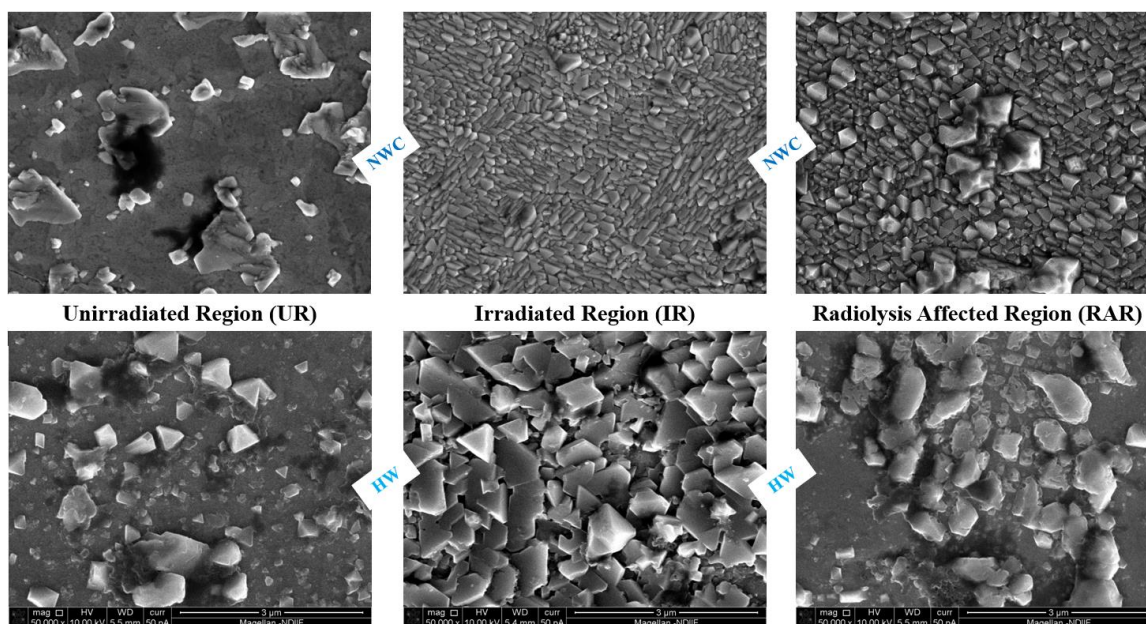


Figure C4: Post-Irradiation SEM images of 24-hour electron-beam T54Y2 sample in NWC (top) and HW (bottom). Representation of the three different regions, UR, IR and RAR.

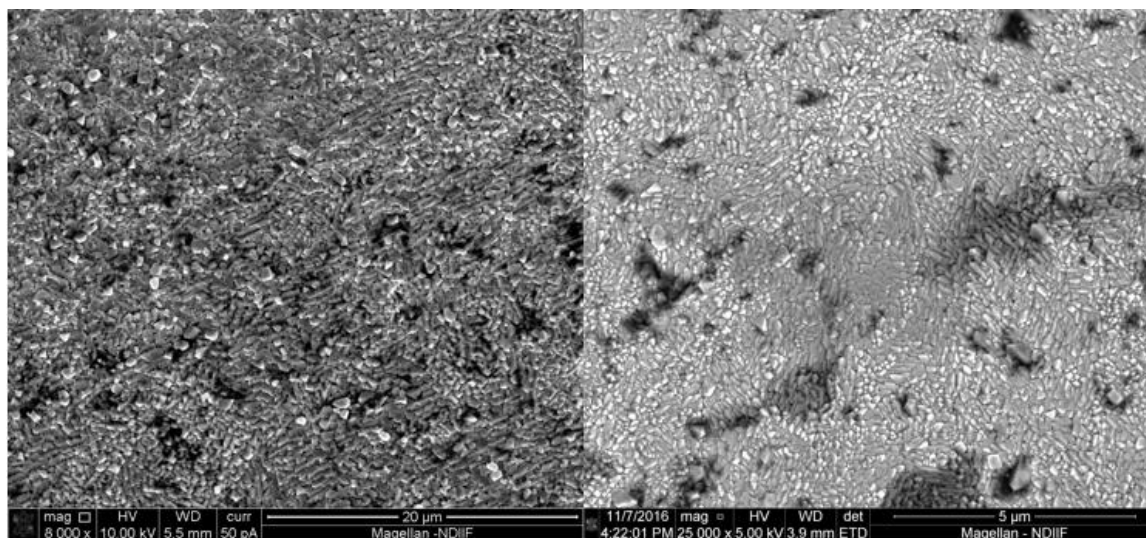


Figure C5: Post-Irradiation SEM images of 24-hour electron-beam T54Y2 sample in HW (left) and NWC (right). Representation of “zig-zag” particle pattern in the irradiated region.

The high magnification SEM images in Figure C6 reveal microcracks present on the surface of both T54Y2 samples that extend up to 200 nm. The images illustrate cracks on the T54Y2 HW (left) and T54Y2 NWC (right) sample. From the SEM images, the T54Y2 HW sample’s surface features deeper cracks while the T54Y2 NWC sample features cracks that appear between grains. This is also evident in the Raman optical images (Figure C14 and C15).

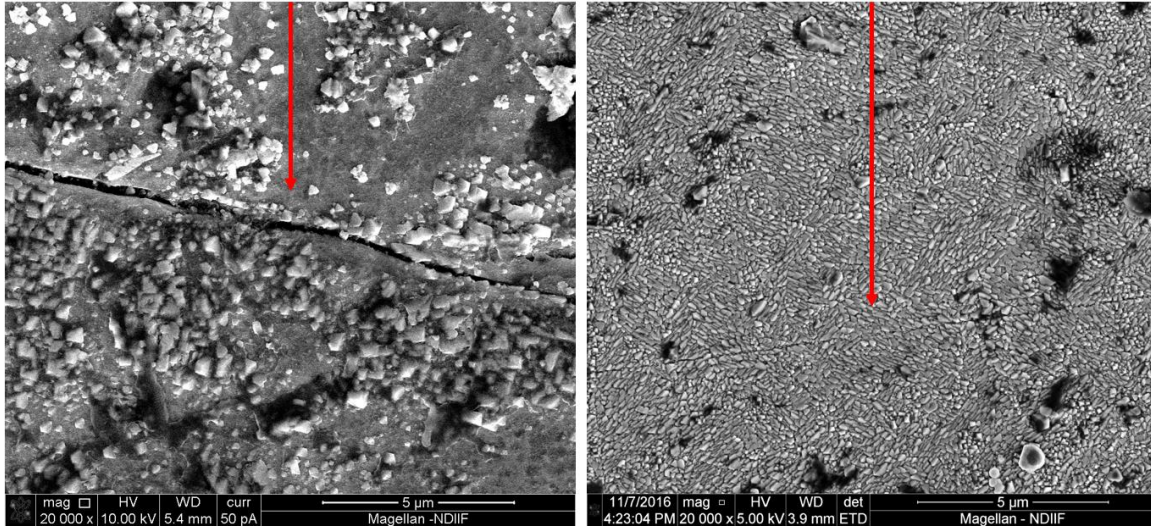


Figure C6: Post-Irradiation SEM images of 24-hour electron-beam T54Y2 sample in NWC (right) and HW (left). The red arrows point toward microcracks on the sample's surface.

b. TEM Imaging and EDX Line scans – Oxide Thickness

Focused ion beam (FIB) lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared for transmission electron microscope (TEM) analysis of the oxide layer thickness and morphology. The FIB lift-outs were prepared using the FEI-HELIOS dual beam FIB and the samples were further investigated via high magnification TEM images and EDX linescans, performed with the Titan TEM (FEI Titan 80/30 TEM) that is equipped with an energy-dispersive X-ray system by which line profiles can be measured; both instruments are located at the Notre Dame Integrated Imaging Facility.

Illustration of the different regions (UR, IR and RAR) via TEM imaging is demonstrated in Figure C7 for T54Y2 NWC sample (top) and HW sample (bottom). As it can be seen in the TEM images, the IR region of T54Y2 HW sample features the largest oxide thickness (about 307 ± 216 nm) which is mostly due to the precipitation oxide layer that is much smaller or absent in the other regions. In the NWC case, the oxide thickness mostly comes from the precipitation oxide layer that is present in all three regions. There is not a clear boundary between the inner and outer oxide layer in the analyzed samples; therefore, the thickness comparison presented in Figure 1 is the overall measured thickness (outer thickness + inner thickness).

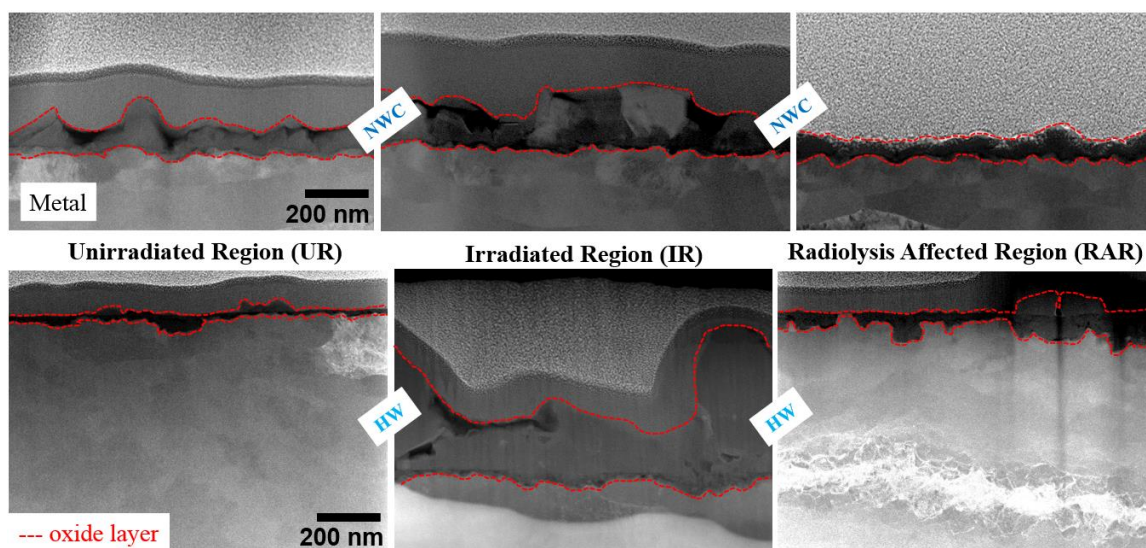


Figure C7: Post-Irradiation TEM images of 24-hour electron-beam T54Y2 sample in Oxygen-saturated water (top) and in Hydrogen-saturated water (bottom). Representation of the three different regions (UR, IR and RAR).

EDX line scans were performed to reveal elemental distribution information about the sample. Multiple EDX line scans were completed on each TEM sample and are shown in the figures below. The line scans of the HW sample are presented in Figures, C8, C9 and C10 and the line scans for the NWC samples are presented in Figures C11, C12 and C13.

The EDX line scan of the UR region of the T54Y2 sample in the Hydrogen-saturated water is presented in Figure C8. The TEM sample included in this scan does not cover a small crystal that is part of the precipitation oxide layer. There is not a clear line boundary between the outer and inner oxide layer as the line scan suggests (about 70-80% atomic concentration of Oxygen in both layers). It is also apparent that this type of steel is Chromium-rich (about 15% atomic concentration of Chromium).

The EDX line scan of the IR region of the T54Y2 sample in the Hydrogen-saturated water is presented in Figure C9. The largest portion of the EDX line scan covers the outer oxide precipitation layer which consists of mostly hematite according to the elemental distribution. About 70 nm of the line scan consists of the inner oxide layer that is Chromium-rich which suggests presence of chromium-iron-oxides or chromium-oxides (about 30% atomic concentration of Chromium). In regards to the T54Y2 metal region, the EDX line scan shows the highest content of Iron with Chromium enrichment as they are constituents of the original metal.

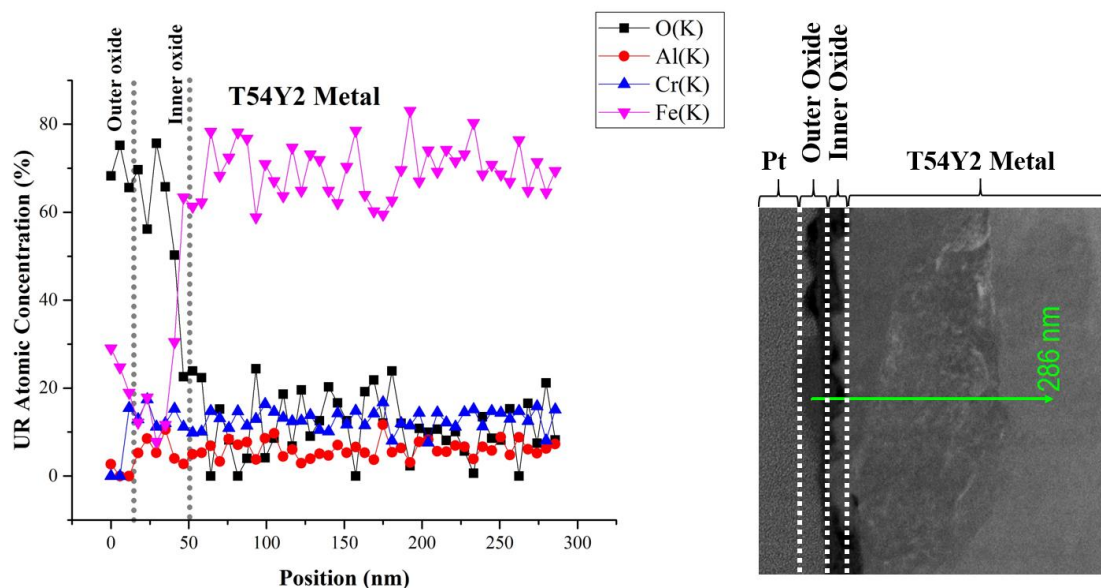


Figure C8: Left: STEM EDX UR line scan results the 24-hour electron-beam irradiated T54Y2 sample in Hydrogen-saturated water, atomic concentration vs. position, representation of outer oxide, inner oxide and metal region of scan. Right: STEM bright field image of UR region (the thin arrow shows the length of the EDX line scan and its direction).

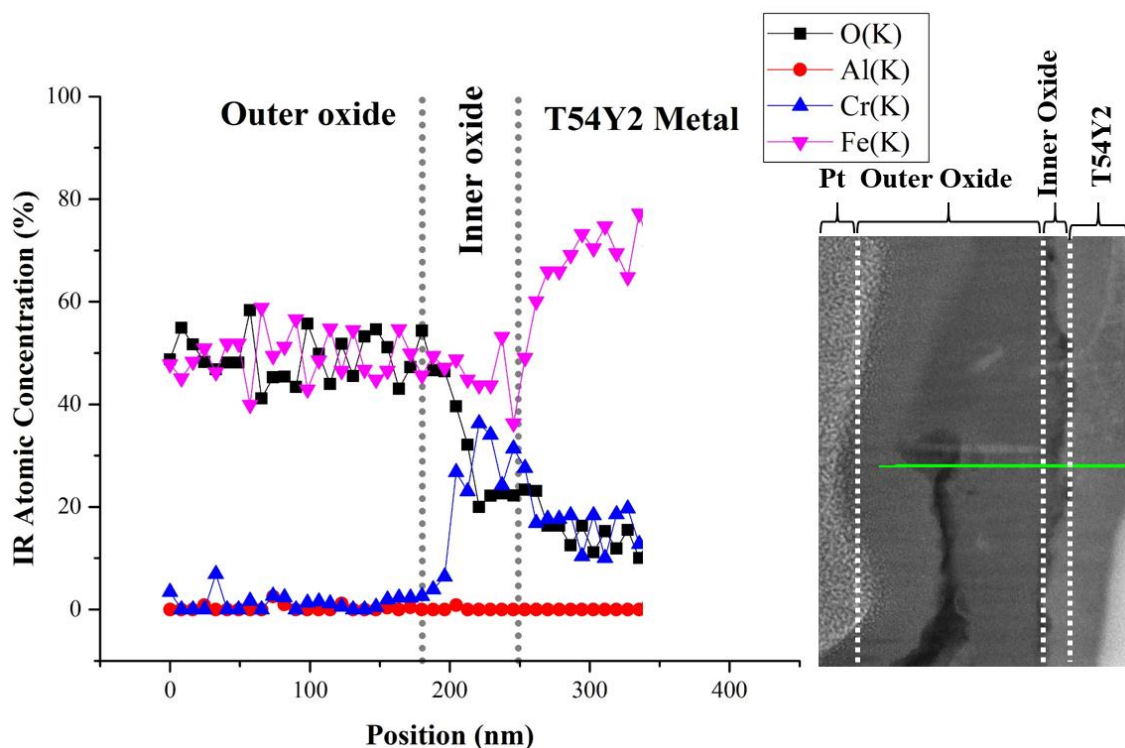


Figure C9: Left: STEM EDX IR line scan results the 24-hour electron-beam irradiated T54Y2 sample in Hydrogen-saturated water, atomic concentration vs. position, representation of outer oxide, inner oxide and metal region of scan. Right: STEM bright field image of IR region (the thin arrow shows EDX line scan direction).

The EDX line scan of the RAR region of the T54Y2 sample in the Hydrogen-saturated water is presented in Figure C10. The EDX line scan of this region does not feature a precipitation oxide layer, though there is not a clear line between the inner oxide layer and the metal region possibly due to overlapping grains in the TEM lamella. This region can be seen in Figure C10 (right) and it is labeled as mixed region (oxide + metal). There is a constant presence of Chromium and Aluminum throughout all regions of the TEM sample. According to the elemental distribution of the RAR inner oxide, it can be concluded that this region is very similar to the oxide layer of the unirradiated region.

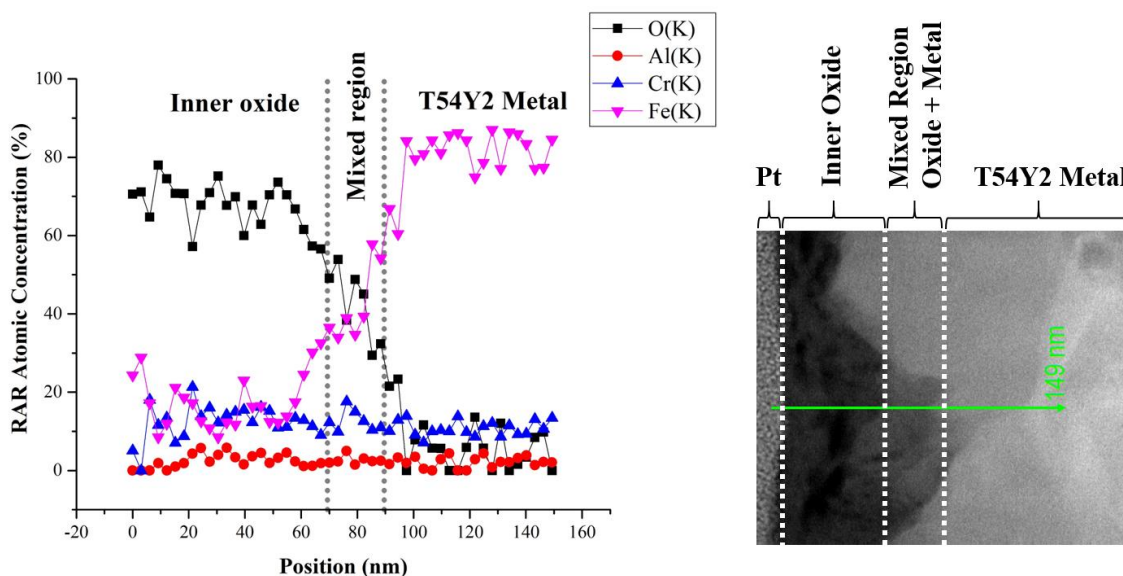


Figure C10: Left: STEM EDX RAR line scan results the 24-hour electron-beam irradiated T54Y2 sample in Hydrogen-saturated water, atomic concentration vs. position, representation of inner oxide, mixed region and metal region of scan. Right: STEM bright field image of RAR region (the thin arrow shows the length of the EDX line scan and its direction).

The EDX line scan of the UR region of the T54Y2 sample in the oxygenated water is presented in Figure C11. The TEM sample included in this scan contains both a precipitation oxide layer and an inner oxide layer, not easily distinguished. The oxide layer as the the line scan suggests contains anywhere from 50 to 70% atomic concentration of oxygen, as well as high concentration of Nickel content. Nickel content is never observed in the hydrogenated water samples because Nickel is not a constituent of T54Y2 steel, and might be a result of the thermocouples corrosion in the flow system, considering the thermocouple sheaths are composed of Inconel alloy 600.

The EDX line scan of the IR region of the T54Y2 sample in the Oxygen-saturated water is presented in Figure C12. The TEM sample included in this scan contains both a precipitation oxide layer and an inner oxide layer. The oxide layer as the the line scan suggests contains anywhere from 40 to 60% atomic concentration of oxygen. The “oxide layer” of this region features a high Nickel atomic concentration, in fact the outermost crystal seems to be entirely nickel oxide. In regards to the T54Y2 metal region, the EDX line scan shows the highest content of Iron with Chromium and Aluminum enrichment as they are constituents of the original metal.

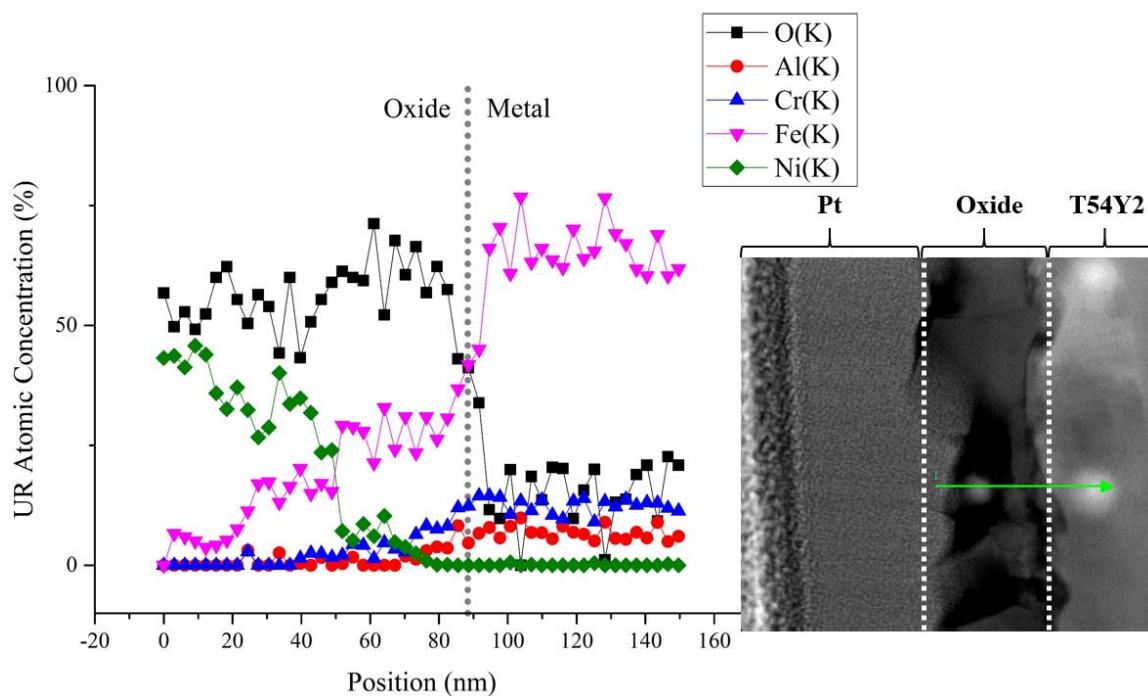


Figure C11: Left: STEM EDX UR line scan results the 24-hour electron-beam irradiated T54Y2 sample in Oxygen-saturated water, atomic concentration vs. position, representation of overall oxide and metal region of scan. Right: STEM bright field image of UR region (the thin arrow shows the EDX line scan direction).

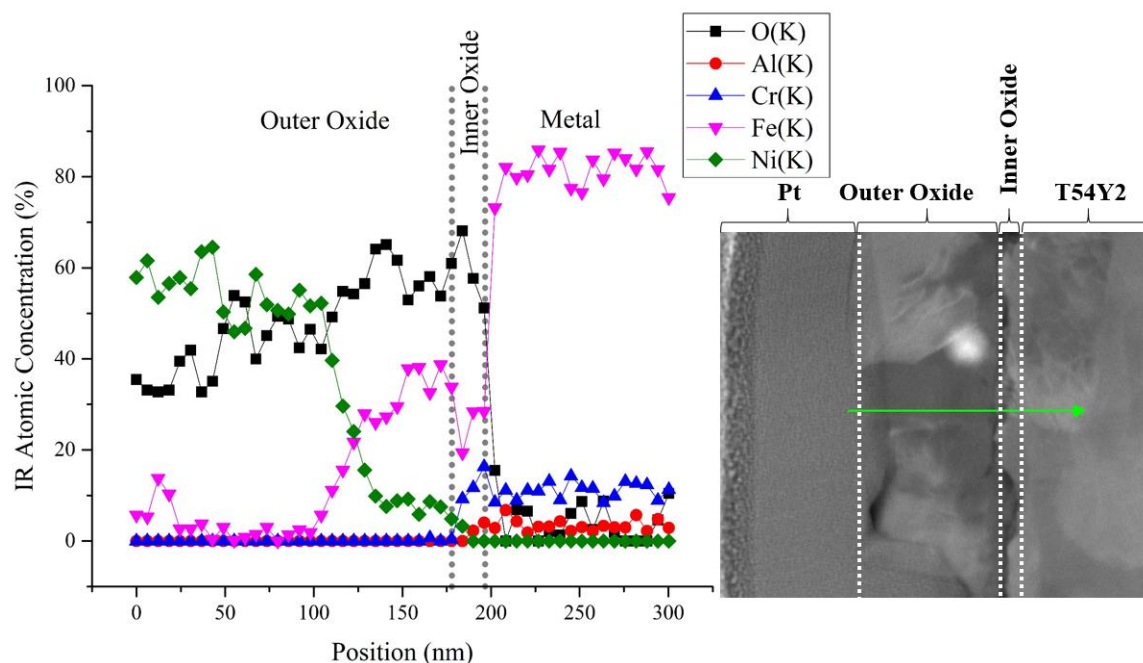


Figure C12: Left: STEM EDX IR line scan results the 24-hour electron-beam irradiated T54Y2 sample in Oxygen-saturated water, atomic concentration vs. position, representation of outer oxide, inner oxide and metal region of scan. Right: STEM bright field image of IR region (the thin arrow shows the EDX line scan direction).

The EDX line scan of the RAR region of the T54Y2 sample in the Oxygen-saturated water is presented in Figure C13. The TEM sample included in this scan contains both a precipitation oxide layer and an inner oxide layer, again not being distinguished from each other. The oxide layer contains approximately 40% atomic concentration of Oxygen, 40% atomic concentration of Iron and about 20% of Nickel atomic concentration.

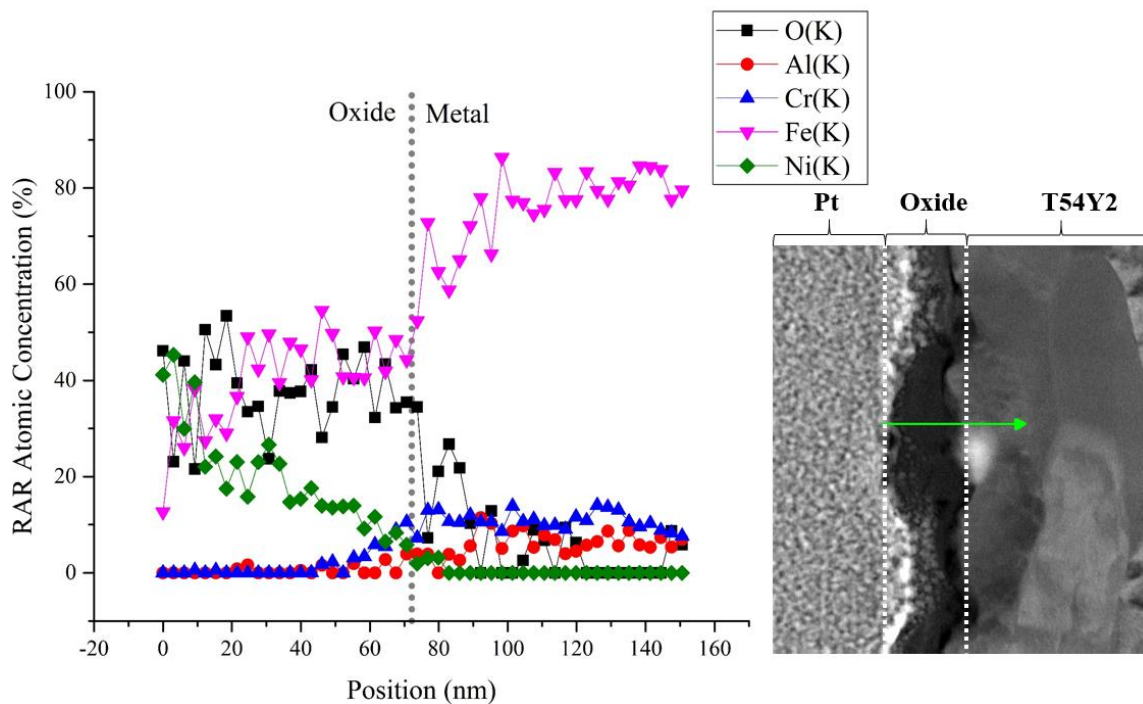


Figure C13: Left: STEM EDX RAR line scan results the 24-hour electron-beam irradiated T54Y2 sample in Oxygen-saturated water, atomic concentration vs. position, representation of inner oxide, mixed region and metal region of scan. Right: STEM bright field image of RAR region (the thin arrow shows the EDX line scan direction).

c. Raman Spectroscopy – Oxide Phase

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated sample. Spectra were recorded using a Micro-Raman Spectrometer (NRS-5100, Jasco). The spectra were collected using a 532 nm wavelength green laser, at a typical laser power of 50 mW, during a total of 180s of exposure time.

Three regions on the irradiated sample were measured using Raman spectroscopy, irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR). Three individual spectra were also taken in each region for data consistency check.

Raman spectra of the UR, RAR and IR region of the T54Y2 sample in the Hydrogen-saturated water and Oxygen-saturated water together with optical images of the sample's regions of interest with red dots indicating locations where the Raman spectrum was taken are presented in Figure C14 and C15, respectively. Raman analysis of corroded steels usually features corrosion products that are mainly composed of a mixture of iron oxides (maghemite, hematite, magnetite). It is assumed the Raman signal is primarily due to a precipitation oxide layer. The formation of hematite is associated with a high corrosion potential, and is generally present in the IR region of HW samples, or all regions of oxygenated NWC samples. In both of the present experiments, there is no presence of the typical Raman peaks related to iron oxides: hematite, magnetite or even maghemite in any of the regions.

Raman analysis in all three regions of the T54Y2 HW sample showed that the corrosion products are mainly composed of a mixture of chromium oxide, iron chromite and nickel chromite. The chromium oxide associated peaks are presented by the orange dashed lines in the plot, the iron chromite peaks by the pink dashed lines and the nickel chromite peaks by the blue dashed lines.

Raman analysis in all three regions of the T54Y2 NWC sample showed that the corrosion products are mainly composed of nickel chromite. The nickel chromite associated peaks are presented by the blue dashed lines in the plot. The presence of Nickel is confirmed in the EDX data. Given that the sample contains no nickel, this nickel oxide must come from corrosion of the hastelloy body or inconel thermocouple sheaths of our flow cell. It makes questionable the utility of this cell for the NWC chemistry conditions.

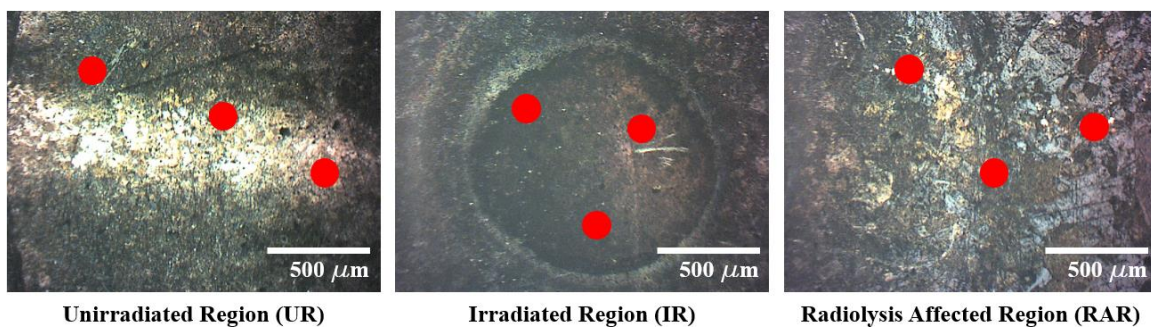
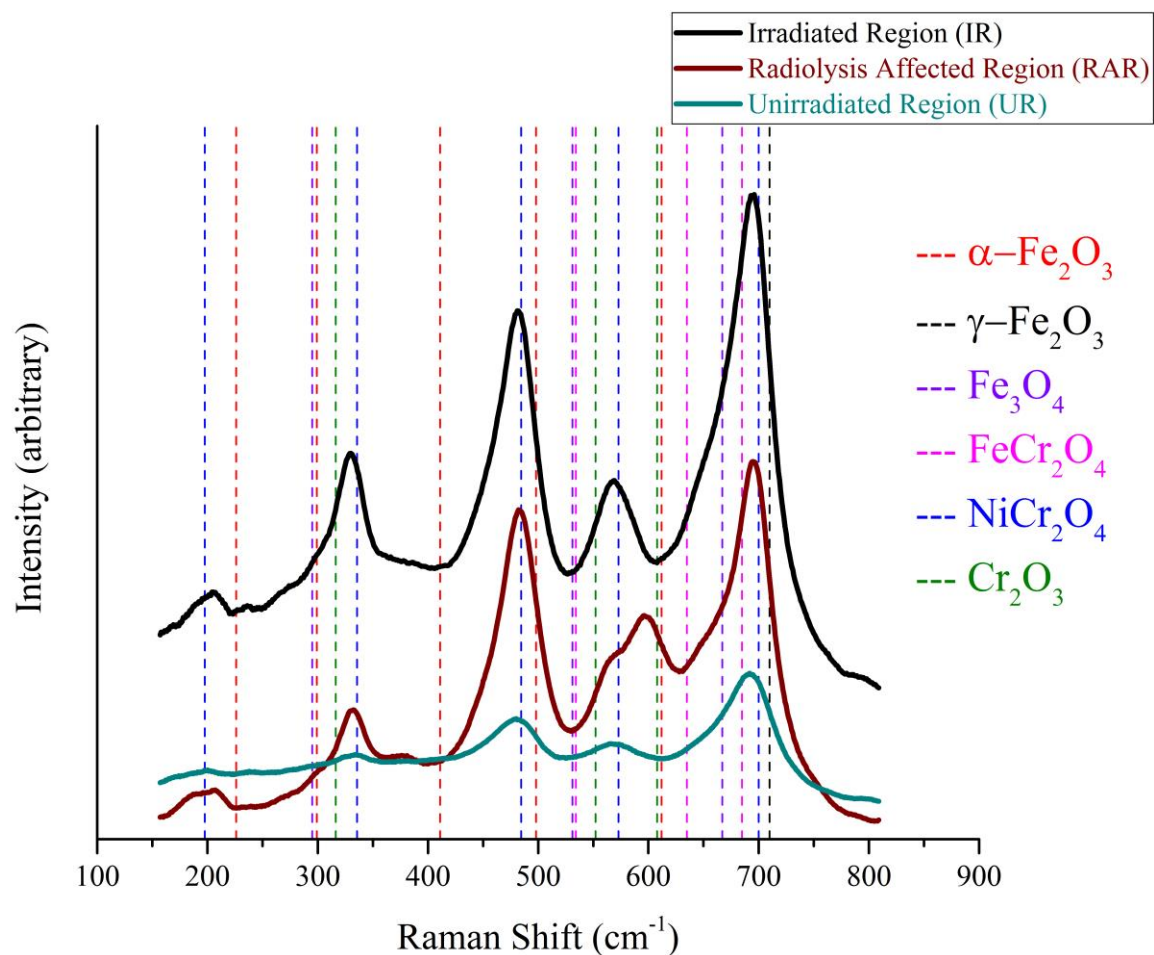


Figure C14: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated T54Y2 sample in Hydrogen-saturated water. Representation of the three different regions (IR, RAR and UR) and associated Raman peaks (top); Post-irradiation optical images of the sample's regions of interest with red dots indicating locations where the Raman spectrum was taken (bottom);

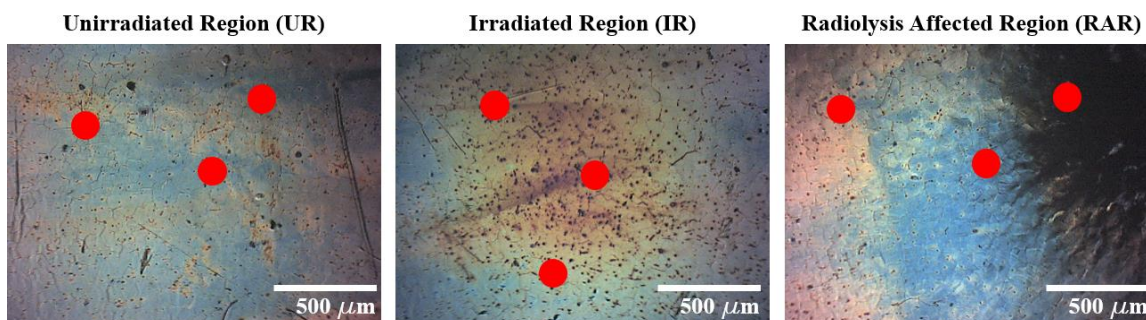
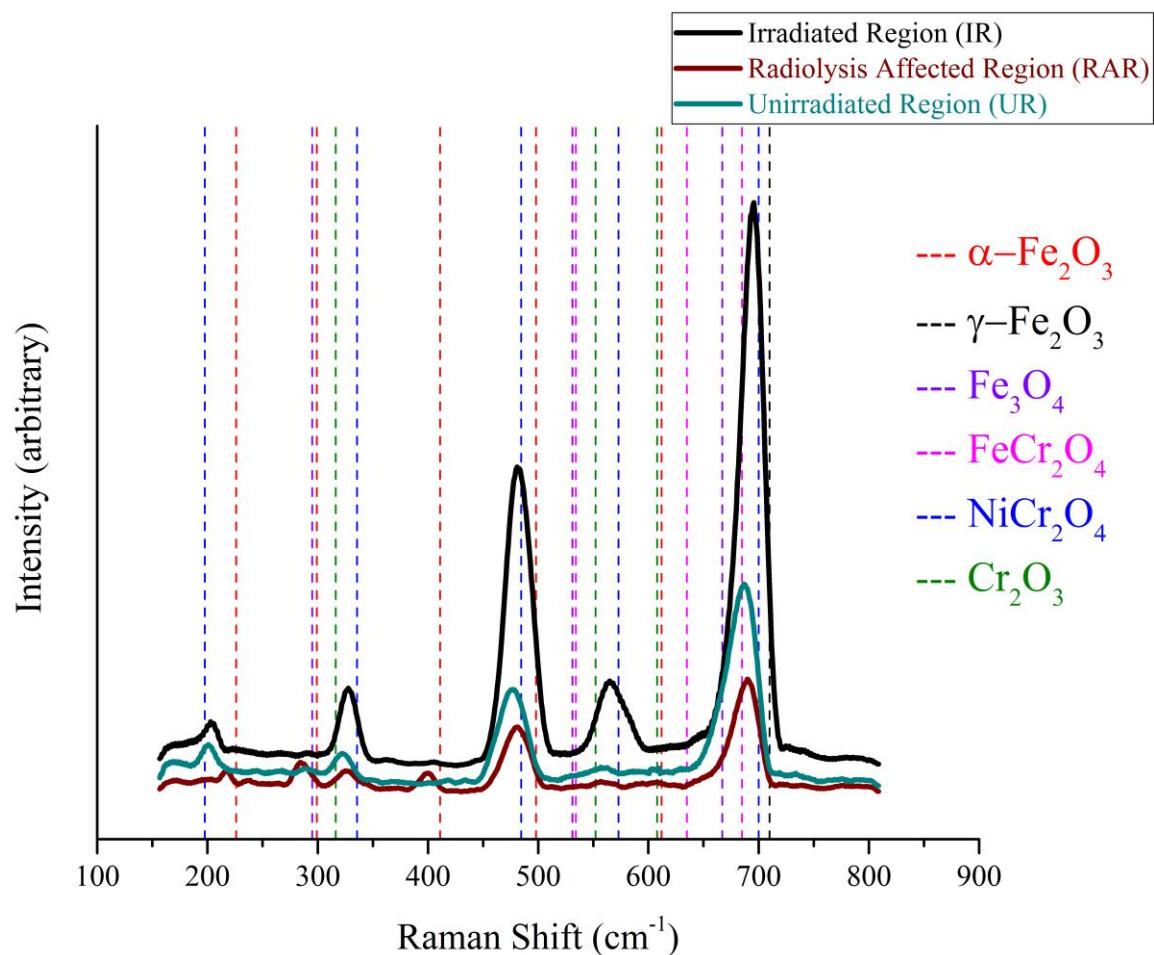


Figure C15: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated T54Y2 sample in Oxygen-saturated water. Representation of the three different regions (IR, RAR and UR) and associated Raman peaks (top); Post-irradiation optical images of the sample's regions of interest with red dots indicating locations where the Raman spectrum was taken (bottom);

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

March 2017 Milestone report for T35Y2 FeCrAl Alloy

Four T35Y2 steel sample irradiations were completed to assess the corrosion behavior of this steel under reactor-like conditions. In this experiment the thin samples actually serve as the interface between the accelerator vacuum system on one side, and water at high pressure and temperature on the other. The samples irradiated at the University of Michigan used high energy protons while at University of Notre Dame an electron beam was used. The protons have energy of ca. 1.7MeV as they pass through the oxide into the water, and electrons have energy of ca. 1.5MeV. The protons have much higher momentum, and so (like high energy neutrons) are capable of causing significant atomic displacement damage in the oxide layer. They also move much more slowly than the relativistic electrons, so their LET (linear energy transfer) is ca. 200x larger than the electrons. To compensate and give nearly the same average energy dose to the sample and water near the surface, the electron beam flux (amps/cm²) is adjusted to be ca. 100x greater than the proton beam. Electrons do essentially no displacement damage to the solid.

Detailed analysis of the several T35Y2 samples is shown below in sections A-C. A summary of oxide thickness generated in the 24 hour irradiated samples is presented in Figure 1. The plot shows comparison between three different regions of interest: unirradiated region upstream of the radiation (UR), the directly irradiated region (IR), and a radiolysis affected region (RAR) downstream of the sample. Samples were irradiated at 320°C with 3ppm hydrogen (HW), and 288°C with 2 ppm oxygen (NWC) or 288°C with argon saturated water in the electron beam case to avoid high nickel content promoted from the hastelloy cell when exposed to oxygen saturated water.

We conclude that T35Y2 steel is a viable candidate cladding material as the corrosion is not dramatically enhanced in the direct radiation zones compared to the unirradiated zones. Its performance is reasonably similar to other candidate steels under these conditions of extreme radiation in either hydrogenated or oxygenated water.

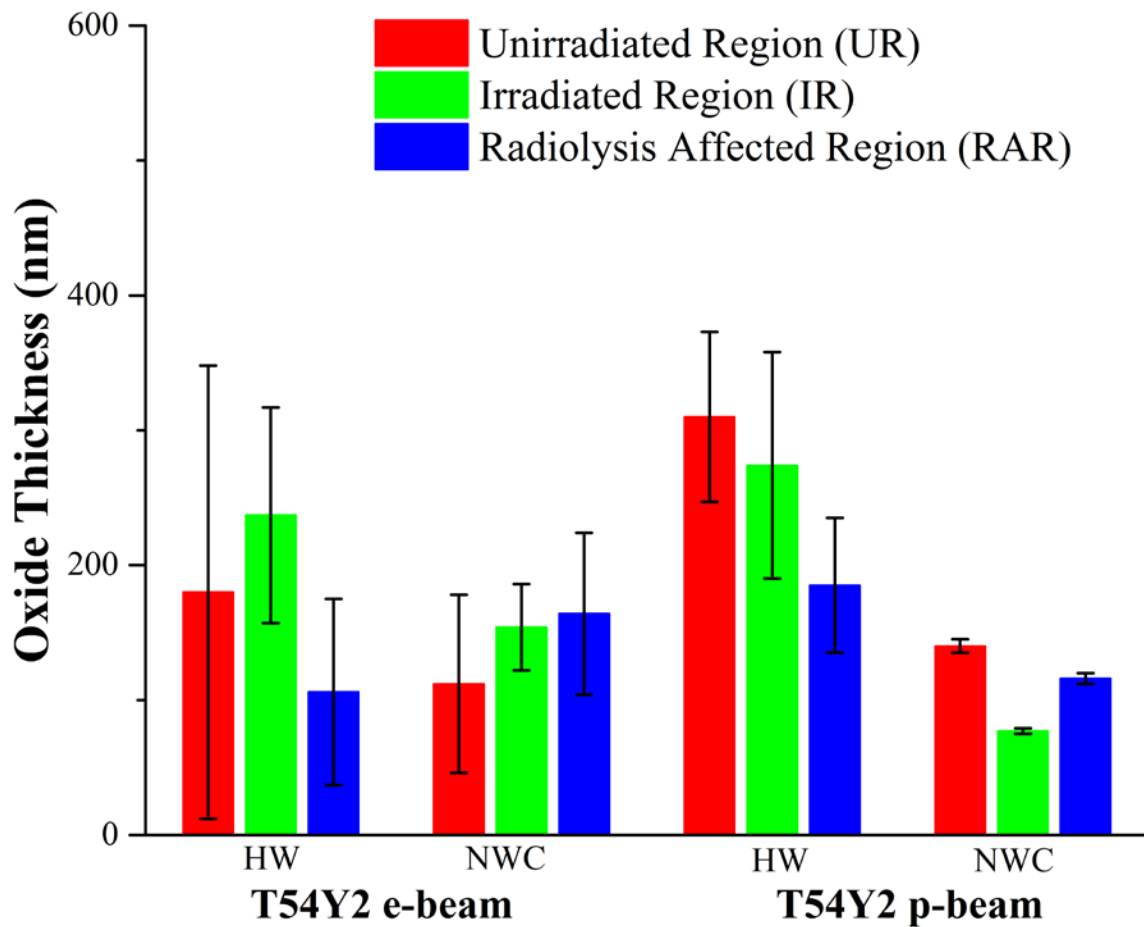


Figure 1: T35Y2 Oxide thickness comparison between ND e-beam and UM p-beam 24 hour irradiated samples. Water chemistry was either 320°C with 3ppm H₂ (HW), or 288°C with 2ppm O₂ (NWC).

A. T35Y2 Base Metal Characterization

The material was cast by a vacuum induction melting from pure element feedstock homogenized at 1200°C, hot-extruded at 1050°C, and then stress-relief annealed at 700°C.

The bulk material was obtained from ORNL, and chemical composition is listed in Table A1.

Table A1. The chemical composition of as-received T35Y2, supplied by ORNL.

Heat	Fe	Cr	Al	Y	C	S	O	N	P
NA	Bal.	13.15	4.44	0.12	0.002	0.003	0.0012	0.0009	<0.002
	Si	B							
	0.01	0.0010							

EDS element analysis was carried out on a FEI NOVA SEM/FIB with EDAX detector. EDS spectrum is shown in Fig. A1. Atomic and weight percentage of each alloy element were shown in Table A2. The concentration of major alloying elements was consistent with the specification received from ORNL, except for Al. A large amount of Al can be found in precipitates which were in the form of aluminum oxide.

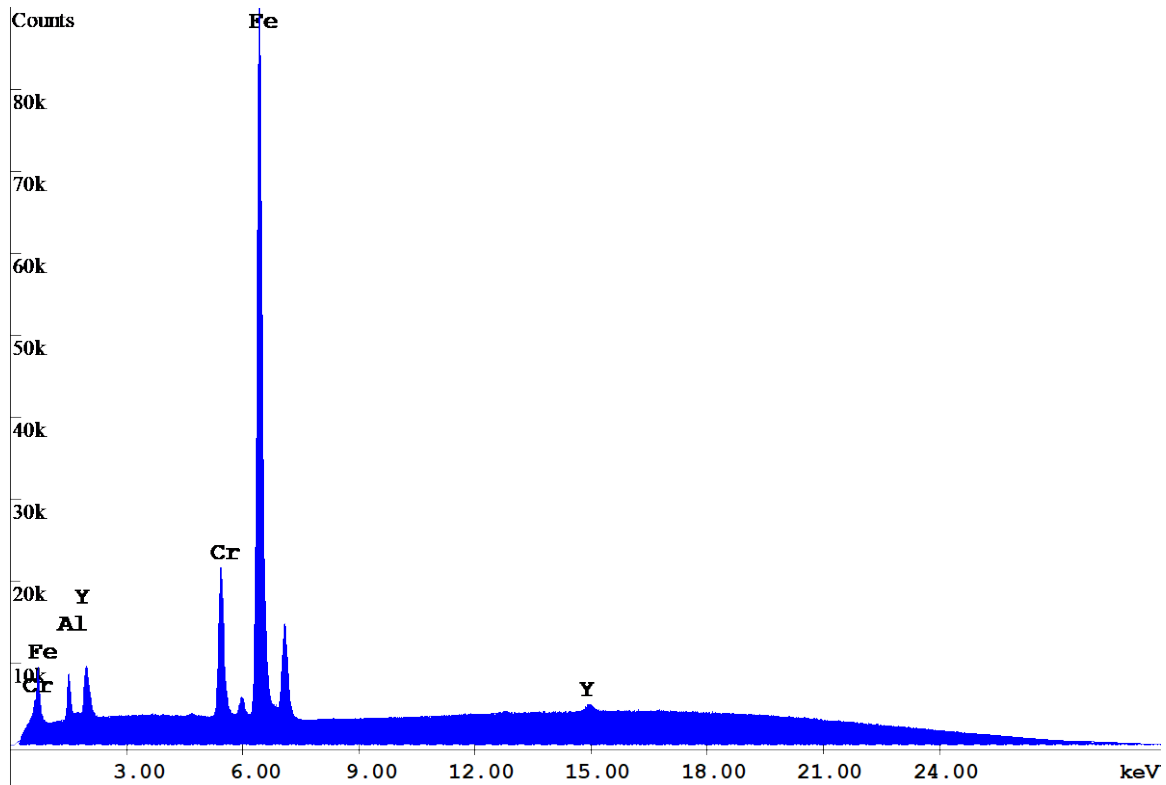


Figure A1. EDS spectrum of as-received T35Y2.

Table A2. Alloy element analysis by EDS.

Element	Wt %	At%
Fe	83.37	79.68
Cr	13.21	13.56
Al	3.42	6.76

Optical image of the polished and etched sample cross-section are shown in Figure A2. The image was taken in the plane perpendicular to the extrusion direction, and equiaxed grains structure were observed from both the extrusion axis and transverse direction. The sample showed typical ferritic steel microstructure with a large number of intermetallic precipitates containing either yttrium or aluminum evenly distributed within the grains. The average particle density and grain size were calculated as $\sim 5 \times 10^4$ particles/cm² and 40 μ m, respectively.

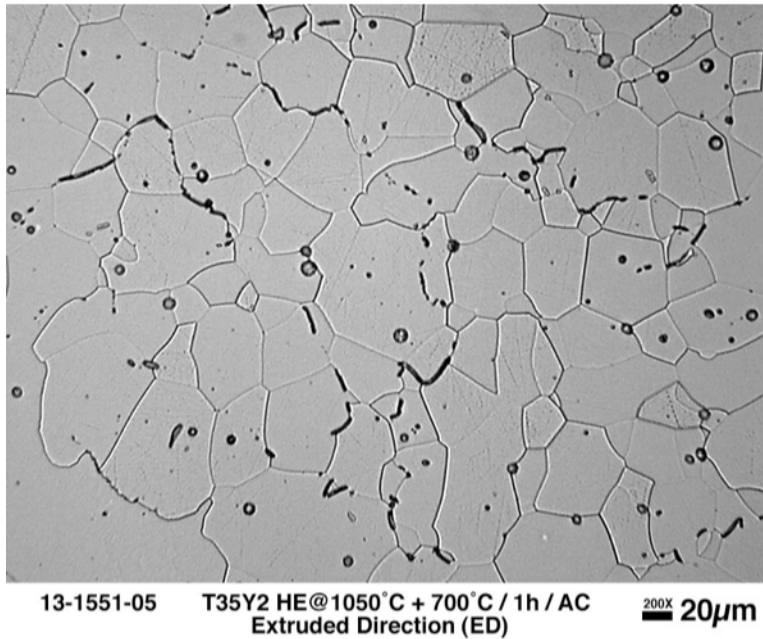


Figure A2: Optical image of a cross-sectional view of the bulk material.

TEM analysis was performed using a JEOL 3011 TEM on twin-jet polished TEM discs. Very clear grain boundaries can be identified but only one-grain boundary was shown in Figure A3, round Y containing precipitates (50-100nm in size) were observed within the grains or at the grain boundaries.

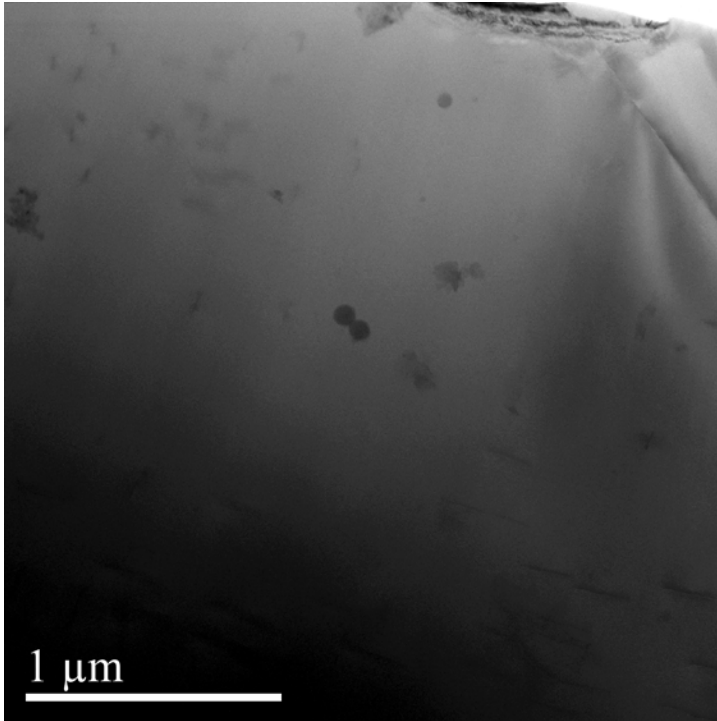


Figure A3. TEM Bright-field images of T35Y2 base metal with Y rich precipitates within the grain.

B. Proton Irradiation Experiments (U. Michigan)

B1. Summary

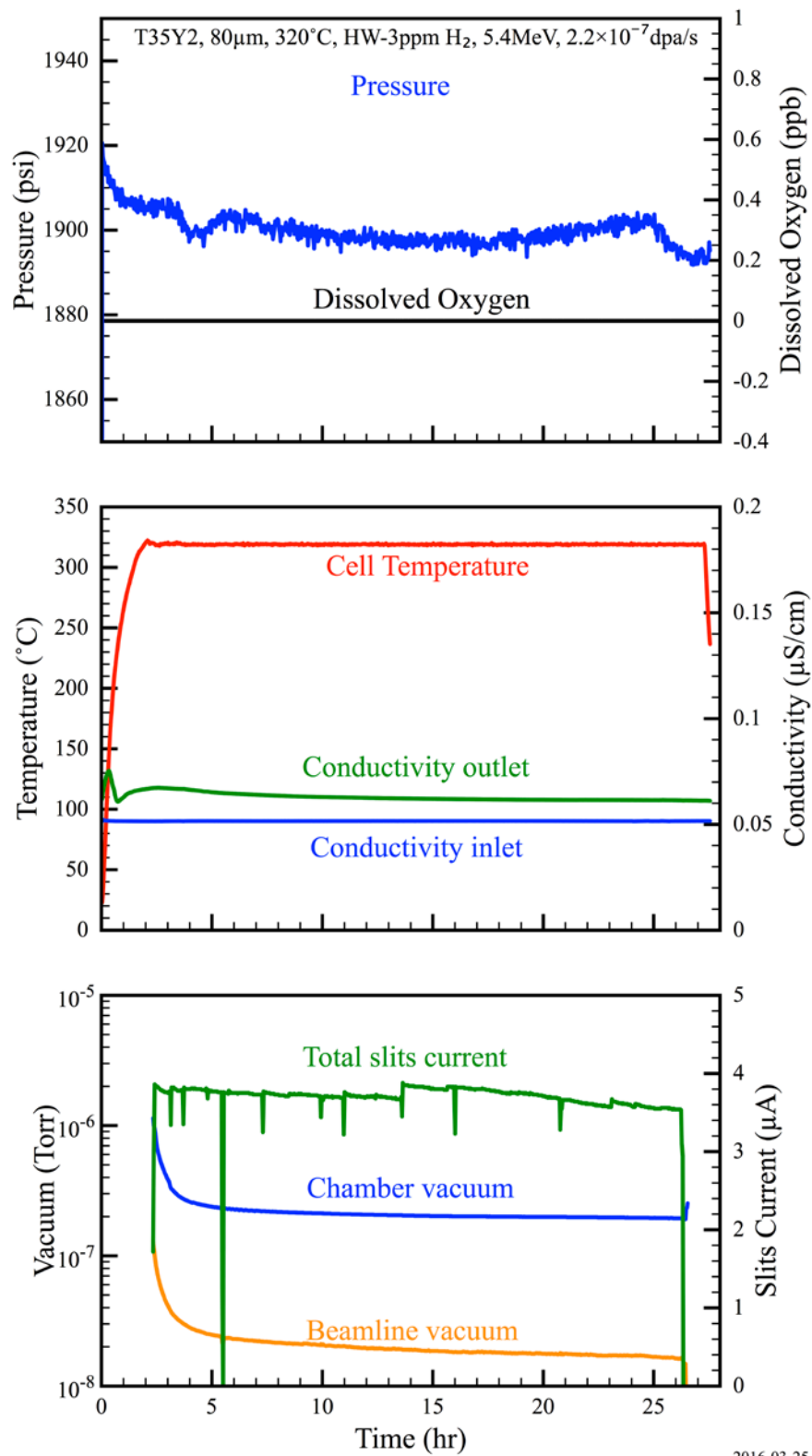
Proton irradiations of T35Y2 were completed in hydrogenated water (HW), and in normal water chemistry (NWC) at 320°C and 288°C, respectively. A 5.4 MeV proton beam at 2 μ A/cm² current density was used for these irradiations. The sample thickness was 80 microns, and the energy of the protons as they cross the oxide layer and enter the water is 1.7MeV. The LET in water is 5.6 x 10⁻¹¹ J/cm/e⁻. The dose rate to the water directly at the interface is 500kJ/kg/s. Various regions of the irradiated sample were analyzed using SEM and Raman Spectroscopy and characterizations of the oxide microstructure were carried out on the TEM.

Table B1: List of irradiation experiments completed for T35Y2.

Sample ID	Proton energy (MeV)	Temp (°C)	Water chemistry	Water dose rate (kGy/s)	Damage rate (dpa/s)	Duration (hr)
T35Y2-HW-24IR	5.4	320	HW (3 ppm H ₂)	500kGy/s	2.2 x10 ⁻⁷	24
T35Y2-NWC-24IR	5.4	288	NWC (2 ppm O ₂)	500kGy/s	2.2 x10 ⁻⁷	24

B2. Proton Irradiation Experimental conditions

Two T35Y2 samples were irradiated for 24 hr under the experimental conditions listed in Table B1. Water loop data and beamline data are shown in Figures B1 for HW condition and Figures B2 for NWC condition. The NWC irradiation was completed in two separate sessions, due to the interruption from a severe power outage. The water system was not affected by this power outage, and the sample was immediately cooled after the proton beam was lost. The irradiation was continued after the beamline vacuum was recovered after the loss of power.



2016-03-25

Figure B1: Water loop and beam current data of 24 hr proton irradiation of T35Y2 in 320°C 3 ppm H_2 water at a damage rate of 2.2×10^{-7} dpa/s.

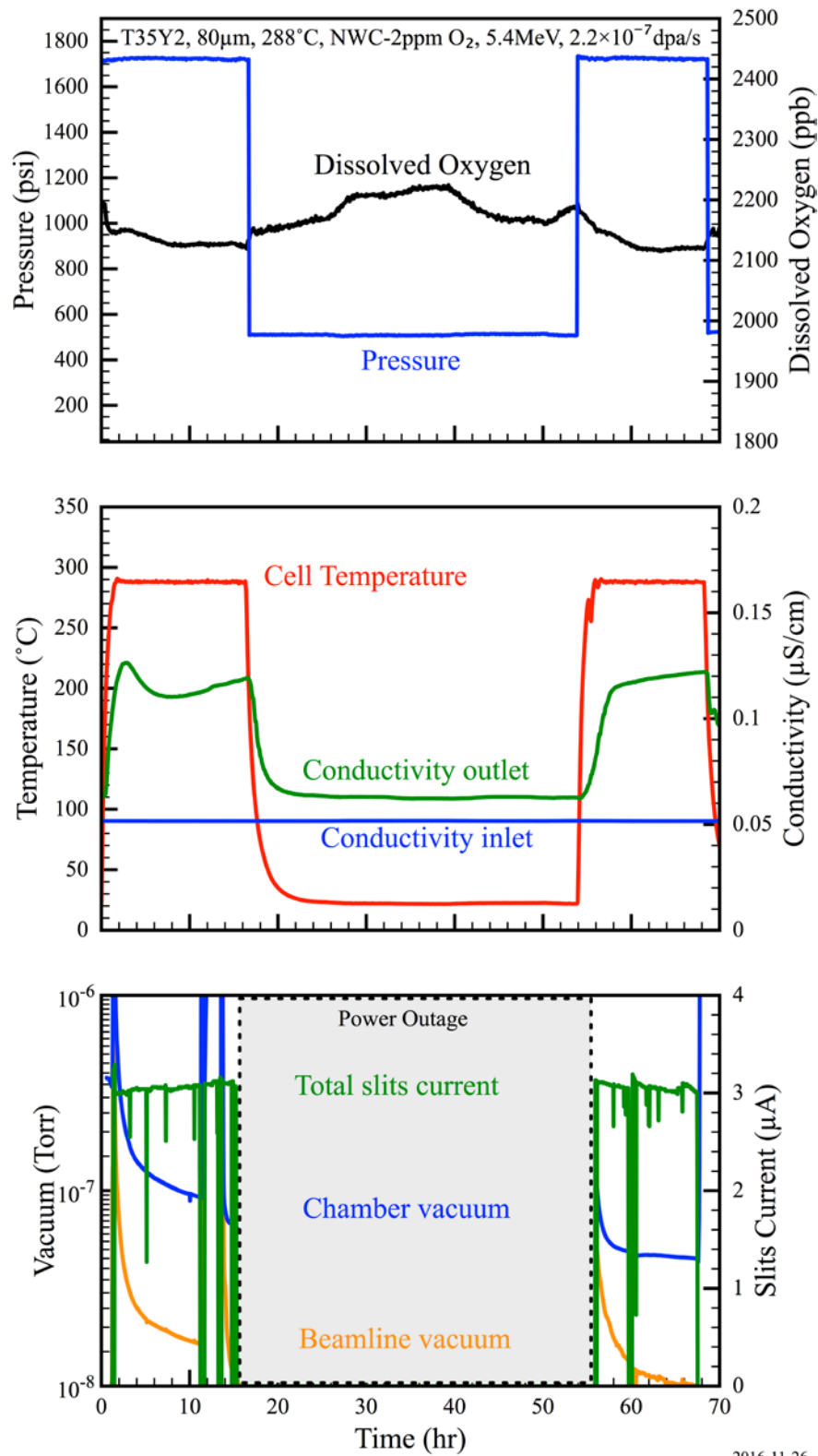


Figure B2: Water loop and irradiation data of 24 hr proton irradiation of T35Y2 in 288°C 2 ppm O₂ water at a damage rate of 2.2×10^{-7} dpa/s.

B3. Post Irradiation Characterization

Three distinctive regions of the sample surface were characterized, namely the Irradiated Region (IR), Radiolysis Affected Region (RAR) and the Unirradiated Region (UR).

Optical Images

Sample T35Y2-HW-24IR remained as shiny as the polished surface in the UR region, as indicated in Figure B3, whereas the IR region has a matte gray appearance. Around the IR region, a noticeable rim of darker oxide was observed, most likely to be the RAR area. However, a distinctive flow region was not found in this sample.

Sample T35Y2-NWC-24IR was discolored and showed interference colors, shown in Figure B3. The lighter orange UR region was observed around the IR region. An IR region with dark blue appearance was observed in the center, and RAR region is not significantly different from the UR region.

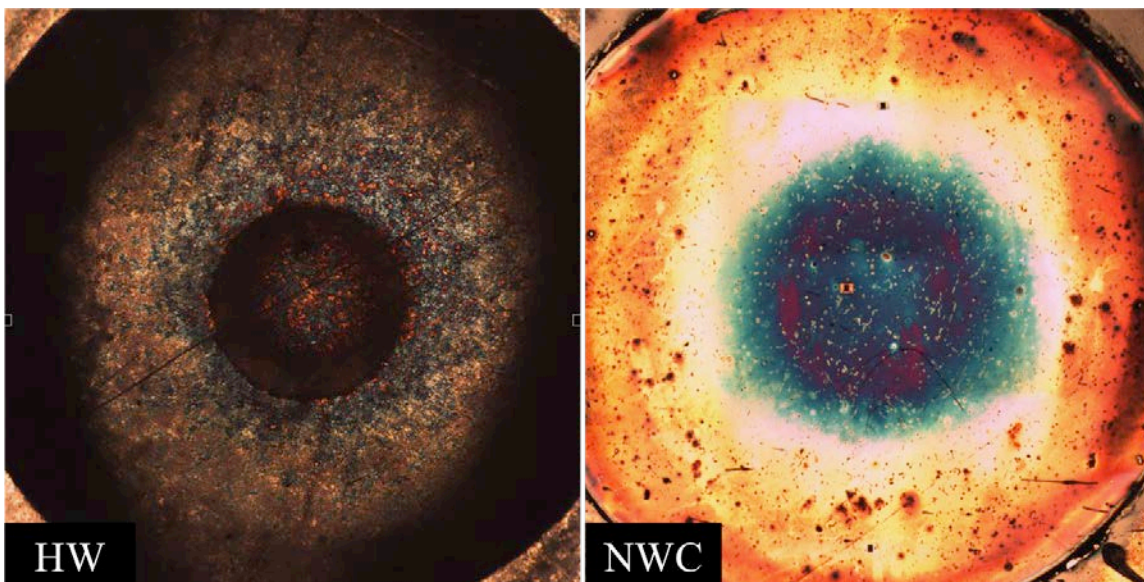


Figure B3: Optical images of irradiated samples T35Y2-HW-24IR and T35Y2-NWC-24IR.

Surface Oxide Morphology Analysis

Sample T35Y2-HW-24IR has a matte gray appearance after 24 hr exposure in primary water condition; a SEM image with circles outlining each region is shown in Figure B4. Oxide morphologies in UR and RAR regions were similar. Outer surface particles in the UR region are more faceted compared with the one in the RAR region. In both regions, a regular shaped outer oxide was observed with the particle size of $\sim 1 \mu\text{m}$. In the IR region, oxide particles consisted of two types, one type is less faceted crystals with a size of $\sim 1 \mu\text{m}$, the other type is much smaller crystals with size less than 200nm as indicated in Figure

B5. Outer oxide particle density was significantly higher in the IR region compared with RAR and UR region.

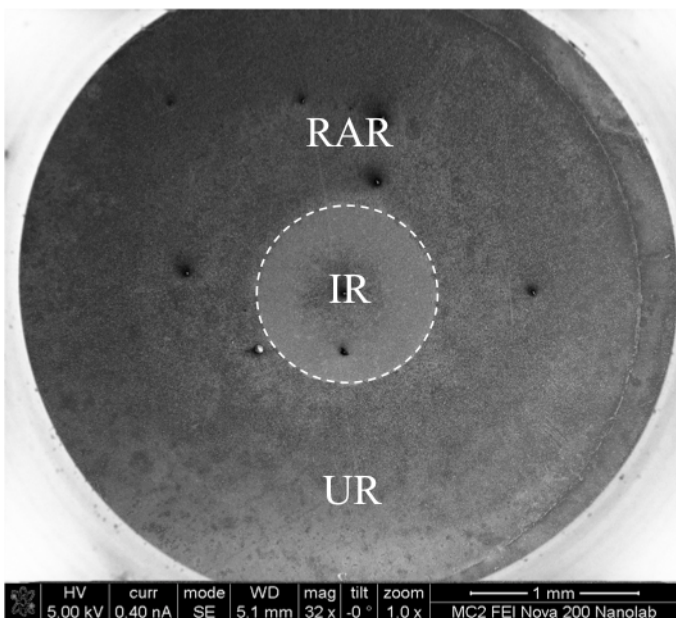


Figure B4: SEM image of sample T35Y2-HW-24IR. The irradiated region (IR) and unirradiated region (UR) are indicated by the dotted line.

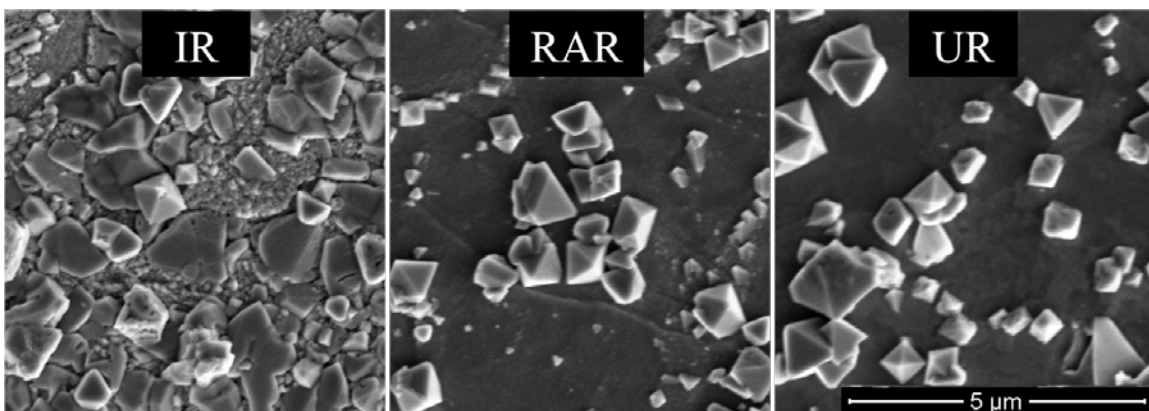


Figure B5: High magnification SEM images of the three regions observed on sample T35Y2-HW-24IR.

Sample T35Y2-NWC-24IR was discolored after 24 hr of exposure in NWC water chemistry. In Figure B6, the IR and RAR regions were difficult to distinguish on the surface of the sample. However, the high magnification SEM images shown in Figure B7 indicated that there was no significant difference regarding oxide particle size (50-200 nm) and morphology in the IR and RAR regions. Oxide particles in the UR region have large aspect ratio compared to the oxides found in the RAR and IR regions. The particle size in the UR region is ~ 200-400 nm.

FIB lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared, and TEM analysis was carried out on these TEM lamellas.

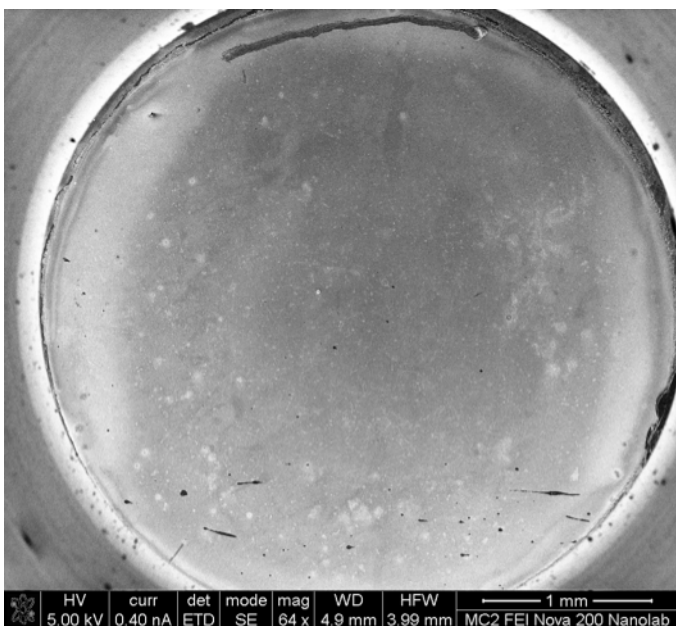


Figure B6: SEM image of sample T35Y2-NWC-24IR. The irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR) are indicated by the dotted line.

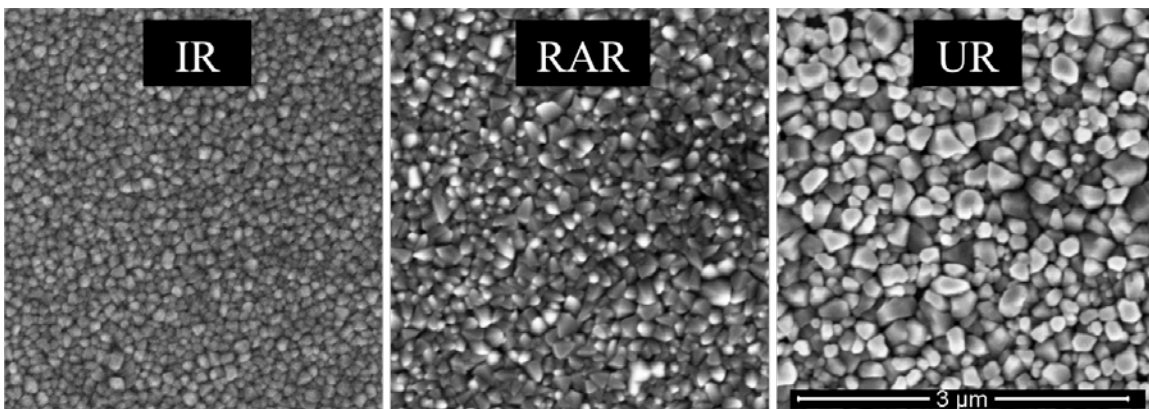


Figure B7: High magnification SEM image of the three regions observed on sample T35Y2-NWC-24IR.

Oxide Phase Analysis with Raman Spectroscopy

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated samples. Spectra were recorded using a Renishaw inVia microscope with a RenCam CCD detector. The spectra were collected using a 633 nm wavelength red laser, at a typical laser power of 50 mW, during a total of 500 s of acquisition time.

All three regions (IR, RAR and UR) on the irradiated samples were measured using Raman spectroscopy. Three individual spectra were also taken in each region for data consistency check.

For **sample T35Y2-HW-24IR**, the Raman peaks related to $\alpha\text{-Fe}_2\text{O}_3$ were observed in the IR region as shown in Figure B8. This observation indicated that when the sample surface was in contact with the radiolysis products of water, the corrosion potential must be high enough for the formation of hematite. The cause of hematite formation could be the presence of short- and long-lived radical species and hydrogen peroxide. The short-lived radiolysis products (e.g. $\text{OH}\cdot$ radicals) are short-lived species, and cannot escape the IR region. However, the product species H_2O_2 can be carried away from the IR region into the RAR region by convection flow of the heated water. This was the primary reason of the region formed around IR region, where oxidizing species could have migrated $\sim 100\ \mu\text{m}$ away from the IR region, but only some of the areas experienced the formation of hematite in the area where convection flow of the heated water took place.

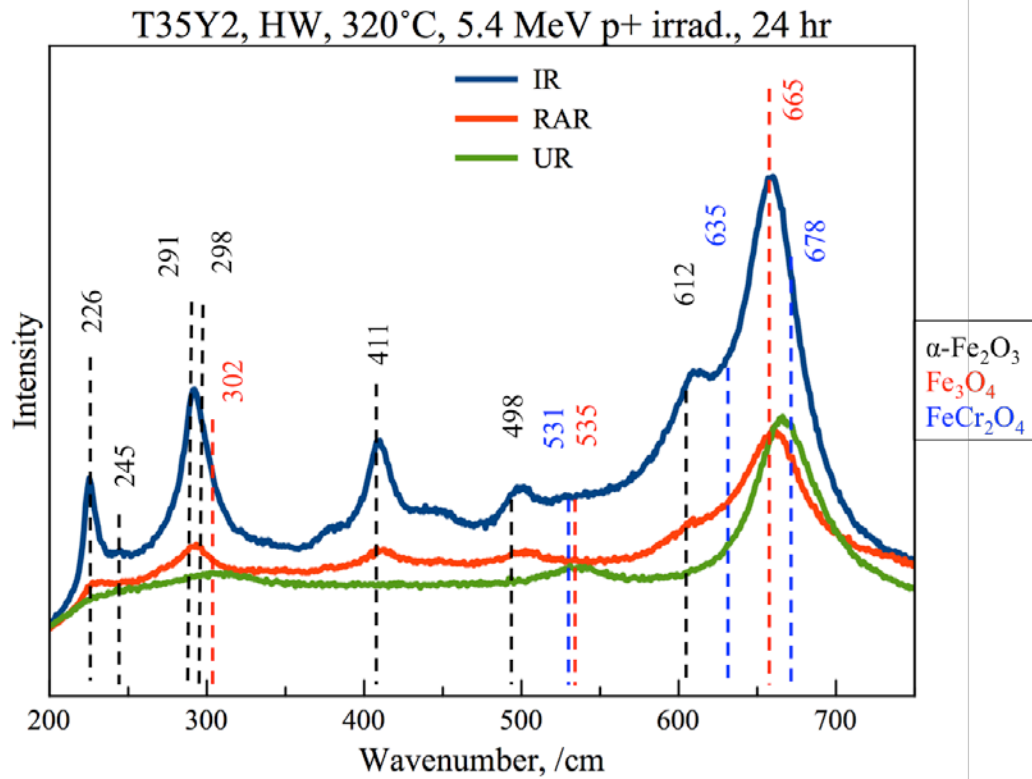


Figure B8: Raman spectra collected from IR, RAR and UR region on the 24 hr irradiated T35Y2 sample in primary water condition.

The UR regions showed a typical Raman spectrum of magnetite (Fe_3O_4). However, the $665\ \text{cm}^{-1}$ peak which was related to magnetite was observed in all regions, indicating that the inner layer may also consist of magnetite phase or a spinel phase which was deficient in Cr content, e.g. $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$. Although, the spinel phase will cause a slight shift in the Raman peak positions, from 665 to a lower wavenumber, e.g. the $635\ \text{cm}^{-1}$ for FeCr_2O_4 . Further compositional analysis of the inner oxide layer is required to confirm the identity of the inner oxide. In the IR region, the oxide consisted of a spinel $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$ inner layer and a Fe_2O_3 outer layer.

For **T35Y2-NWC-24IR**, the Raman peaks related to Fe_2O_3 are present in all the regions as shown in Figure B9. Also, some of the peaks cannot be fitted by a single peak of Fe_2O_3 , spinel or Fe_3O_4 , which suggests multiple oxide phases may be present in the spectra. However, in NWC water chemistry, Fe_2O_3 is still the dominant oxide, with possible Fe substituting Cr in FeCr_2O_4 .

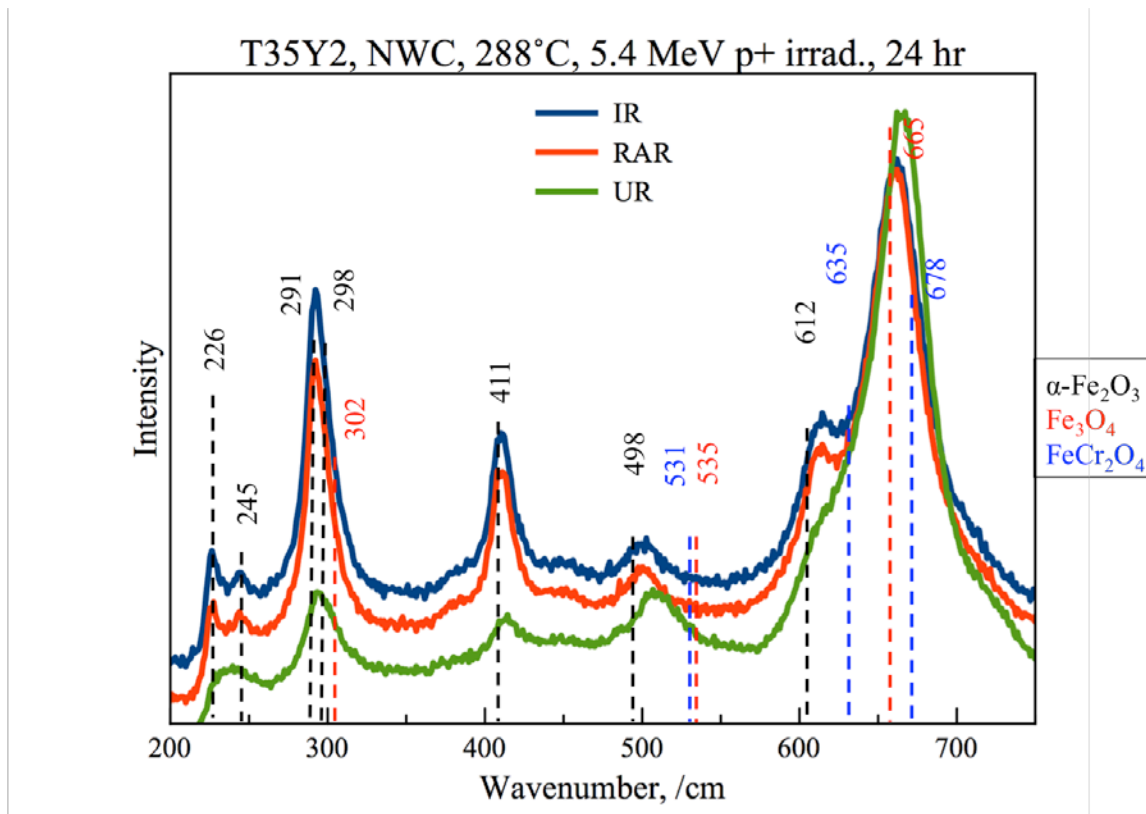


Figure B9: Raman spectra collected from irradiated region, unirradiated regions and the radiolysis affected region on the 24 hr irradiated T35Y2 sample in NWC water condition.

Oxide Morphology with TEM

TEM lamellas from IR and UR regions were prepared using FIB, and a JEOL 3100R05 TEM/STEM was used for TEM analysis.

The high angle annular dark field (HAADF) images were collected for oxide thickness analysis. Under such imaging conditions, the oxide would have a dark contrast compared to a light-colored metal substrate or platinum protective coating. There is also a slight contract shift between the inner spinel oxide and the outer particles.

On sample **T35Y2-HW-24IR**, as shown in Figure B10, the inner oxide layer appeared to be very thin, with an appearance of a dark line at the metal/oxide interface. A complete coverage of the IR region with outer oxide was observed. However, the original metal surface was not observed in the IR region. In the UR region, only partial outer oxide coverage was observed. Although original metal surface was oxidized, the flat shape of the

interface can still be observed in the UR and RAR regions. Average total oxide thickness for different regions was listed in Table B2.

For **T35Y2-NWC-24IR**, the HAADF STEM images shown in Figure B11, had indicated that the oxide layers were similar in term of oxide thickness compared with the hydrogenated (and higher temperature) condition. The interface of inner and outer oxide layer became indistinguishable under NWC condition, indicating possible inner oxide dissolution had occurred. Large undulation of the metal/oxide interface was also observed. This was caused by heterogeneous inner oxide growth rate. The complete outer oxide coverage was observed in all cases. However, the overall thickness of the oxide is thinnest in the IR region and thickest in the UR region.

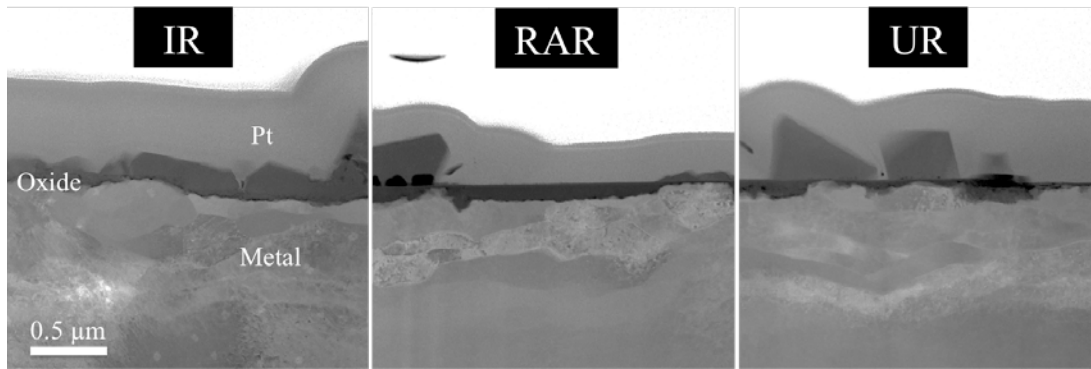


Figure B10: High Angle Annular Dark Field STEM (HAADF-STEM) images of the FIB lamellas taken from the irradiated sample T35Y2-HW-24IR.

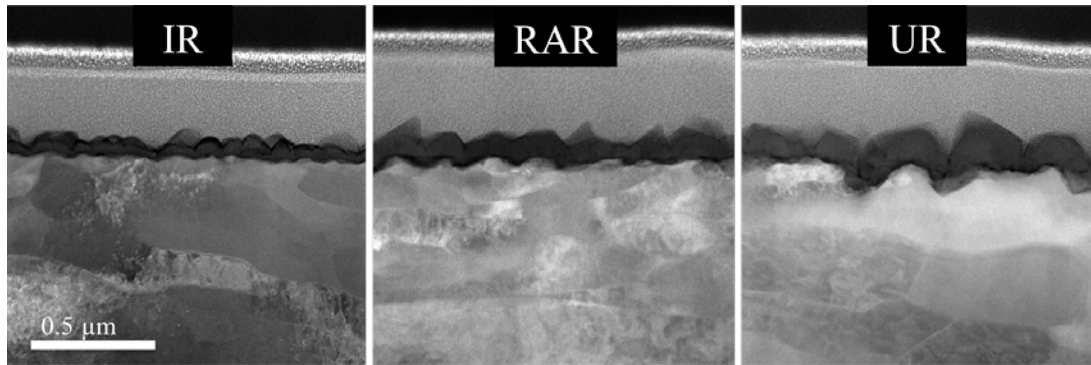


Figure B11: HAADF-STEM images of the FIB lamellas taken from the irradiated sample T35Y2-NWC-24IR.

Table B2: Oxide thickness observed on samples irradiated in both HW and NWC conditions.

Sample	Region	Total Oxide (nm)
T35Y2-HW-24IR	IR	274 ± 84
	RAR	185 ± 50
	UR	310 ± 63
T35Y2-NWC-24IR	IR	77 ± 2
	RAR	116 ± 4
	UR	140 ± 5

Oxide Composition Analysis with EDS

Energy Dispersive X-ray Spectroscopy (EDS) was used to determine the oxide compositions. The EDS spectra were collected on JEOL 2010F STEM with EDAX detector.

For **sample T35Y2-HW-24IR**, EDS results of IR and UR region are shown in Figure B12 and B13. The IR region oxide composition was consistent with Fe_2O_3 , which was 40 at% Fe and 60 at% O for the outer oxide, the thin inner oxide was observed but the composition of the inner layer was not determined due to the limited resolution of EDS for the thin oxide. EDS result from the UR region had confirmed that the inner oxide was a Cr-deficient FeCr_2O_4 -spinel phase (line-scan A) and outer precipitates were Fe_3O_4 of 43 at% Fe and 57 at% O.

The inner oxide of UR region consist of a spinel phase; its composition slightly deviates from FeCr_2O_4 . Some aluminum was also present in this inner layer (line-scan A), however, its oxidation state and which oxide constituent it belongs to was unknown.

The RAR region has a mixture of outer particles, both hematite and spinel were present suggested by its Raman response in Fig. B8. EDS line scans in Figure B14, indicated that the outer oxide was Fe_2O_3 (line-scan B) and the inner oxide was Cr-deficient FeCr_2O_4 -spinel with large aluminum content (line-scan A).

Direct irradiation has a direct impact on the stability of the inner oxides. Without irradiation, a spinel phase was observed in the inner oxide; with irradiation, the inner oxide became thinner, indicating oxide dissolution may be occurred.

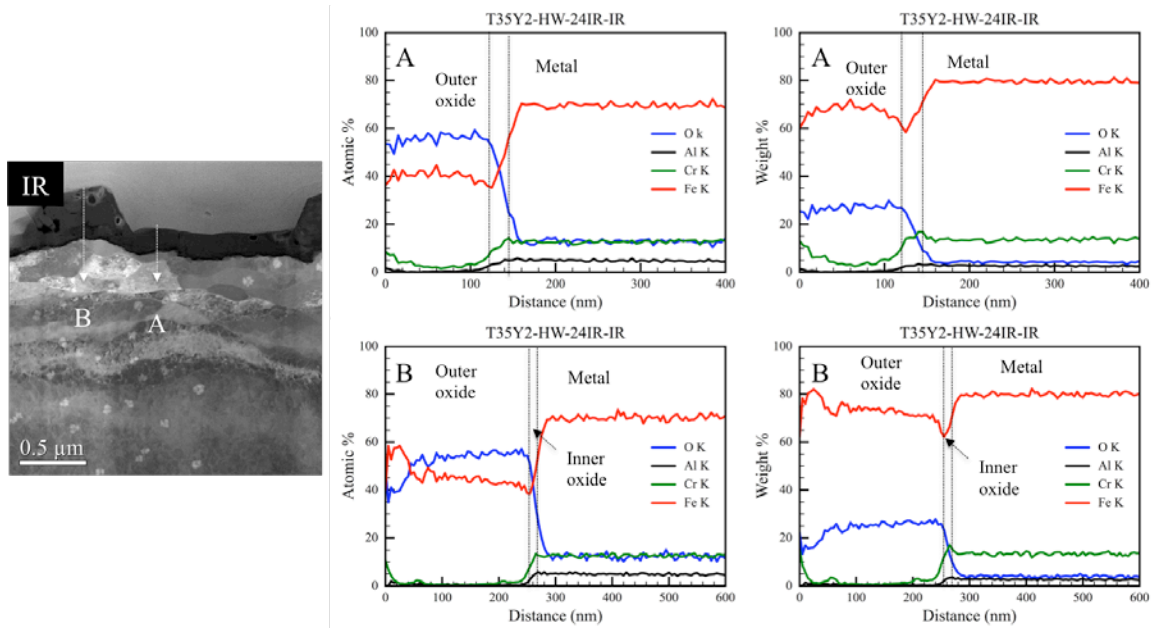


Figure B12: EDS line scans of oxide regions (IR) formed on sample T35Y2-HW-24IR.

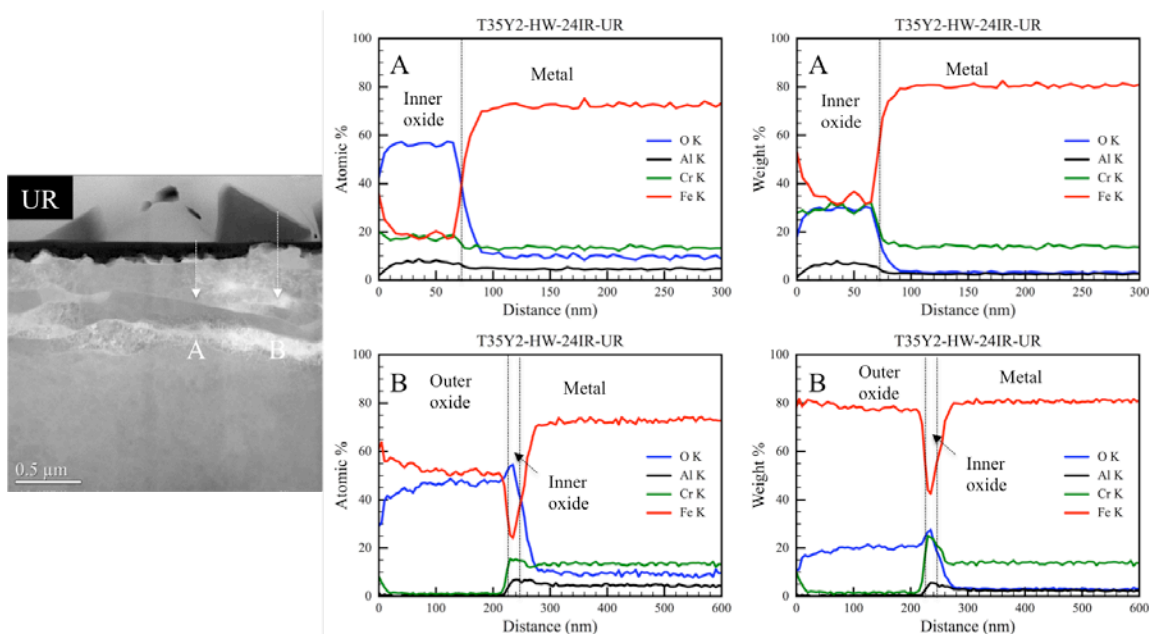


Figure B13: EDS line scans of oxide regions (UR) formed on sample T35Y2-HW-24IR.

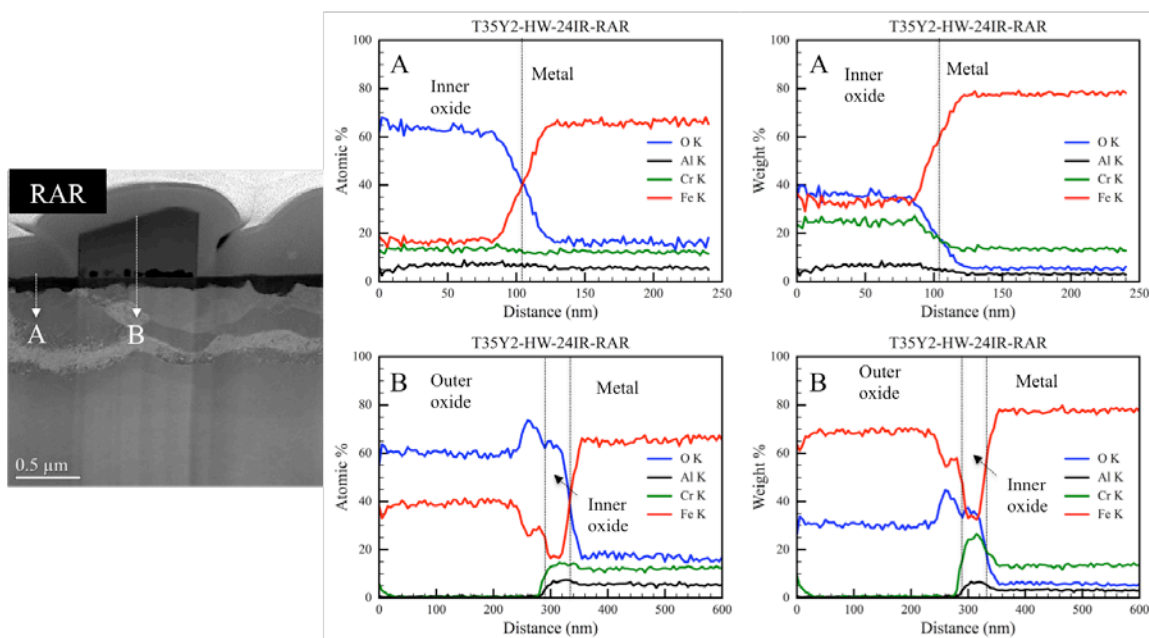


Figure B14: EDS line scans of oxide regions (RAR) formed on sample T35Y2-HW-24IR.

For the NWC condition of **sample T35Y2-NWC-24IR**, EDS results of IR and UR region are shown in Figure B15 and B16. In the IR regions, the outer oxide particle showed a hematite composition; the inner layer was very thin and its composition changed over thickness. In the UR region, the outer oxide consisted of a Fe-rich Fe-Cr spinel phase; no aluminum was found. In the RAR region (Fig. B17), hematite phase was observed which is consistent with the Raman results for this region.

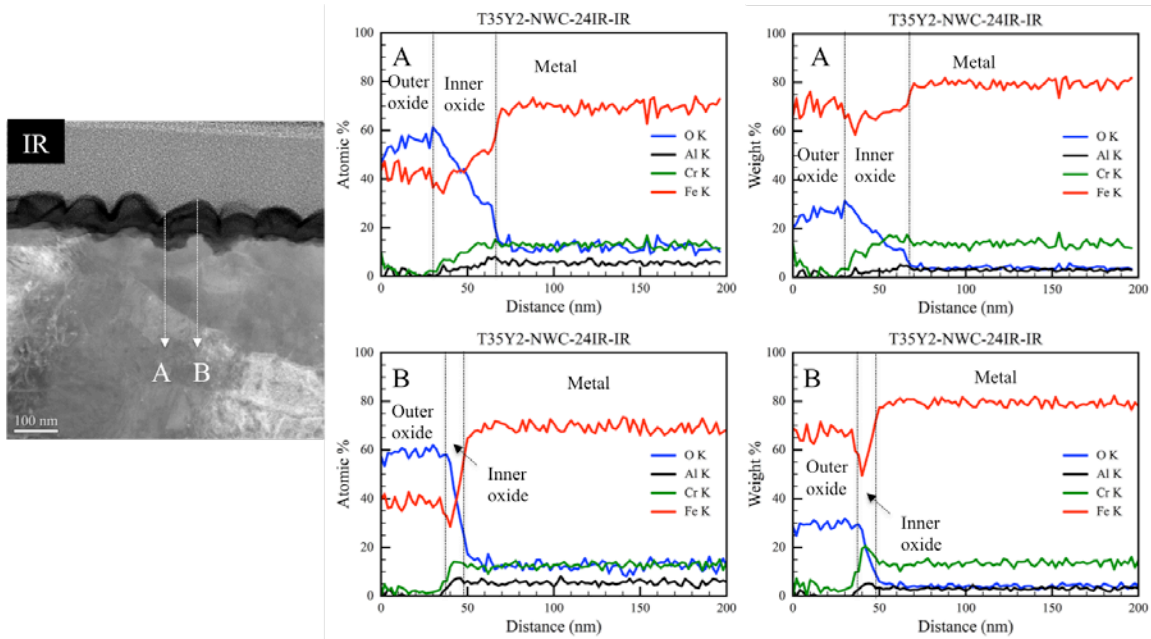


Figure B15: EDS line scans of oxide regions (IR) formed on sample T35Y2-NWC-24IR.

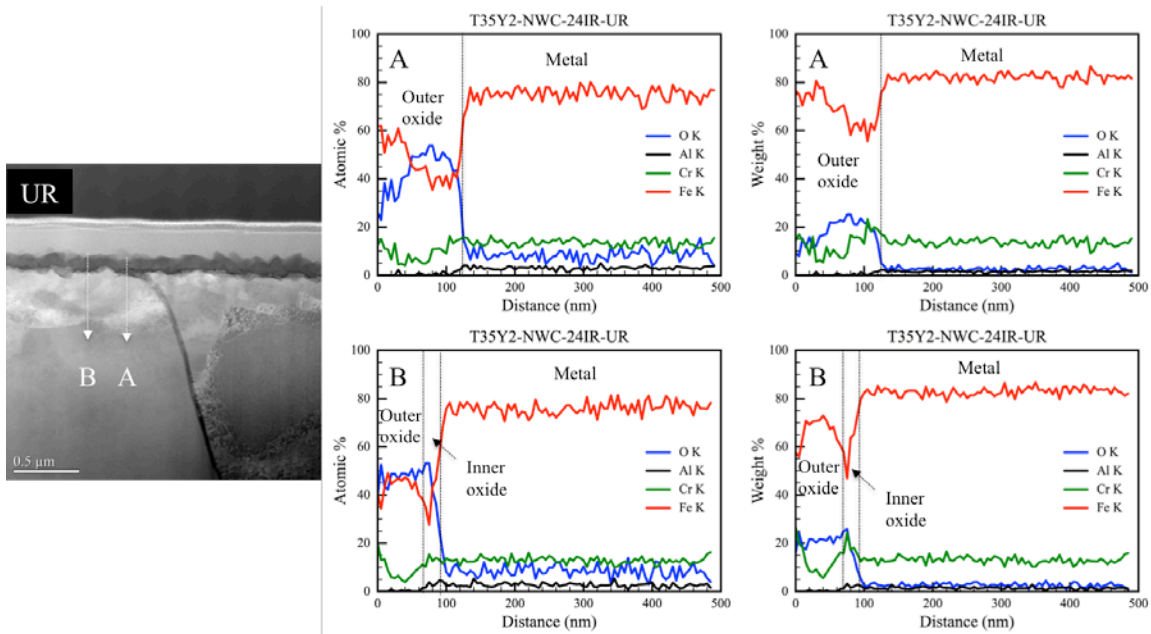


Figure B16: EDS line scans of oxide regions (UR) formed on sample T35Y2-NWC-24IR.

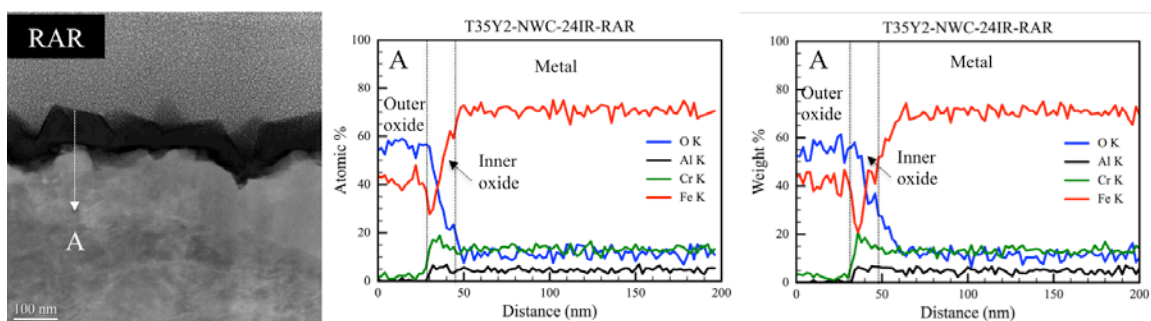


Figure B17: EDS line scans of oxide regions (RAR) formed on sample T35Y2-NWC-24IR.

Proton Post Irradiation Characterization Summary

The oxide species found on irradiated samples under different conditions were confirmed using Raman and the findings were summarized in Table B3.

Table B3: Summary of the oxide species found on T35Y2 in HW and NWC conditions under proton irradiation.

Samples	Regions	Outer Oxide/Inner Oxide	
		NWC 288°C, 2 ppm O ₂	HW 320°C, 3 ppm H ₂
T35Y2	IR	$\alpha\text{-Fe}_2\text{O}_3$ /Fe(Cr, Fe) ₂ O ₄	$\alpha\text{-Fe}_2\text{O}_3$ /Fe(Cr, Fe) ₂ O ₄
	RAR		Fe_3O_4 /Fe(Cr, Fe) ₂ O ₄
	UR		

Reference:

- [1] J. Ouyang, et al., Supersaturation-controlled shape evolution of $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals and their facet-dependent catalytic and sensing properties, ACS, Appl. Mater. Interfaces 2014, Vol. 6, pp. 12505-12514.
- [2] L. Chen, et al., Shape-evolution and growth mechanism of Fe_3O_4 polyhedrons, Advances in Materials Science and Engineering, Vol. 2015, Article ID 763124.

C. Electron Irradiation Experiments (U. of Notre Dame)

C1. Summary

Electron irradiations of T35Y2 were completed (samples ID and conditions are listed in Table C1) in PWR conditions – 3 ppm hydrogenated water (HW) at 320°C, and in BWR conditions – argon saturated water for normal water chemistry (NWC) at 288°C. A 2.5 MeV and 3.0 MeV electron beam were used for these irradiations. Given the ~250 micron sample thickness, energy of electrons as they cross the oxide layer and enter the water is ca. 1.5 MeV, so that they are still relativistic, and have LET of 1.9×10^6 eV/cm/e-. Dose rate to the water at the surface is ca. 170 kGy/s. Post-irradiation characterization of various regions of the irradiated samples was completed by means of SEM, TEM imaging and EDX line scans and Raman spectroscopy.

Table C1: List of irradiation experiments completed for T35Y2

Sample ID	e- Energy (MeV)	Temp (°C)	Water chemistry	Duration (hr)
T35Y2-HW	2.5	320	3 ppm H ₂	24
T35Y2-NWC	3.0	288	Argon-sat	24

Water loop data for the 24 hr e-beam irradiated T35Y2 HW and NWC experiments are shown in Figures C1 and C2, respectively. In the T35Y2 HW experiment, note that the outlet conductivity dropped from 3.5 to 1.5 $\mu\text{S/cm}$ during the course of the experiment compared to the unchanged inlet conductivity at 0.09 $\mu\text{S/cm}$. In the T35Y2 NWC experiment, the outlet conductivity dropped from 0.28 to 0.14 $\mu\text{S/cm}$ during the course of the experiment compared to the unchanged inlet conductivity at 0.06 $\mu\text{S/cm}$. This indicates that as the sample surface developed a layer of oxide, the amount of dissolved metal that goes into solution decreases.

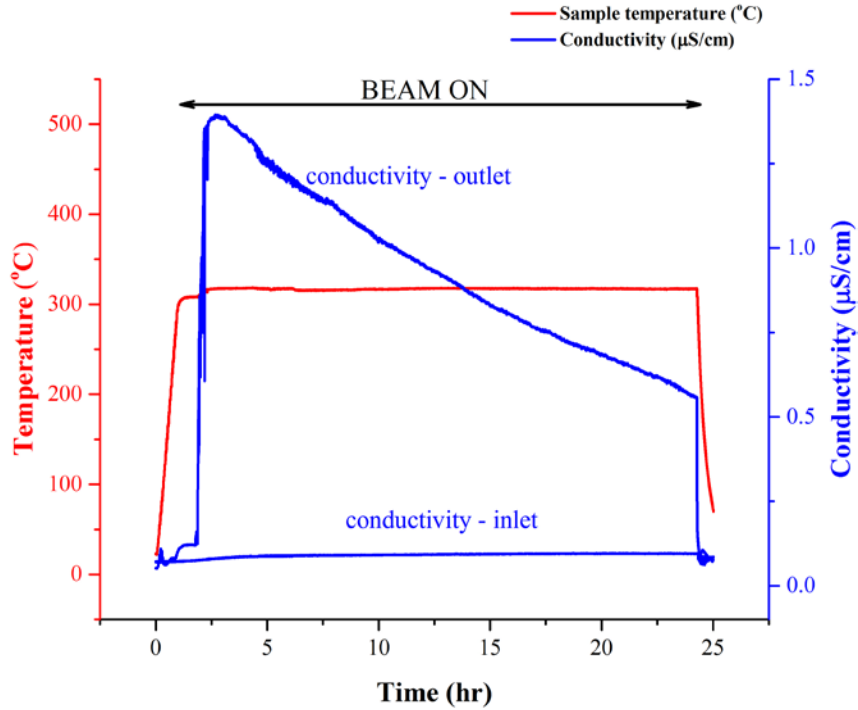


Figure C1: Water loop data of 24 hr electron irradiation of T35Y2 HW in 320°C 3 ppm H_2 water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

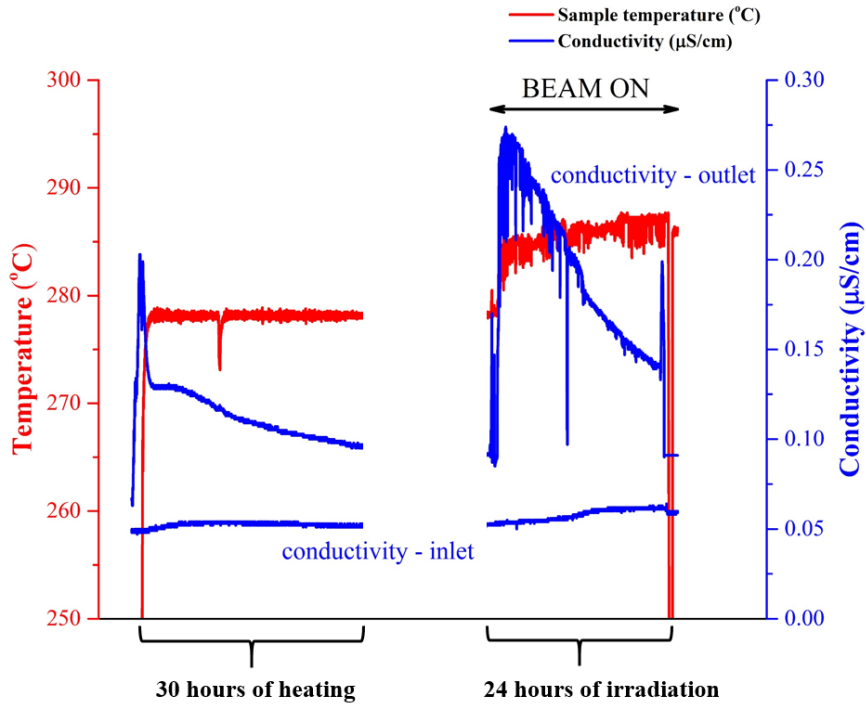


Figure C2: Water loop data of 24 hr electron irradiation of T35Y2 NWC in 288°C Argon saturated water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

C2. Post Irradiation Characterization of T35Y2 samples

a. Optical Microscopy and SEM Imaging – Oxide Morphology

Both T35Y2 steel samples (e-beam irradiated) were analyzed via microscopy. Both samples were discolored after 24 hr of e-beam exposure. Under the optical microscopy, three distinctive regions can be identified on the sample surface, Irradiated Region (IR), Radiolysis Affected Region (RAR) and Unirradiated Region (UR), shown in Figure C3 (left) for the T35Y2 HW sample and Figure C3 (right) for the T35Y2 NWC sample. The sample's irradiated region was discolored after 24 hr of e-beam exposure, observed as a darker circular region in the HW case and a maroon circular region in the NWC case.

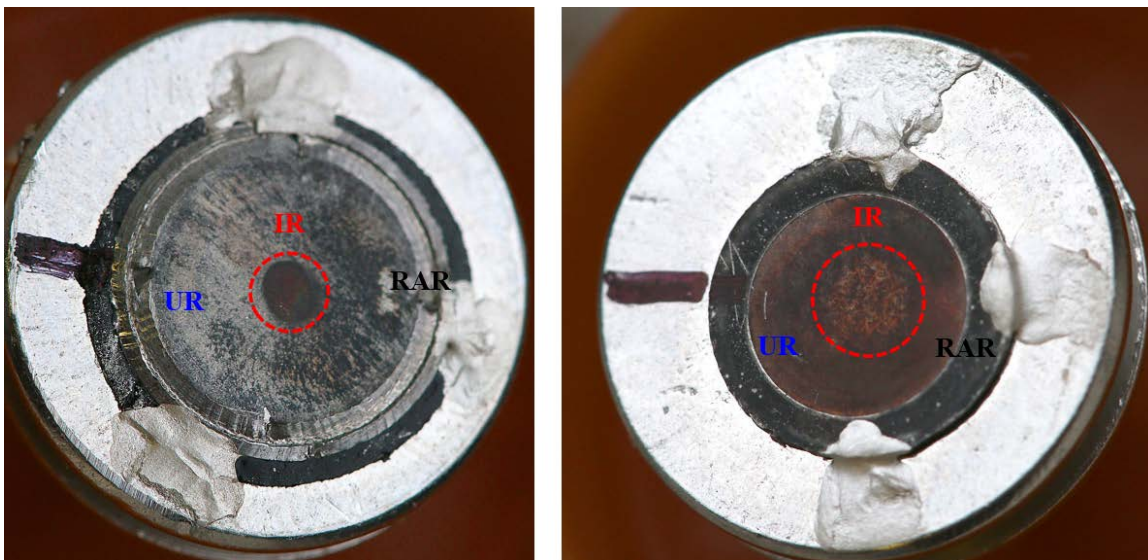


Figure C3: Post-irradiation optical image of 24-hour electron-beam irradiated T35Y2 sample in HW (left) and NWC (right). Representation of unirradiated region (UR), irradiated region (IR) and radiolysis affected region (RAR).

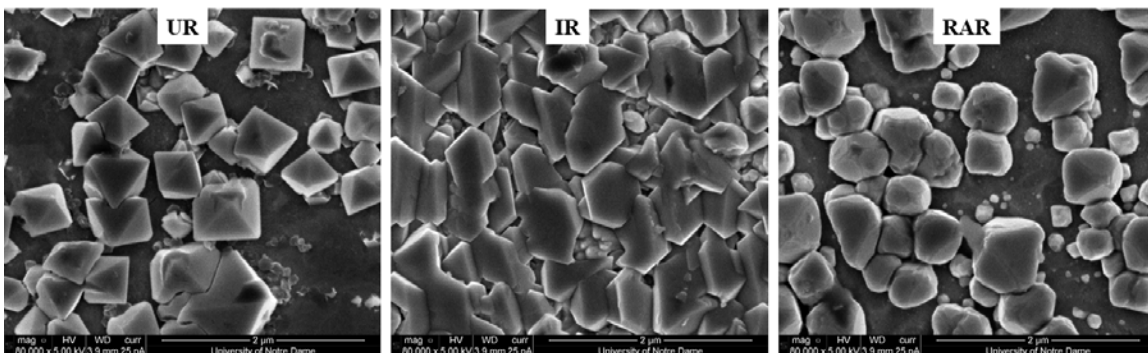


Figure C4: Post-Irradiation SEM images of 24-hour electron-beam T35Y2 sample in HW. Representation of the three different regions, UR, IR and RAR.

The high magnification SEM images in Figure C4 and Figure C5 represent the oxide particles of the three different regions (UR, IR and RAR) in the T35Y2 Hydrogen-saturated sample and T35Y2 Argon-saturated sample, respectively. There are similarities in the population density of the particles when comparing the regions of the different irradiating conditions; the IR region features the most densely populated particles, then the RAR region and the UR region. In both cases, the IR region features small particles that tend to grow in different direction, forming something similar to a “zig-zag” pattern.

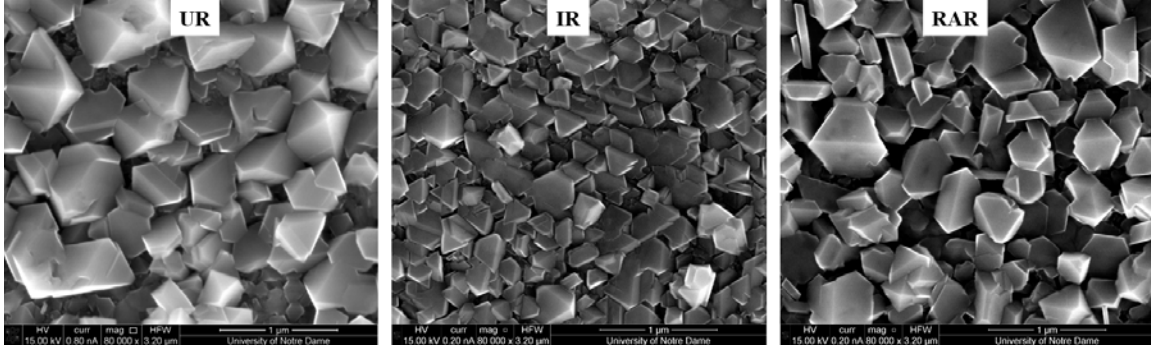


Figure C5: Post-Irradiation SEM images of 24-hour electron-beam T35Y2 sample in NWC. Representation of the three different regions, UR, IR and RAR.

b. TEM Imaging and EDX Line scans – Oxide Thickness

Focused ion beam (FIB) lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared for transmission electron microscope (TEM) analysis of the oxide layer thickness and morphology. The FIB lift-outs were prepared using the FEI-HELIOS dual beam FIB and the samples were further investigated via high magnification TEM images and EDX linescans, performed with the Titan TEM (FEI Titan 80/30 TEM) that is equipped with an energy-dispersive X-ray system by which line profiles can be measured; both instruments are located at the Notre Dame Integrated Imaging Facility.

TEM images of the different regions (UR, IR and RAR) are presented in Figure C6 for T35Y2 HW sample and Figure C7 for T35Y2 NWC sample. As it can be seen in the TEM images, the UR and IR region of T35Y2 HW sample features similar oxide thickness which is mostly due to the precipitation oxide. In the NWC case, the oxide thickness mostly comes from the precipitation oxide layer that is present in all three regions. There is not a clear boundary between the inner and outer oxide layer in the analyzed samples; therefore, the thickness comparison presented in Figure 1 is the overall measured thickness (outer thickness + inner thickness). Average thickness measurements are presented in Table C2.

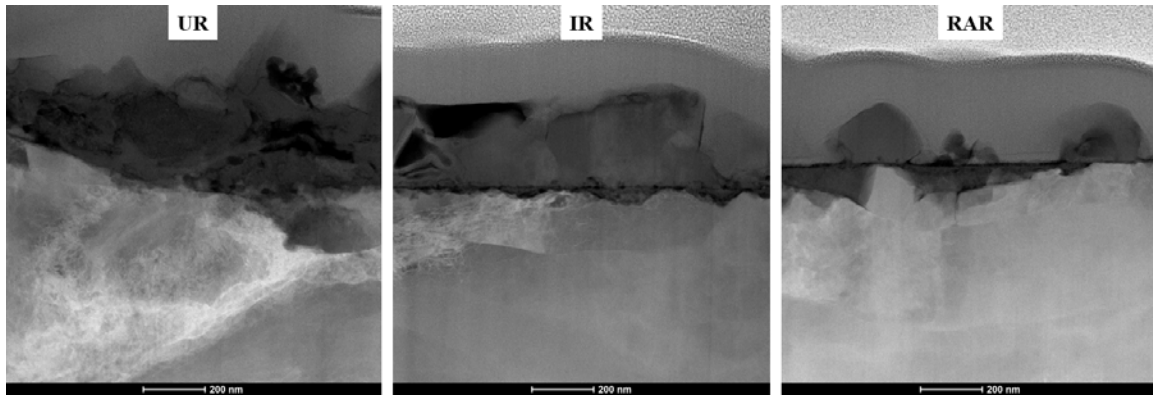


Figure C6: Post-Irradiation TEM images of 24-hour electron-beam T35Y2 sample in Hydrogen-saturated water. Representation of the three different regions (UR, IR and RAR).

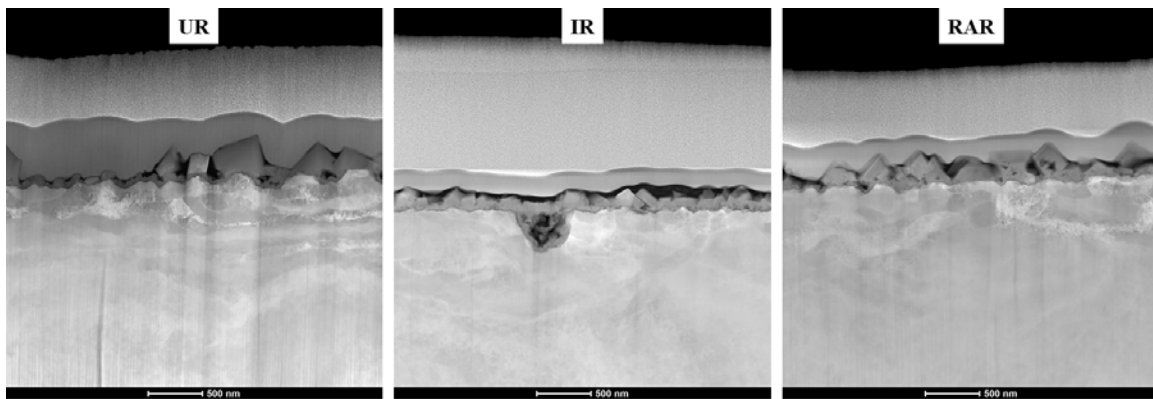


Figure C7: Post-Irradiation TEM images of 24-hour electron-beam T35Y2 sample in Argon-saturated water. Representation of the three different regions (UR, IR and RAR).

Table C2: Oxide thickness observed on samples irradiated in both HW and NWC conditions.

Sample	Region	Total Oxide (nm)
T35Y2-HW-24IR	IR	237 ± 80
	RAR	106 ± 115
	UR	180 ± 168
T35Y2-NWC-24IR	IR	154 ± 32
	RAR	164 ± 60
	UR	112 ± 66

EDX line scans were performed to reveal elemental distribution information about the sample. Multiple EDX line scans were completed on each TEM sample and are shown in the figures below. The line scans of the HW sample are presented in Figures, C8, C9 and C10 and the line scans for the NWC samples are presented in Figures C11, C12 and C13.

Two EDX line scans of the UR region of the T35Y2 sample in the Hydrogen-saturated water are presented in Figure C8. The TEM sample included in these scans covers a bit of the precipitation layer. The boundary between the outer and inner oxide layer as the the line scan suggests can be determined by the increase of Aluminum and Chromium in the inner oxide layer. Both outer and inner oxide layers consist of about 60 to 70% atomic concentration of Oxygen. It is also apparent that this type of steel is Chromium-rich (about 15% atomic concentration of Chromium).

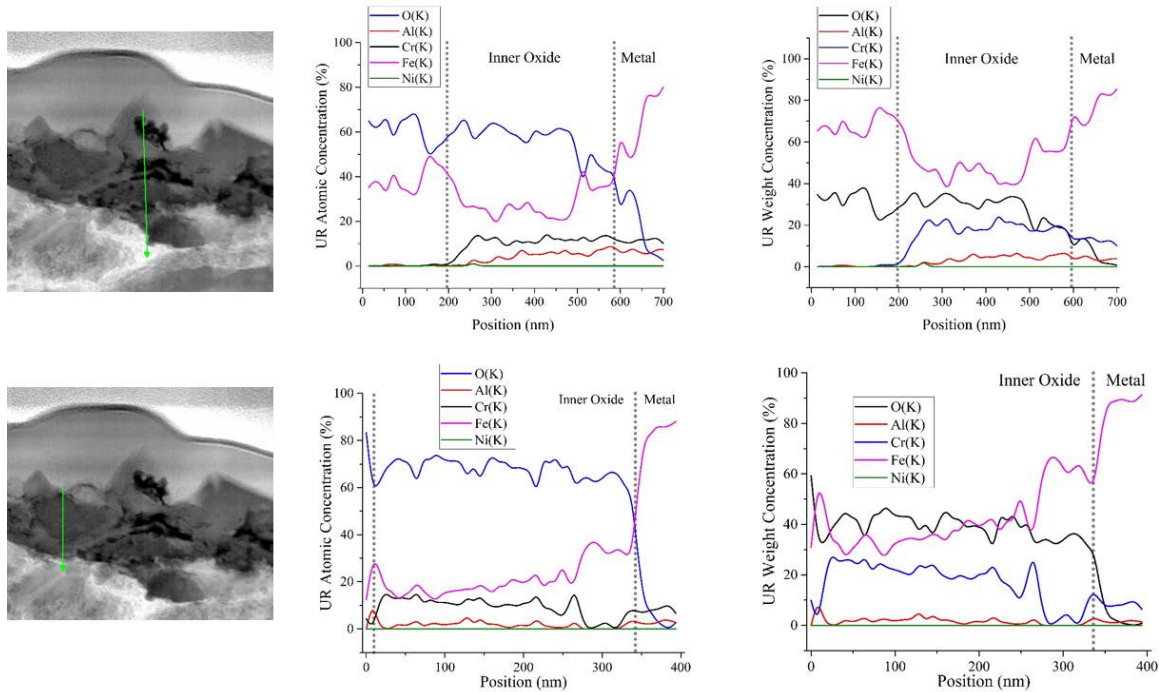


Figure C8: Left: STEM bright field image of UR region (the thin arrow shows the length of the EDX line scan and its direction), 24-hour electron-beam irradiated T35Y2 sample in Hydrogen-saturated water; **STEM EDX UR line scan results** - Middle: atomic concentration vs. position, representation of inner oxide and metal region of scan. Right: weight concentration vs. position.

The EDX line scans of the IR region of the T35Y2 sample in the Hydrogen-saturated water are presented in Figure C9. The largest portion of the EDX line scans cover the outer oxide precipitation layer which consists of mostly nickel-iron-oxide according to the elemental distribution. The inner oxide feature a spinel phase of FeCr_2O_4 , as well as some aluminum present.

The EDX line scans of the RAR region of the T35Y2 sample in the Hydrogen-saturated water are presented in Figure C10. The EDX line scans of this region focus more on the inner oxide layer rather than the precipitation layer, though there is somewhat a clear line between the outer and inner oxide layer as well as the inner oxide and the metal region. According to the elemental distribution of the RAR inner oxide, it can be concluded that this region is very similar to the oxide layer of the unirradiated region.

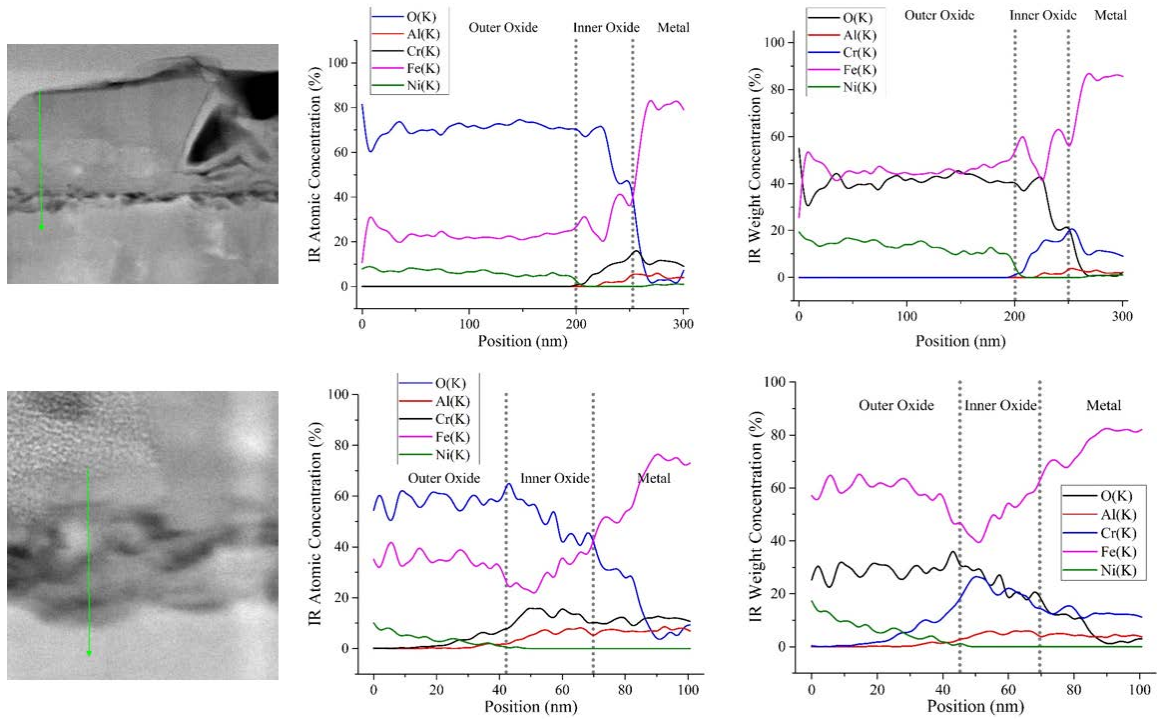


Figure C9: Left: STEM bright field image of IR region (the thin arrow shows the length of the EDX line scan and its direction), 24-hour electron-beam irradiated T35Y2 in Hydrogen-saturated water; **STEM EDX IR line scan results** - Middle: atomic concentration vs. position, representation of outer, inner oxide and metal region of scan. Right: weight concentration vs. position.

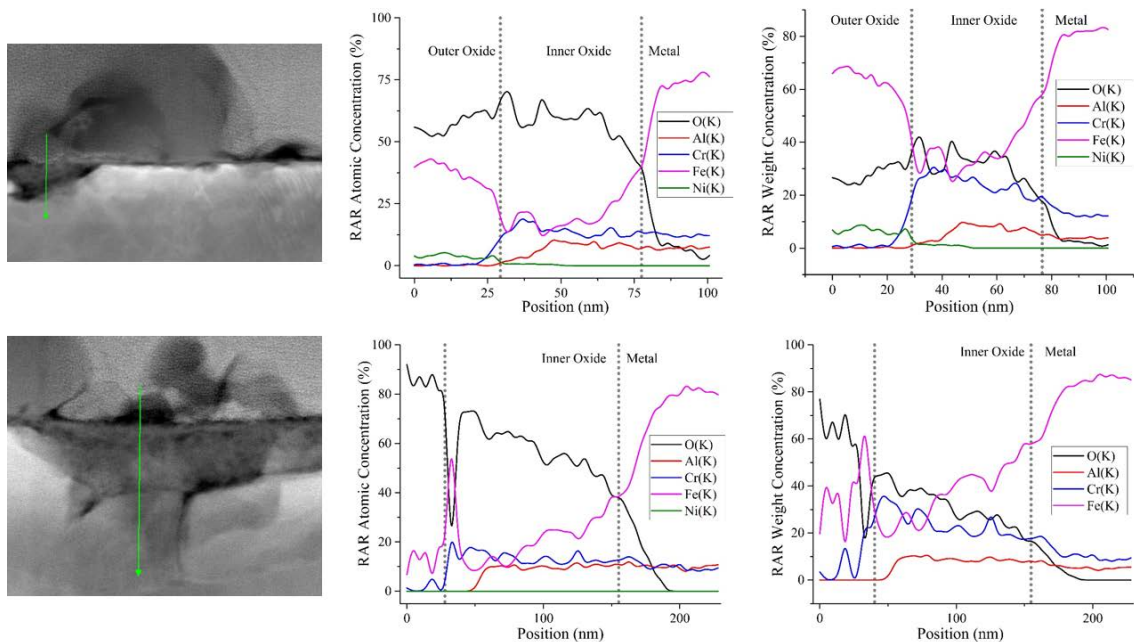


Figure C10: Left: STEM bright field image of RAR region (the thin arrow shows the length of the EDX line scan and its direction), 24-hour electron-beam irradiated T35Y2 sample in Hydrogen-saturated water; **STEM EDX RAR line scan results** - Middle: atomic concentration vs. position, representation of inner oxide and metal region of scan. Right: weight concentration vs. position.

The EDX line scan of the UR region of the T35Y2 sample in Argon-saturated water is presented in Figure C11. The TEM sample included in this scan contains both a precipitation oxide layer and an inner oxide layer, not easily distinguished. The oxide layer as the the line scan suggests contains anywhere from 50 to 60% atomic concentration of oxygen, as well as some (about 10%) Nickel precipitation. Nickel is not a constituent of T35Y2 steel, and might be a result of the Hastelloy corrosion cell.

The EDX line scan of the IR region of the T35Y2 sample in the Argon-saturated water is presented in Figure C12. The TEM sample included in this scan contains both a precipitation oxide layer and an inner oxide layer. The oxide layer as the line scan suggests contains about 60% atomic concentration of oxygen and about 20% Nickel atomic concentration on its surface which decreases throughout the line. The inner oxide layer features enrichment of Chromium and Aluminum and the metal region shows the highest content of Iron.

The EDX line scan of the RAR region of the T35Y2 sample in the Argon-saturated water is presented in Figure C13. The TEM sample included in this scan contains both a precipitation oxide layer and an inner oxide layer, not being distinguished from each other. The oxide layer contains approximately 60% atomic concentration of Oxygen, 40% atomic concentration of Iron and about 20% of Nickel atomic concentration only at its surface.

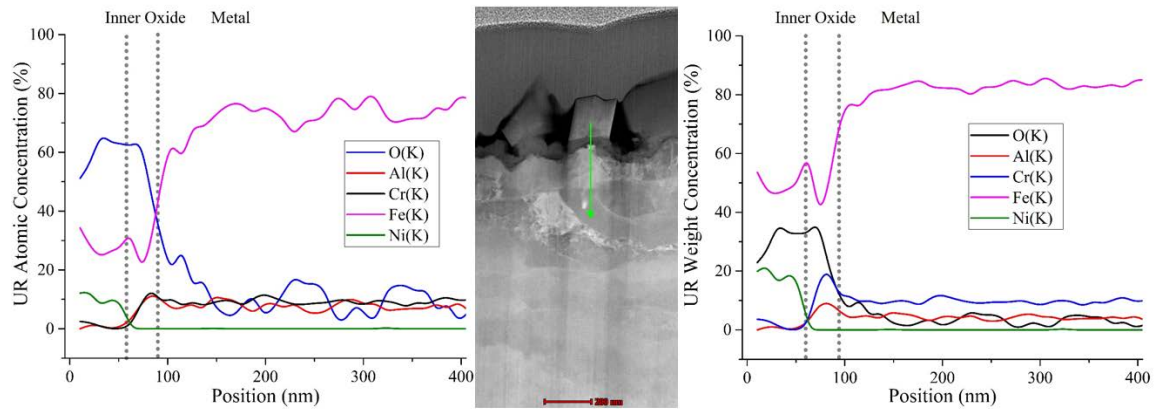


Figure C11: Left: STEM EDX UR line scan results the 24-hour electron-beam irradiated T35Y2 sample in Argon-saturated water, atomic concentration vs. position, representation of inner oxide and metal region of scan. Middle: STEM bright field image of UR region (the thin arrow shows the EDX line scan direction). Right: STEM EDX UR line scan results, weight concentration vs. position.

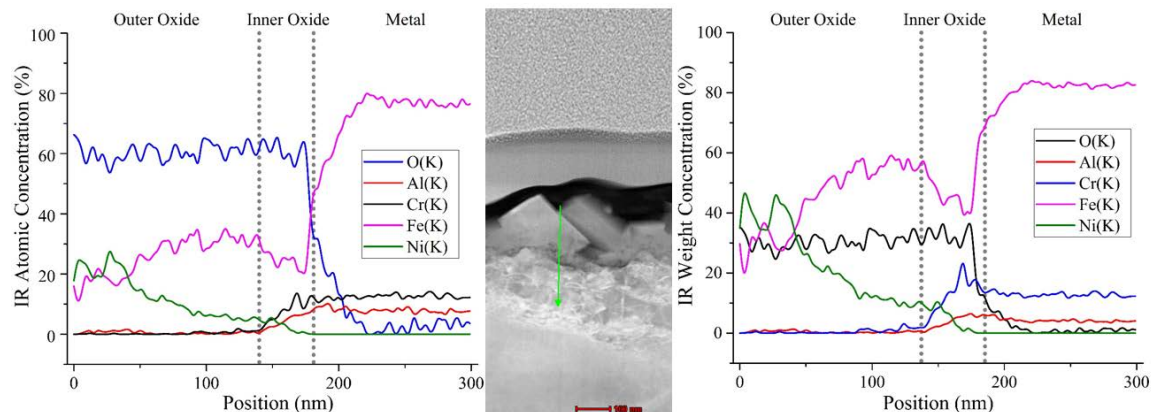


Figure C12: Left: STEM EDX IR line scan results the 24-hour electron-beam irradiated T35Y2 sample in Argon-saturated water, atomic concentration vs. position, representation of outer, inner oxide and metal region of scan. Middle: STEM bright field image of IR region (the thin arrow shows the EDX line scan direction). STEM EDX UR line scan results, weight concentration vs. position.

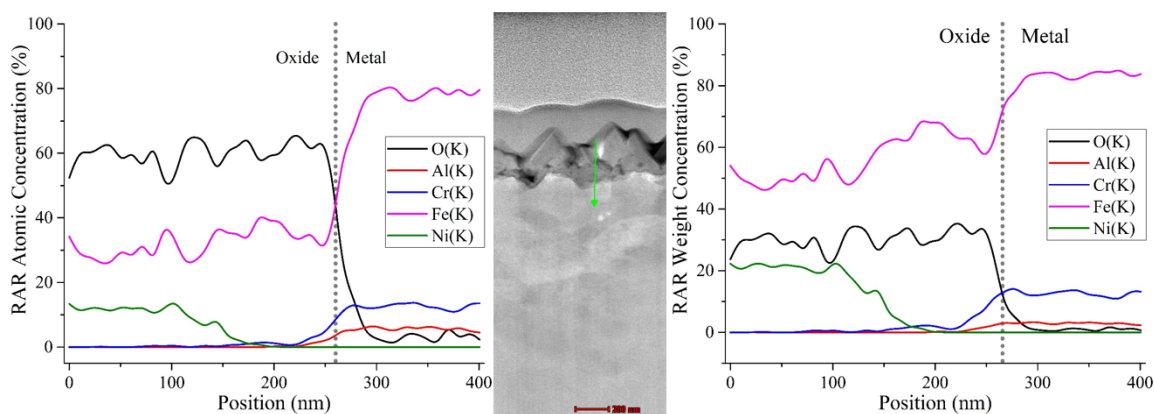


Figure C13: Left: STEM EDX RAR line scan results the 24-hour electron-beam irradiated T35Y2 sample in Argon-saturated water, atomic concentration vs. position, representation of oxide and metal region of scan. Middle: STEM bright field image of RAR region (the thin arrow shows the EDX line scan direction). STEM EDX UR line scan results, weight concentration vs. position.

c. Raman Spectroscopy – Oxide Phase

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated sample. Spectra were recorded using a Micro-Raman Spectrometer (NRS-5100, Jasco). The spectra were collected using a 532 nm wavelength green laser, at a typical laser power of 50 mW, during a total of 240s of exposure time.

Three regions on the irradiated sample were measured using Raman spectroscopy, irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR). Three individual spectra were also taken in each region for data consistency check.

Raman spectra of the UR, RAR and IR region of the T35Y2 sample in the Hydrogen-saturated water (left) and Argon-saturated water (right) are presented in Figure C14. Raman analysis of corroded steels usually features corrosion products that are mainly composed of a mixture of iron oxides (maghemite, hematite, magnetite). It is assumed the Raman signal is primarily due to a precipitation oxide layer. The formation of hematite is associated with a high corrosion potential, and is generally present in the IR region of HW samples, or all regions of NWC samples. In both of the present experiments, there is no presence of the typical Raman peaks related to iron oxides.

Raman analysis of the IR region of the T35Y2 HW sample showed that the corrosion products are mainly composed of a mixture of chromium oxide, iron chromite and nickel chromite. The chromium oxide associated peaks are presented by the green dashed lines in the plot, the iron chromite peaks by the pink dashed lines and the nickel chromite peaks by the blue dashed lines. The UR and RAR regions of the HW sample feature a strong magnetite peak and there is no presence of Nickel spinels.

Similar to the HW case, Raman analysis of the IR case of the T35Y2 NWC sample showed that the corrosion products are mainly composed of nickel chromite. The nickel chromite associated peaks are presented by the blue dashed lines in the plot. The presence of Nickel is confirmed in the EDX data. Given that the sample contains no nickel, this nickel oxide must come from corrosion of the hastelloy body. The UR and RAR regions of the NWC sample feature strong hematite and magnetite peaks.

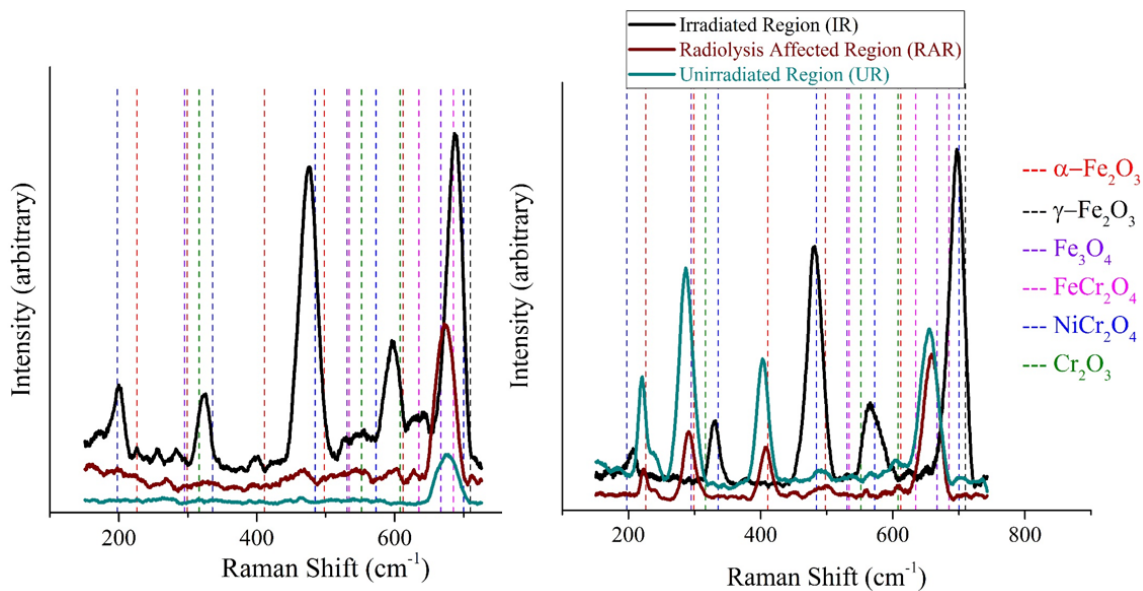


Figure C14: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated T35Y2 sample in Hydrogen-saturated water (left) and T35Y2 sample in Argon-saturated water (right). Representation of the three different regions (IR, RAR and UR) and associated Raman peaks;

Assessment of Corrosion Resistance of Candidate Alloys for Accident Tolerant Fuel Cladding under Reactor Conditions

September 2017 Milestone report for APMT FeCrAl Alloy

Four APMT steel sample irradiations were completed to assess the corrosion behavior of this steel under reactor-like conditions. In these experiments the thin samples actually serve as the interface between the accelerator vacuum system on one side, and water at high pressure and temperature on the other. The samples irradiated at the University of Michigan used high energy protons while at University of Notre Dame an electron beam was used. The protons have energy of ca. 1.7MeV as they pass through the oxide into the water, and electrons have energy of ca. 1.5MeV. The protons have much higher momentum, and so (like high energy neutrons) are capable of causing significant atomic displacement damage in the oxide layer. They also move much more slowly than the relativistic electrons, so their LET (linear energy transfer) is ca. 200x larger than the electrons. To compensate and give nearly the same average energy dose to the sample and water near the surface, the electron beam flux (amps/cm²) is adjusted to be ca. 100x greater than the proton beam. Electrons do essentially no displacement damage to the solid.

Detailed analysis of the several APMT samples is shown below in sections A-C. A summary of oxide thickness generated in the 24 hour irradiated samples is presented in Figure 1. The plot shows comparison between three different regions of interest: unirradiated region upstream of the radiation (UR), the directly irradiated region (IR), and a radiolysis affected region (RAR) downstream of the sample. Samples were irradiated at 320°C with 3ppm hydrogen (HW), and 288°C with 2 ppm oxygen (NWC) or 288°C with argon saturated water (ArW) in the electron beam case to avoid high nickel content promoted from the hastelloy cell when exposed to oxygen saturated water.

We conclude that APMT steel is a viable candidate cladding material as the corrosion is not dramatically enhanced in the direct radiation zones compared to the unirradiated zones. Its performance is reasonably similar to other candidate steels under these conditions of extreme radiation in either hydrogenated or oxygenated water.

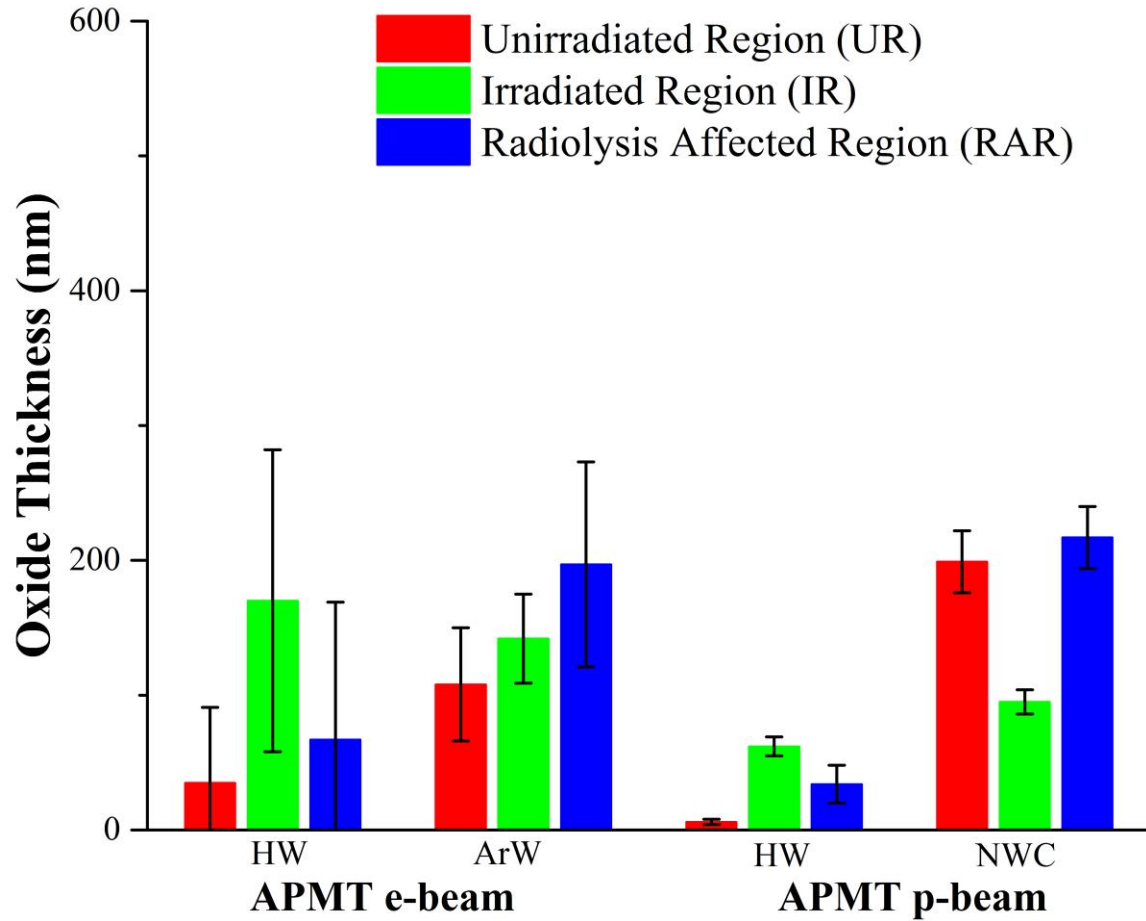


Figure 1: APMT oxide thickness comparison between ND e-beam and UM p-beam 24 hour irradiated samples. Water chemistry was either 320°C with 3ppm H₂ (HW), 288°C with 2ppm O₂ (NWC) or 288°C with Argon saturated water (ArW).

A. APMT Base Metal Characterization

The bulk material was obtained from Sandvik, and chemical composition is listed in Table A1.

Table A1. The chemical composition (wt.%) of as-received APMT, supplied by Sandvik.

Heat	Fe	Cr	Al	Mo	C	S	O	N	P
NA	69	21	5	3	0.08	-	-	-	-
	Si	B	Mn	Y					
	<0.7	-	0.4	-					

EDS element analysis was carried out on a FEI NOVA SEM/FIB with EDAX detector. EDS spectrum is shown in Fig. A1. Atomic and weight percentage of each alloy element were shown in Table A2. The concentration of major alloying elements was consistent with the specification received from Sandvik.

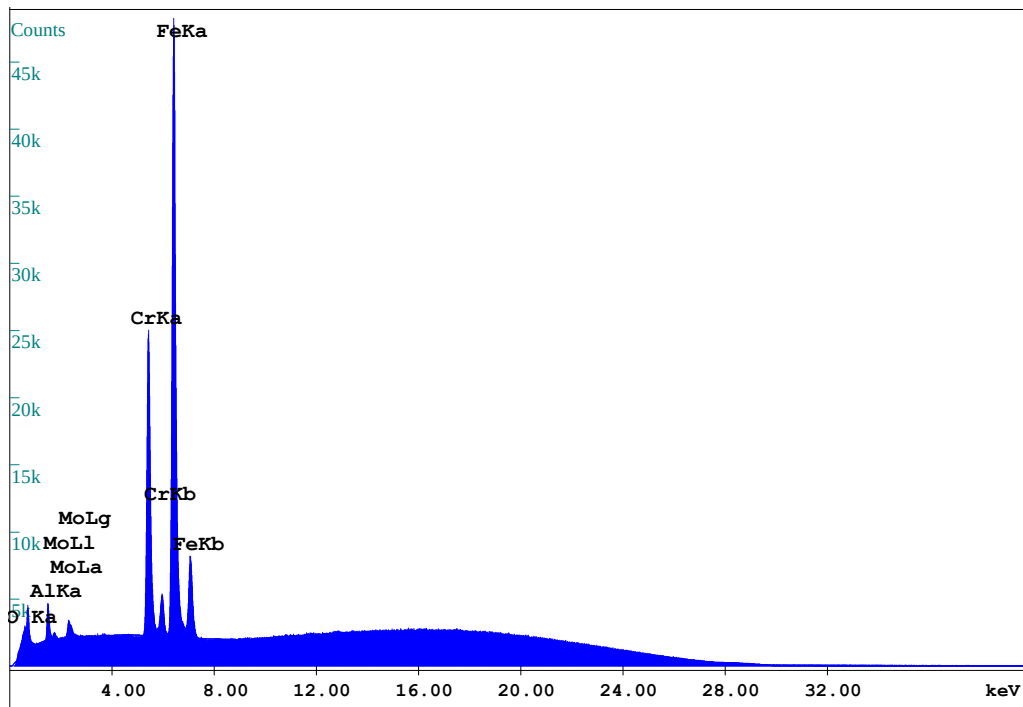


Figure A1. EDS spectrum of as-received APMT.

Table A2. Alloy element analysis of APMT by EDS.

Element	Weight %	Atomic %
Fe	70.69	64.03
Cr	21.41	20.83
Al	3.69	6.92
Mo	1.93	1.02

TEM analysis was performed using a JEOL 3011 TEM on a twin-jet polished TEM disc. Very clear grain boundaries can be identified, however only a few grain boundaries were shown in Figure A2. Grain size was in the order of 2 ~ 5 μ m.

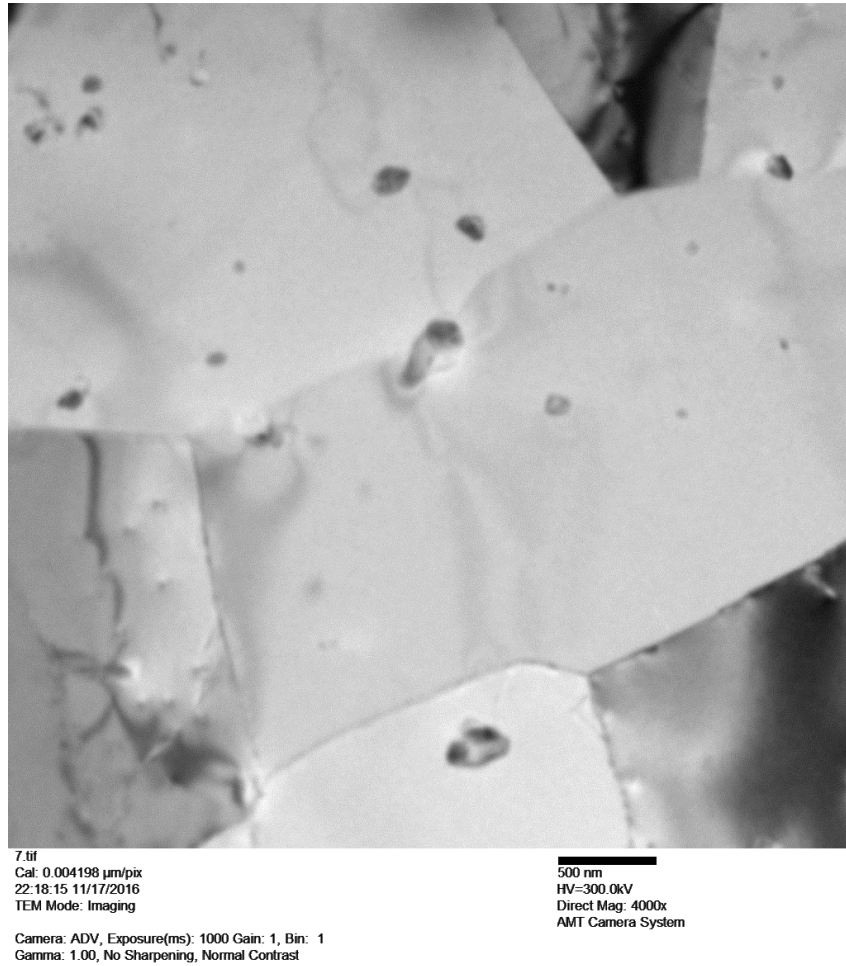


Figure A2. TEM Bright-field images of APMT base metal.

B. Proton Irradiation Experiments (U. Michigan)

B1. Summary

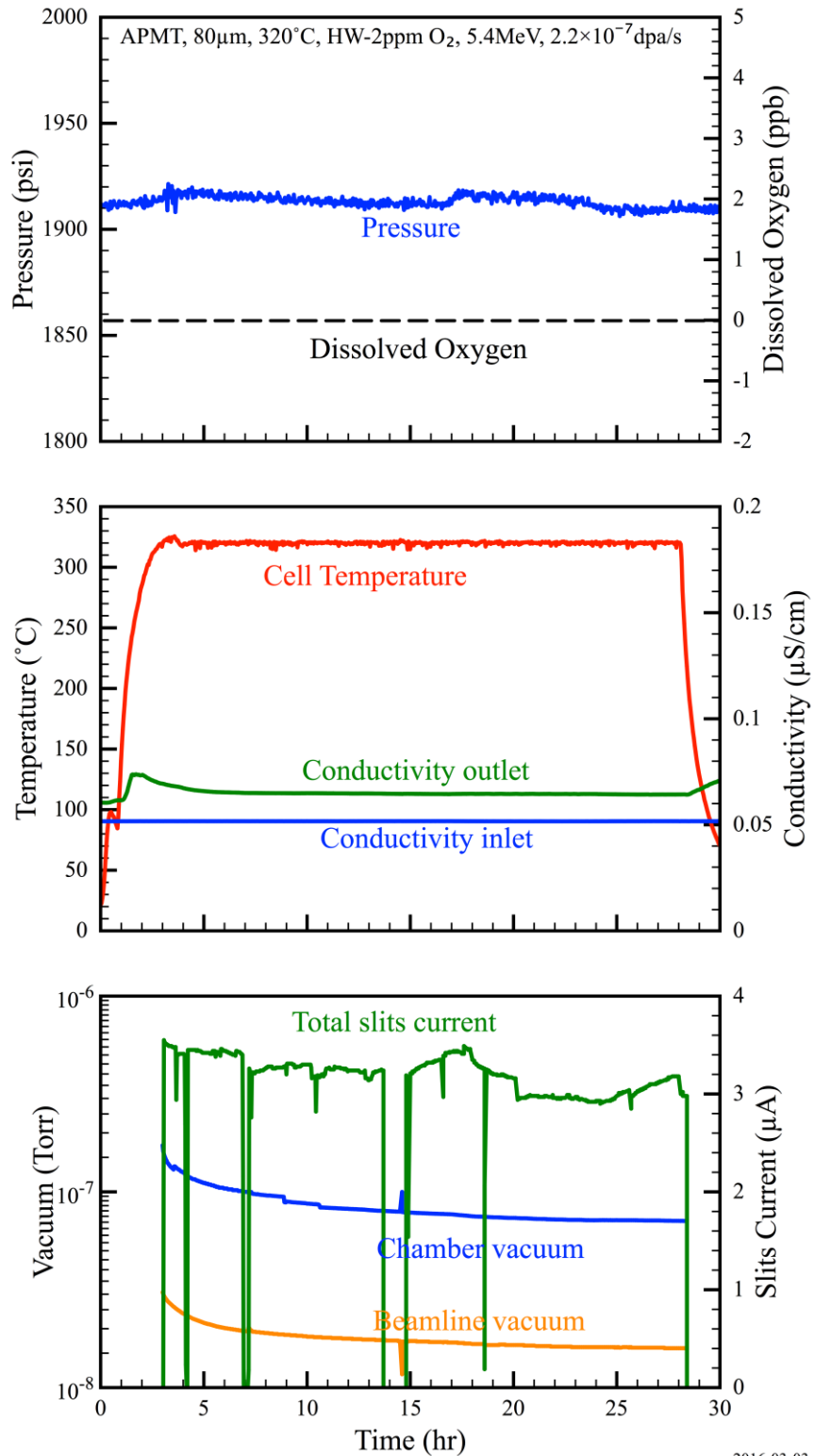
Proton irradiations of APMT were completed in hydrogenated water (HW), and in normal water chemistry (NWC) at 320°C and 288°C, respectively. A 5.4 MeV proton beam at a current density of 2 $\mu\text{A}/\text{cm}^2$ was used for these irradiations. The sample thickness was 80 microns, and the energy of the protons as they cross the oxide layer and enter the water is 1.7 MeV. The LET in water is $5.6 \times 10^{-11} \text{ J}/\text{cm}/\text{e}^-$. The dose rate to the water directly at the interface is 500 kJ/kg/s. Various regions of the irradiated sample were analyzed using SEM and Raman Spectroscopy and characterizations of the oxide microstructure were carried out on the TEM.

B2. Proton Irradiation Experimental conditions

Two APMT samples were irradiated for 24 hr under the experimental conditions listed in Table B1. Water loop data and beamline data are shown in Figures B1 for HW condition and Figures B2 for NWC condition.

Table B1: List of irradiation experiments completed for APMT.

Sample ID	p-energy (MeV)	Temp (°C)	Water chemistry	Water dose rate (kGy/s)	Damage rate (dpa/s)	Duration (h)
APMT-HW-24IR	5.4	320	HW (3 ppm H ₂)	500kGy/s	2.2×10^{-7}	24
APMT-NWC-24IR	5.4	288	NWC (2 ppm O ₂)	500kGy/s	2.2×10^{-7}	24



2016-03-03

Figure B1: Water loop and beam current data of 24 h proton irradiation of APMT in 320°C 3 ppm H₂ water at a damage rate of 2.2×10^{-7} dpa/s.

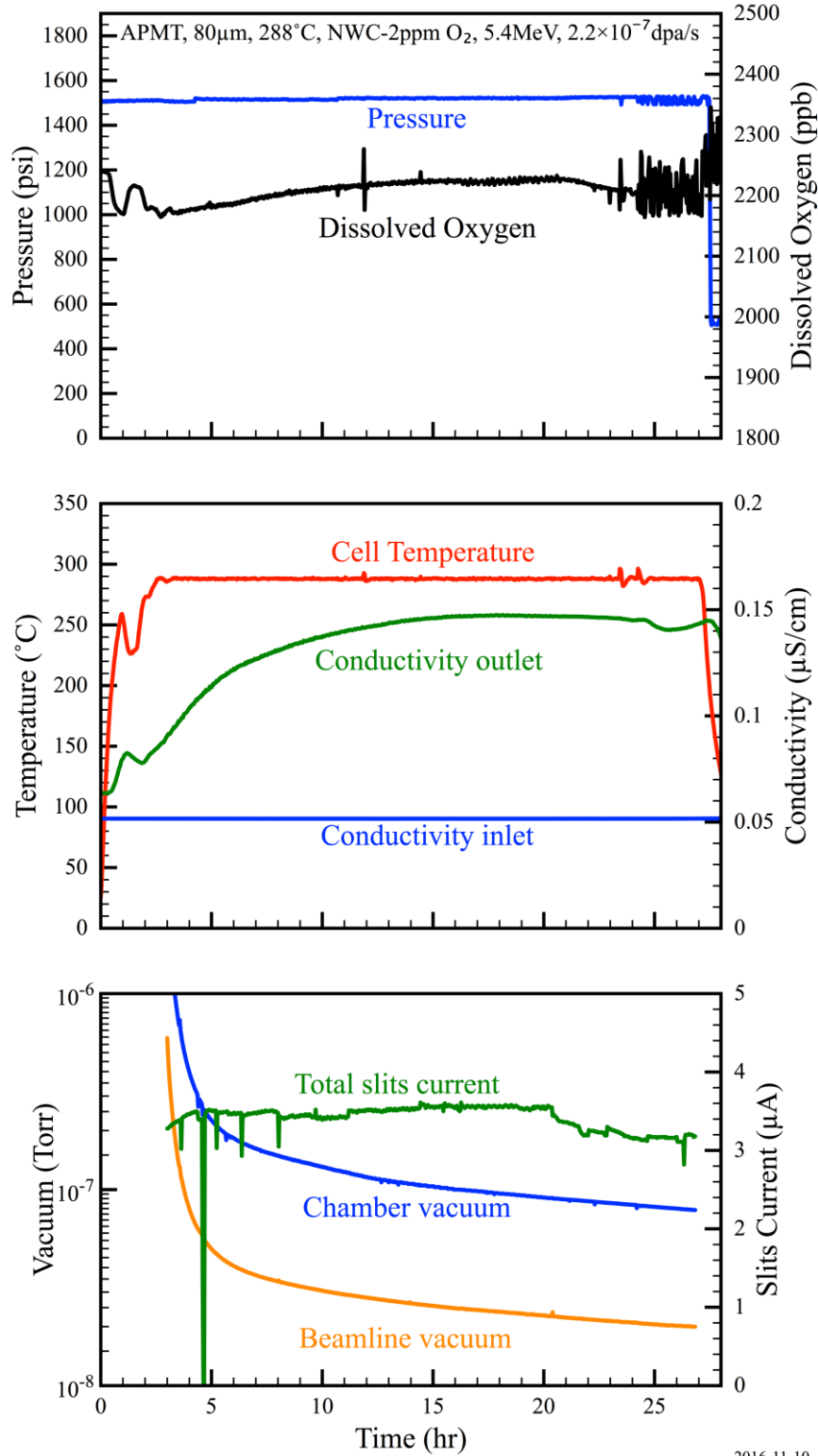


Figure B2: Water loop and irradiation data of 24 h proton irradiation of APMT in 288 $^{\circ}$ C 2 ppm O₂ water at a damage rate of 2.2×10^{-7} dpa/s.

2016-11-10

B3. Post Irradiation Characterization

Three distinctive regions of the sample surface were characterized, namely the Irradiated Region (IR), Radiolysis Affected Region (RAR) and the Unirradiated Region (UR).

Optical Images

Sample APMT-HW-24IR remained as shiny as the polished surface in the UR region, as indicated in Figure B3, whereas the IR region has a matte gray appearance. A distinctive flow region was not found in this sample.

Sample APMT-NWC-24IR was discolored and showed interference colors, shown in Figure B3. The lighter orange UR region was observed around the IR region. An IR region with dark blue appearance was observed in the center, and RAR region is not significantly different from the UR region.

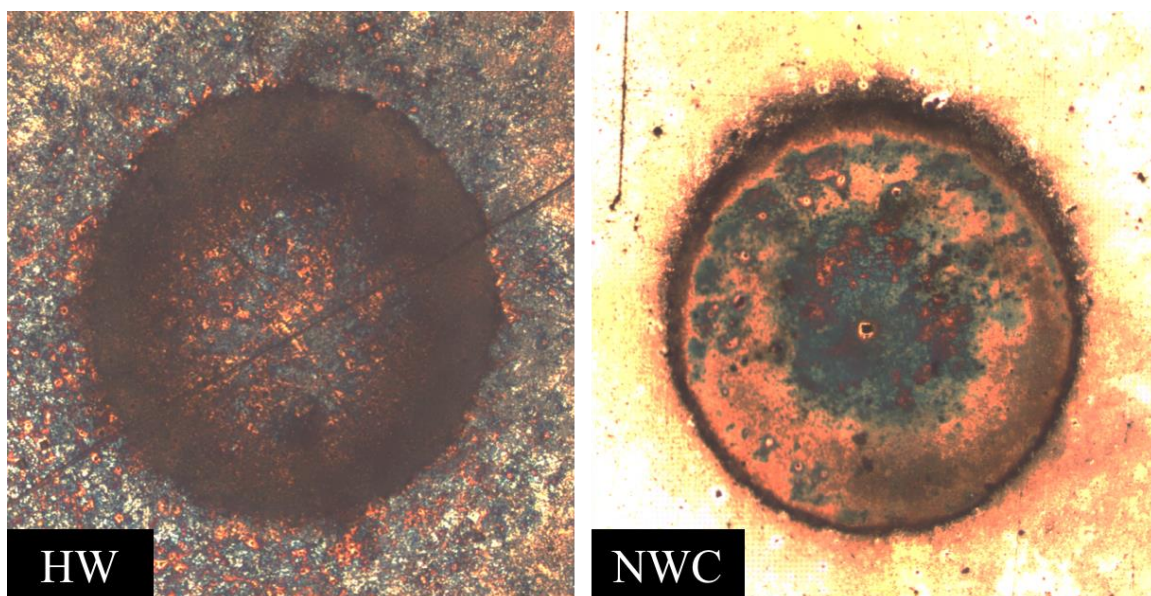


Figure B3: Optical images of irradiated samples APMT-HW-24IR and APMT-NWC-24IR.

Surface Oxide Morphology Analysis

Sample APMT-HW-24IR has a matte gray appearance after 24 h exposure in hydrogen water condition; a SEM image with circles outlining each region is shown in Figure B4. Oxide morphologies in UR and RAR regions were similar. Outer surface particles in the UR region are more faceted compared with the one in the RAR region. In both regions, a regular shaped outer oxide was observed with the particle size of $\sim 0.5 \mu\text{m}$. In the IR region, oxide particles consisted of two types, one type is less faceted crystals

with a size of $\sim 0.5 \mu\text{m}$, the other type is much smaller crystals with size less than 200nm as indicated in Figure B5. Outer oxide particle density was significantly higher in the IR region compared with RAR and UR region.

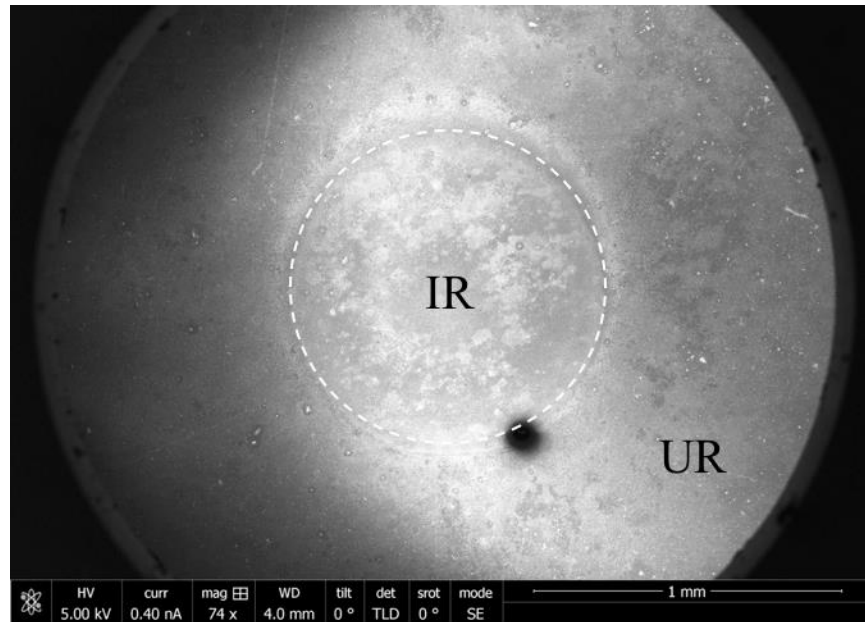


Figure B4: SEM image of sample APMT-HW-24IR. The irradiated region (IR) and unirradiated region (UR) are indicated by the dotted line.

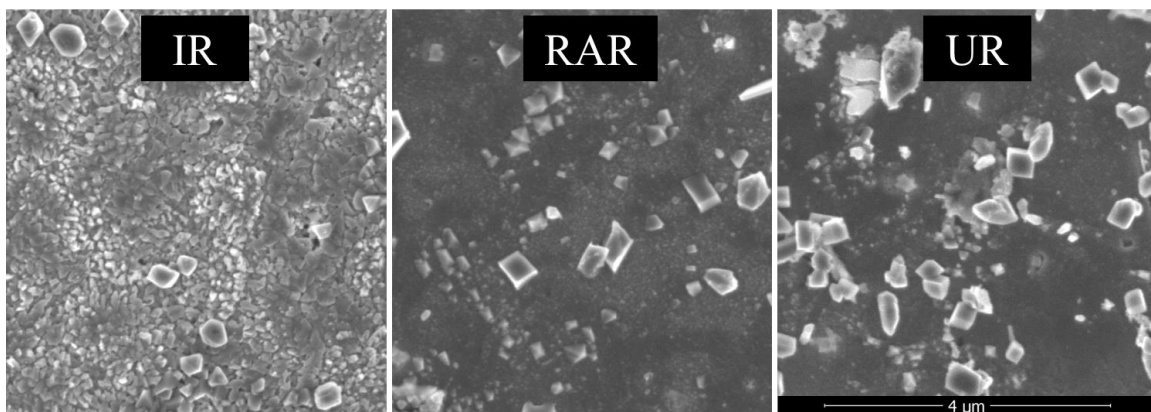


Figure B5: High magnification SEM images of the three regions observed on sample APMT-HW-24IR.

Sample APMT-NWC-24IR was discolored after 24 h of exposure in NWC water chemistry. In Figure B6, the IR and RAR regions were difficult to distinguish on the surface of the sample. However, the high magnification SEM images revealed that outer oxide particles from RAR and UR regions have the morphology of a flake or a needle shape, which were significantly different from the IR outer oxide shown in Figure B7. Oxide particles in the RAR and UR regions have large aspect ratio compared to the oxides found in the IR region. The particle size in the UR region is $\sim 0.5\text{-}2 \mu\text{m}$.

FIB lift-outs from three distinctive regions (IR, RAR and UR) on each sample were prepared, and TEM analysis was carried out on these TEM lamellas.

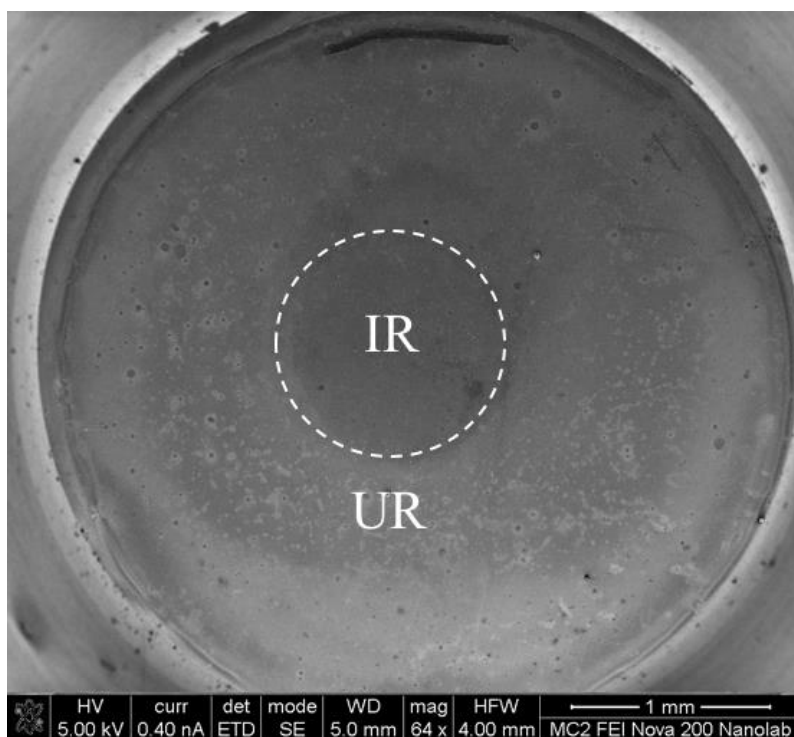


Figure B6: SEM image of sample APMT-NWC-24IR. The irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR) are indicated by the dotted line.

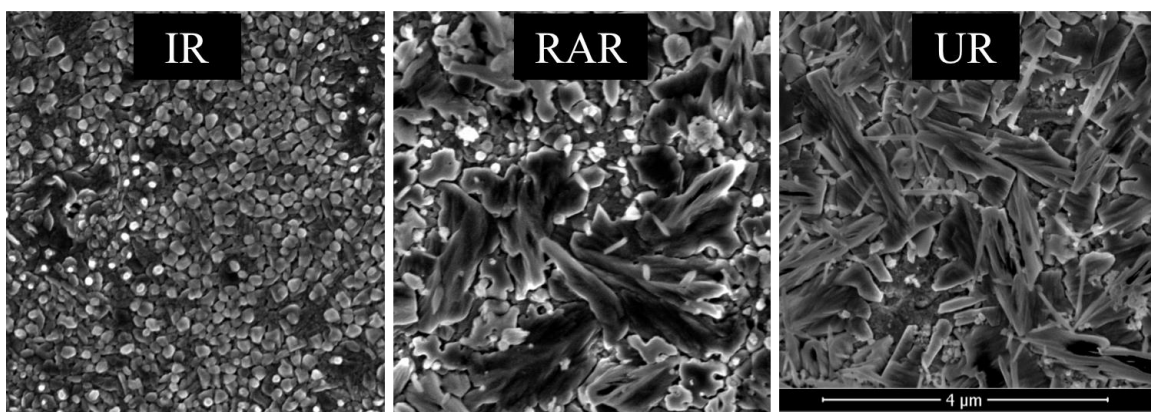


Figure B7: High magnification SEM image of the three regions observed on sample APMT-NWC-24IR.

Oxide Phase Analysis with Raman Spectroscopy

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated samples. Spectra were recorded using a Renishaw inVia microscope with a RenCam CCD detector. The spectra were collected using a 633 nm wavelength red laser, at a typical laser power of 50 mW, during a total of 500 s of acquisition time.

All three regions (IR, RAR and UR) on the irradiated samples were measured using Raman spectroscopy. Three individual spectra were also taken in each region for data consistency check.

For **sample APMT-HW-24IR**, the Raman peaks related to α -Fe₂O₃ were observed in the IR region as shown in Figure B8. This observation indicated that when the sample surface was in contact with the radiolysis products of water, the corrosion potential was high enough for the formation of hematite. The cause of hematite formation could be the presence of short- and long-lived radical species and hydrogen peroxide. The short-lived radiolysis products (e.g. OH[•] radicals) cannot escape the IR region. However, H₂O₂ can be carried away from the IR region into the RAR region by convection flow of the heated water. However, outer oxide precipitation was limited in the RAR region, indicated that precipitation of outer oxide was rather difficult due to lack of Fe/Cr ions in the nearby water phase.

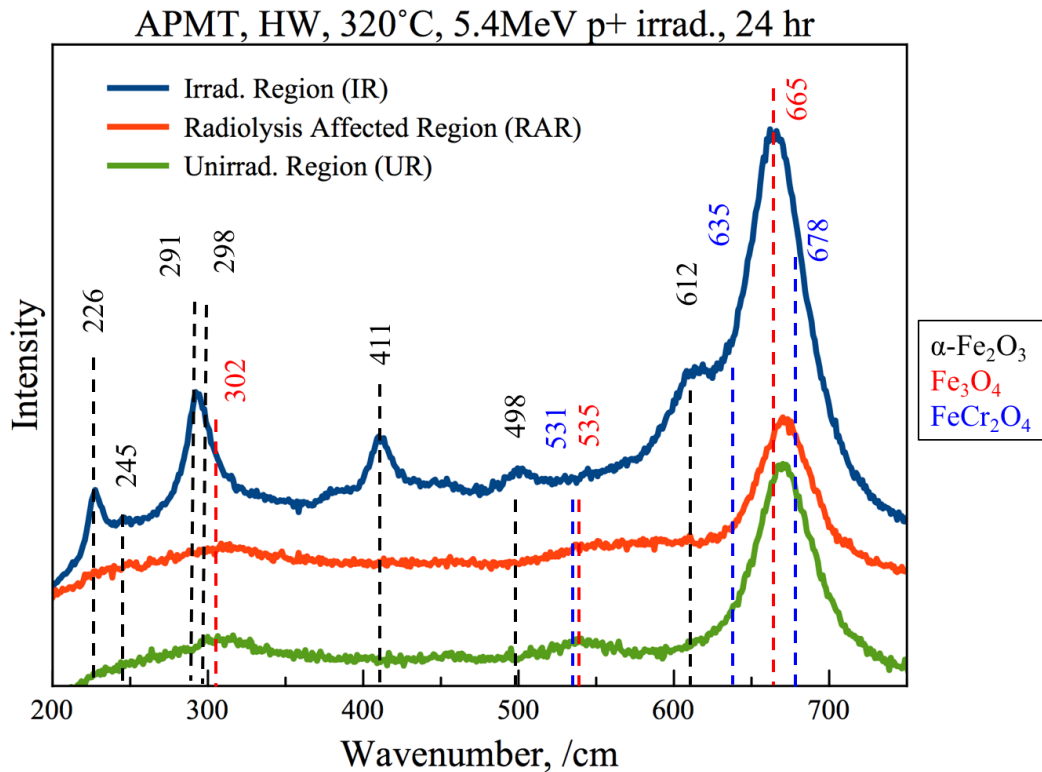


Figure B8: Raman spectra collected from IR, RAR and UR region on the 24 h irradiated APMT sample in primary water condition.

The UR regions showed a typical Raman spectrum of magnetite (Fe_3O_4). However, the 665 cm^{-1} peak which was related to magnetite was observed in all regions, indicating that the inner layer may also consist of magnetite phase or a spinel phase which has a chemical composition of iron chromite e.g. $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$. The spinel phase will cause a slight shift in the Raman peak positions, from 665 to a lower wavenumber, e.g. the 635 cm^{-1} for FeCr_2O_4 . Further compositional analysis of the inner oxide layer is required to confirm the identity of the inner oxide. In the IR region, the oxide consisted of a spinel $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$ inner layer and a Fe_2O_3 outer layer.

For **APMT-NWC-24IR**, the Raman peaks related to Fe_2O_3 are present in all the regions as shown in Figure B9. Also, some of the peaks cannot be fitted by a single peak from the $\alpha\text{-Fe}_2\text{O}_3$, spinel or Fe_3O_4 spectra, which suggested multiple oxide phases may be present in the spectra. However, in NWC water chemistry, $\alpha\text{-Fe}_2\text{O}_3$ is still the dominant oxide specie, with possibility that Cr maybe substituting Fe in $\alpha\text{-Fe}_2\text{O}_3$. Yogi and Varshney had demonstrated that as hematite was doped with increase amount of Cr, characteristic Raman peaks of hematite can shift to a higher wavenumber, or even disappear [1]. This Cr doping mechanism can be a valid explanation for the slight peak shift from the typical hematite value to a higher wavenumber in the UR and RAR case.

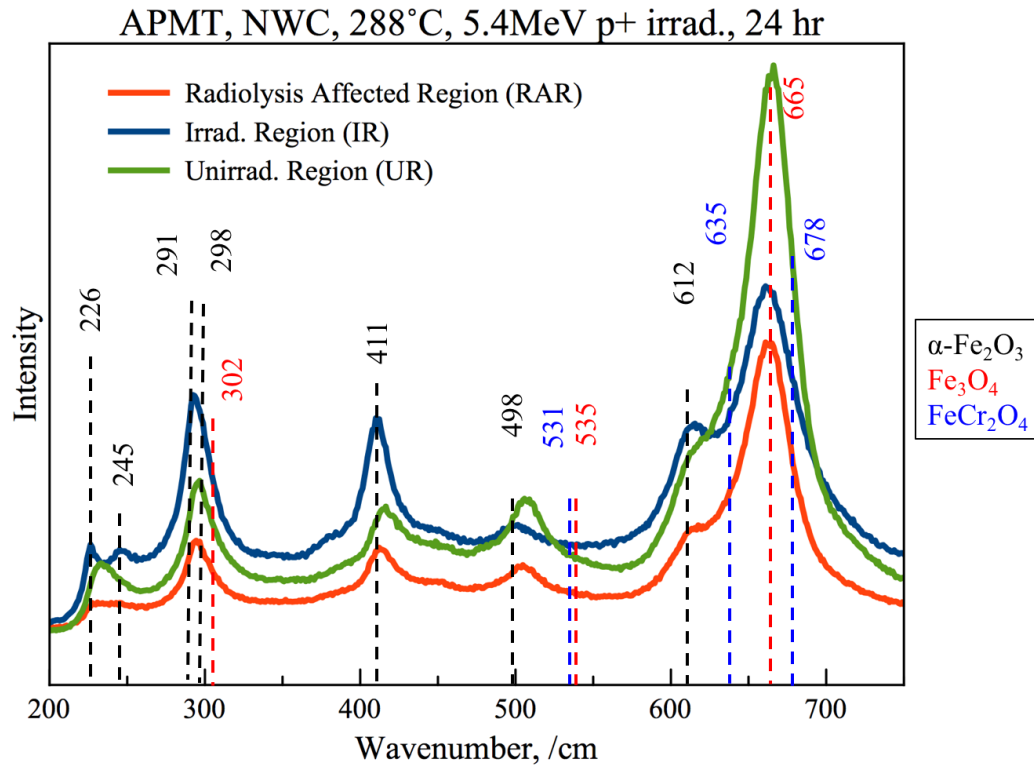


Figure B9: Raman spectra collected from irradiated region, unirradiated regions and the radiolysis affected region on the 24 h irradiated APMT sample in NWC water condition.

Oxide Morphology with TEM

TEM lamellas from IR and UR regions were prepared using FIB, and a JEOL 2100F TEM/STEM was used for TEM analysis.

The high angle annular dark field (HAADF) images were collected for oxide thickness analysis. Under such imaging conditions, the oxide would have a dark contrast compared to a light-colored metal substrate or platinum protective coating (darker gray layer on top of the oxide layer).

On sample **APMT-HW-24IR**, as shown in Figure B10, the inner oxide layer appeared to be very thin, with an appearance of a dark line at the metal/oxide interface. A non-complete outer oxide coverage was observed in the IR region. Furthermore, some of the original oxidized metal surface (covered to inner oxide) was reserved in some part of the IR region. In the UR region, only inner oxide coverage was observed. Although original metal surface was oxidized, the flat shape of the interface can still be observed in the UR and RAR regions. Average total oxide thickness for different regions was listed in Table B2.

For **APMT-NWC-24IR**, the HAADF STEM images shown in Figure B11, had indicated that the oxide layers were much different compared with the hydrogenated (and higher temperature) condition. The interface of inner and outer oxide layer became indistinguishable under NWC condition, indicating possible inner oxide dissolution had occurred. Large undulation of the metal/oxide interface was also observed. This was caused by heterogeneous inner oxide growth rate. The complete outer oxide coverage was observed in IR and RAR case, while only partial coverage was observed in UR case.

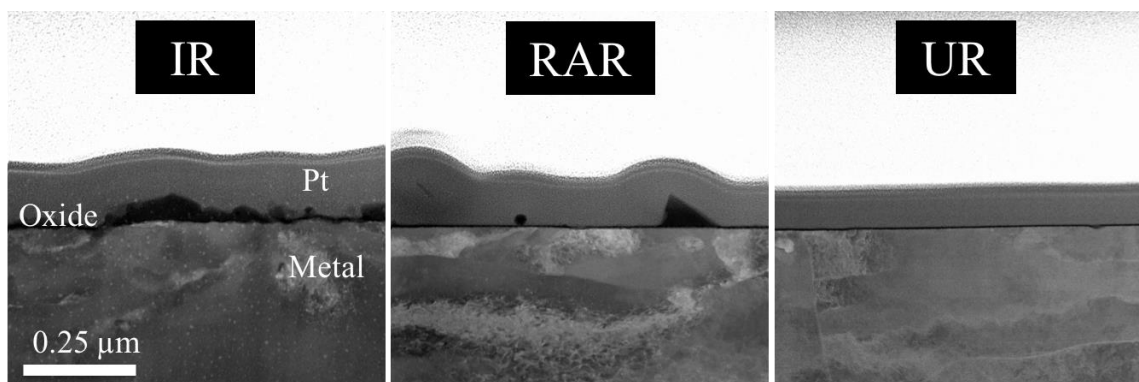


Figure B10: High Angle Annular Dark Field STEM (HAADF-STEM) images of the FIB lamellas taken from the irradiated sample APMT-HW-24IR.

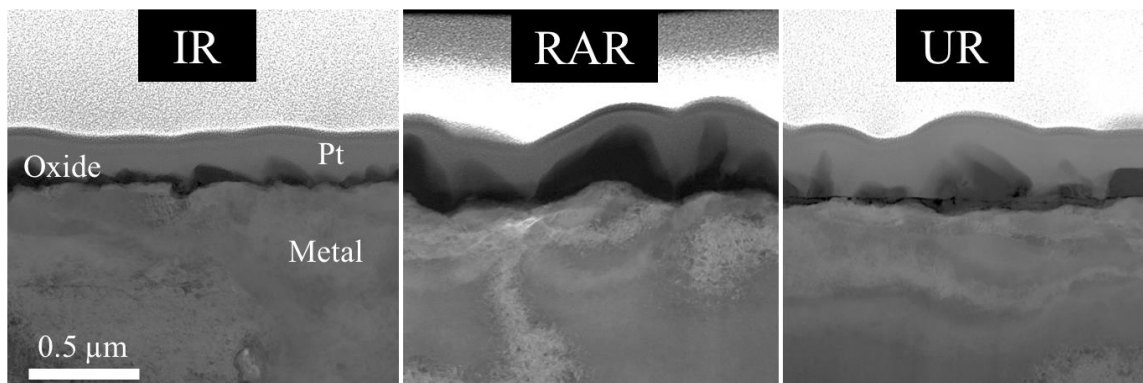


Figure B11: HAADF-STEM images of the FIB lamellas taken from the irradiated sample APMT-NWC-24IR.

Table B2: Oxide thickness observed on samples irradiated in both HW and NWC conditions.

Sample	Region	Total Oxide (nm)
APMT-HW-24IR	IR	62 ± 7
	RAR	34 ± 14
	UR	6 ± 2
APMT-NWC-24IR	IR	95 ± 9
	RAR	217 ± 23
	UR	199 ± 23

Oxide Composition Analysis with EDS

Energy Dispersive X-ray Spectroscopy (EDS) was used to determine the oxide compositions. The EDS spectra were collected on JEOL 2100F STEM with EDAX detector and TEAM data acquisition software. The Cr-*l* and O-*k* peaks were overlapping at ~ 0.5 keV, which resulted the overestimate of the oxygen concentration in the metal portion. This artifact was corrected by removing the Cr-*l* contribution from the EDS spectra, dropping the oxygen concentration to the level that was normally found in the bulk metal. This correction was only done to the metal region, but not applied in the oxide region due to less contribution from the Cr-*l* peak in the oxide where O-*k* peak is significantly larger.

For **sample APMT-HW-24IR**, EDS results of IR and UR region are shown in Figure B12 and B13. The IR region oxide composition was consistent with Fe_2O_3 , which was 40 at% Fe and 60 at% O for the outer oxide, the thin inner oxide was observed but the composition of the inner layer was not determined due to the limited resolution of EDS for the thin oxide. EDS result from the UR region had confirmed that the inner oxide was a Cr-deficient FeCr_2O_4 -spinel phase and outer precipitates were Fe_3O_4 of 43 at% Fe and 57 at% O.

The inner oxide of UR region consists of a spinel phase; its composition slightly deviates from FeCr_2O_4 . Some aluminum was also present in this inner layer, however, its oxidation state and which oxide constituent it belongs to was unknown.

The RAR region has very little coverage of the outer oxide. EDS line scans in Figure B14, indicated that the inner oxide was Cr-deficient FeCr_2O_4 -spinel with large aluminum content.

Irradiation has a direct impact on the thickness of the outer oxide layer, possibly due to enhanced Fe/Cr dissolution from the oxide. Without irradiation, a generally thin spinel oxide was observed in UR and RAR with very little outer oxide coverage.

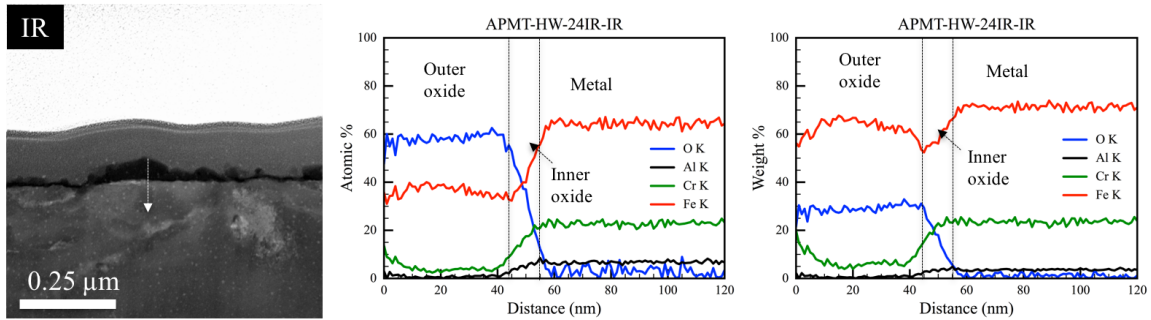


Figure B12: EDS line scans of oxide regions (IR) formed on sample APMT-HW-24IR.

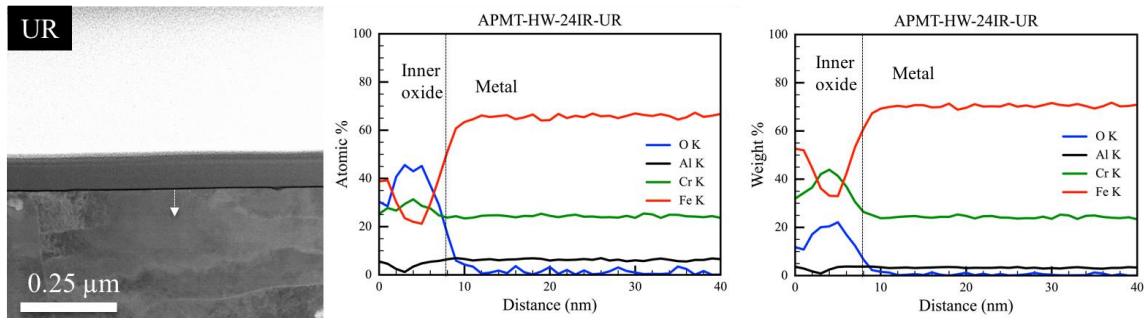


Figure B13: EDS line scans of oxide regions (UR) formed on sample APMT-HW-24IR.

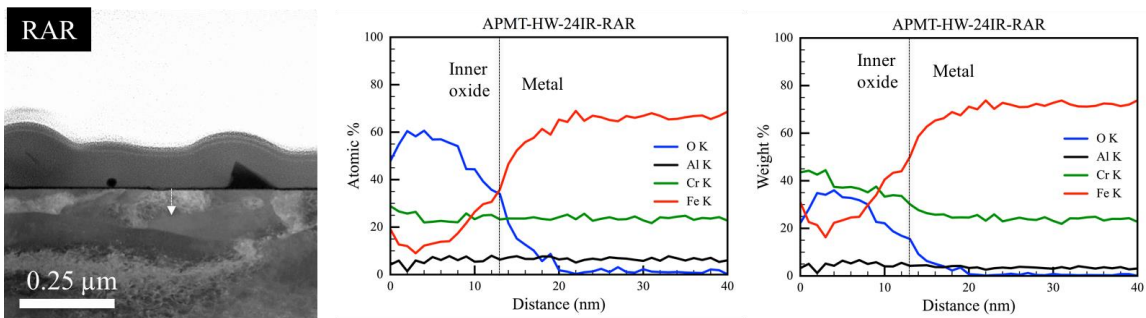


Figure B14: EDS line scans of oxide regions (RAR) formed on sample APMT-HW-24IR.

For the NWC condition of **sample APMT-NWC-24IR**, EDS results of IR and UR region are shown in Figure B15 and B16. In the IR regions, the outer oxide particle showed a hematite composition with about 5% Cr concentration; the inner layer was very thin and its composition changed over thickness which could be an artifact of the EDS technique

due to the finite electron beam size. In the UR region, the outer oxide consisted of a Cr doped hematite with higher amount of Cr concentration, $\sim 10\%$; no aluminum was found in the outer oxide. In the RAR region (Fig. B17), Cr doped hematite phase was observed which is consistent with the Raman results for this region.

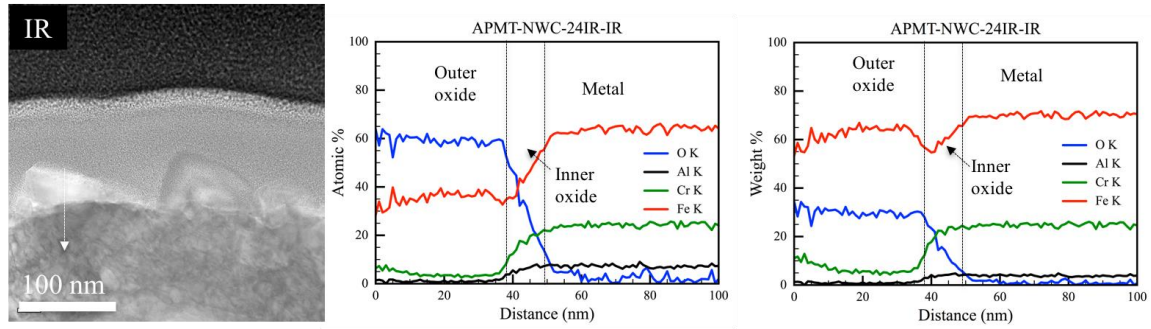


Figure B15: EDS line scans of oxide regions (IR) formed on sample APMT-NWC-24IR.

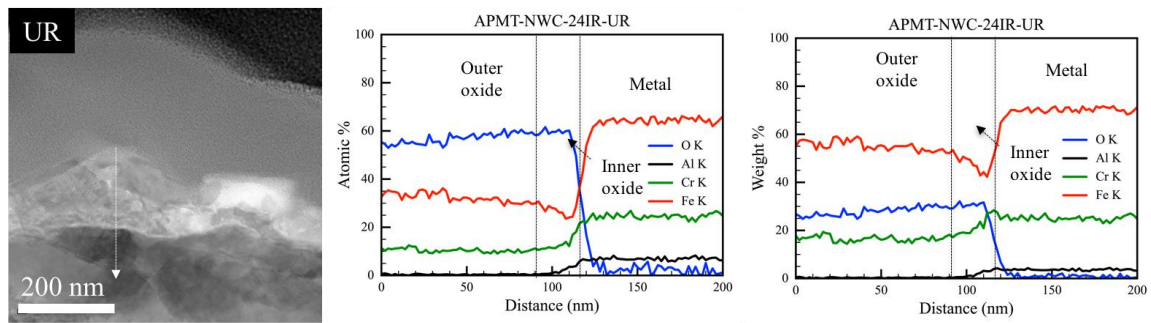


Figure B16: EDS line scans of oxide regions (UR) formed on sample APMT-NWC-24IR.

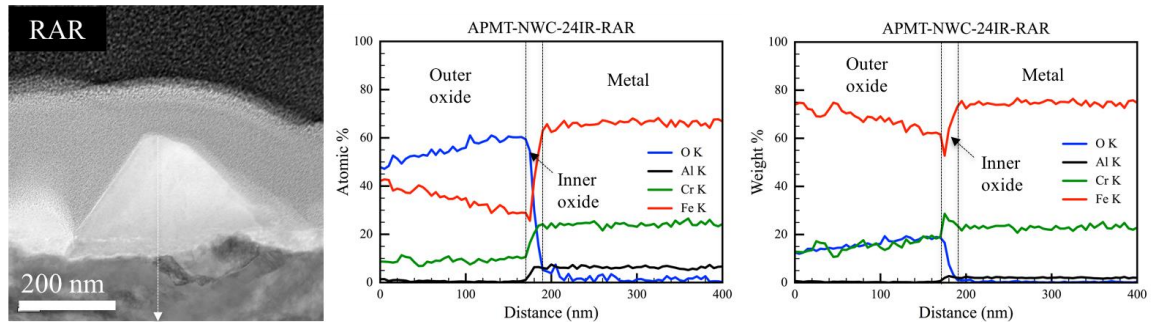


Figure B17: EDS line scans of oxide regions (RAR) formed on sample APMT-NWC-24IR.

Proton Post Irradiation Characterization Summary

The oxide species found on irradiated samples under different conditions were confirmed using Raman and the findings were summarized in Table B3.

Table B3: Summary of the oxide species found on APMT in HW and NWC conditions under proton irradiation.

Samples	Regions	Outer Oxide/Inner Oxide	
		NWC 288°C, 2 ppm O ₂	HW 320°C, 3 ppm H ₂
APMT	IR	$\alpha\text{-Fe}_{2-x}\text{Cr}_x\text{O}_3$ $/\text{Fe}(\text{Cr, Fe, Al})_2\text{O}_4$	$\alpha\text{-Fe}_{2-x}\text{Cr}_x\text{O}_3$ $/\text{Fe}(\text{Cr, Fe, Al})_2\text{O}_4$
	RAR		$\text{Fe}(\text{Cr, Fe, Al})_2\text{O}_4$
	UR		

Reference:

[1] A. Yogi and D. Varshney, “Magnetic and structural properties of pure and Cr-doped hematite: $\alpha\text{-Fe}_{2-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 1$)”, J. Adv. Ceramics, Vol. 2(4), 2013, pp. 360-369.

C. Electron Irradiation Experiments (U. of Notre Dame)

C1. Summary

Electron irradiations of APMT alloy were completed in PWR conditions – 3 ppm hydrogenated water (HW) at 320°C, and in BWR conditions – argon saturated water (ArW) at 288°C. A 3.0 MeV electron beam was used for these irradiations. Given the ~300 microns sample thickness, energy of electrons as they cross the oxide layer and enter the water is ca. 1.5 MeV, so that they are still relativistic, and have LET of 1.9×10^6 eV/cm/e-. Dose rate to the water at the surface is ca. 170 kGy/s. Post-irradiation characterization of various regions of the irradiated samples was completed by means of SEM, TEM imaging and EDX line scans and Raman spectroscopy.

C2. Experiments

Two APMT samples were irradiated under the experimental conditions listed in Table C1. Water loop data for the 24 hr and 22 hr e-beam irradiated APMT HW and ArW experiments are shown in Figures C1 and C2, respectively.

In the APMT HW experiment, note that the outlet conductivity varied between 0.15 to 0.18 $\mu\text{S}/\text{cm}$ during the course of the experiment compared to the almost unchanged inlet conductivity at 0.09 $\mu\text{S}/\text{cm}$. It can be seen from the plot that the outlet conductivity has dropped to very low value on multiple occasions. This occurred due to high-vacuum interlock interruptions and shutdown of the accelerator. These were quickly resolved, and the experiment continued.

In the APMT ArW experiment (shown in Figure C2), the outlet conductivity dropped from 0.50 to 0.15 $\mu\text{S}/\text{cm}$ during the course of the experiment compared to the unchanged inlet conductivity at 0.07 $\mu\text{S}/\text{cm}$. This indicates that as the sample surface developed a layer of oxide, the amount of dissolved metal that goes into solution decreases. However, there was a decrease of the outlet conductivity a couple of times during the course of the experiment. These events were due to beam drift and the subsequent necessity to readjust the beam to achieve a maximum beam current, or random instances of too-high vacuum pressure, which could have been due to micro leaks in the sample or the sample weld. After about 22 hours of irradiation the accelerator shut down and we were not able to recover the beam (apparently cathode failure), therefore the experiment was terminated.

Table C1: List of irradiation experiments completed for APMT.

Sample ID	e-energy (MeV)	Temp (°C)	Water chemistry	Duration (hr)
APMT-HW-24IR	3.0	320	3 ppm H ₂	24
APMT-ArW-22IR	3.0	288	Argon-sat	22

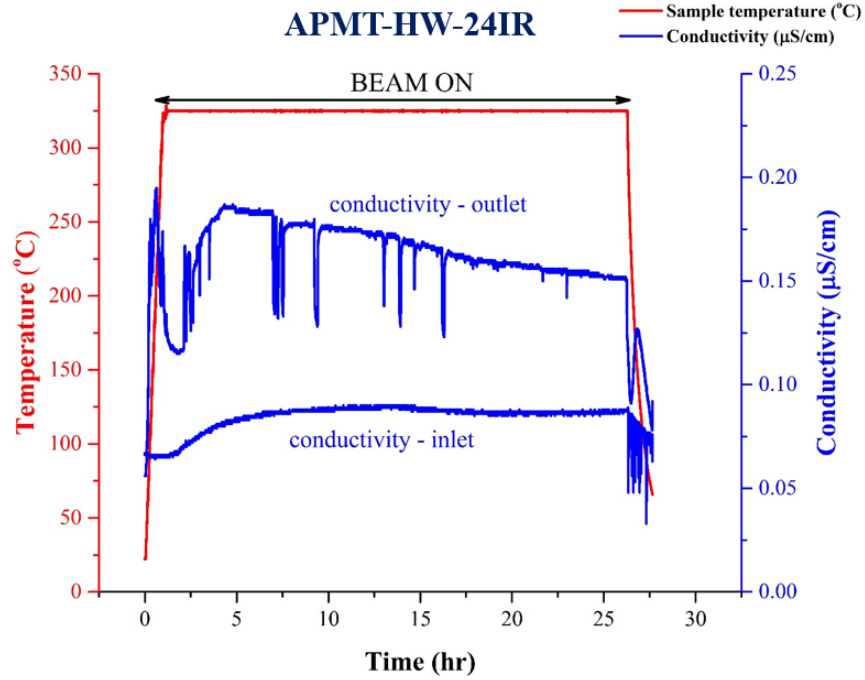


Figure C1: Water loop data of 24 hr electron irradiation of APMT HW in 320°C 3 ppm H₂ water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

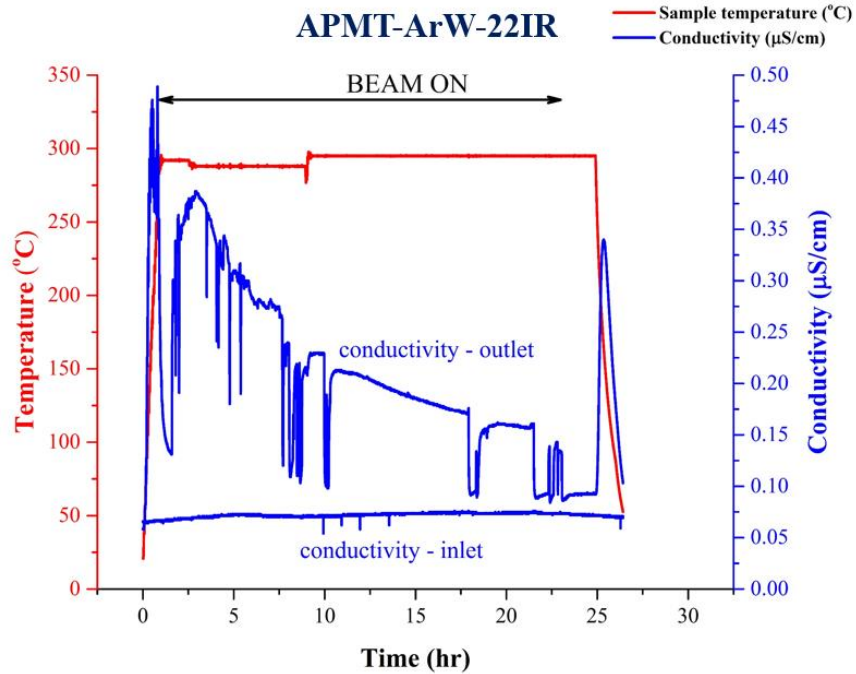


Figure C2: Water loop data of 22 hr electron irradiation of APMT NWC in 288°C Argon saturated water; Sample temperature and pressure of water during irradiation (left axis), conductivity of water (right axis).

C3. Post Irradiation Characterization of APMT samples

Optical Microscopy

Both APMT steel samples (e-beam irradiated) were analyzed via microscopy. APMT HW sample was fairly clean and there was slight discoloration after 24 hr of e-beam exposure only in the central irradiated region. The ArW case showed discoloration throughout the sample's surface after 22 hr of e-beam irradiation.

Under the optical microscopy, the irradiated region and the water flow direction can be identified, shown in Figure C3 (left) for the APMT HW sample and Figure C3 (right) for the APMT ArW sample. Both samples' irradiated region was discolored after 24 hr of e-beam exposure, observed as a darker circular region in the HW case and a maroon circular region in the ArW case.

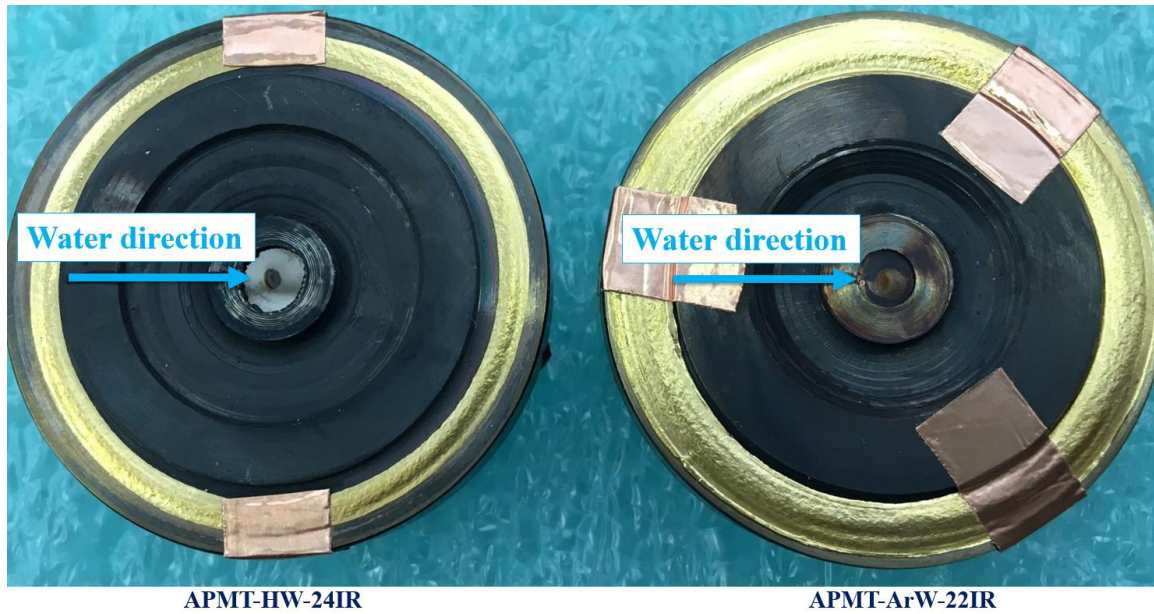


Figure C3: Post-irradiation optical images of electron-beam irradiated APMT sample in HW 24-hour (left) and ArW 22-hour (right). Blue arrow represents the water flow direction during irradiation.

Surface Oxide Morphology Analysis

Under the SEM microscopy, three distinctive regions can be identified on the sample surface, Irradiated Region (IR), Radiolysis Affected Region (RAR) and Unirradiated Region (UR), shown in Figure C4 (left) for the APMT HW sample and Figure C4 (right) for the APMT ArW sample.

The oxide morphologies in the UR and RAR regions in both samples are very similar. Outer surface particles in the UR region are more faceted compared with the one in the RAR region. In both regions, a regular shaped outer oxide was observed with the particle size of $\sim 0.5\ \mu\text{m}$ to $1\ \mu\text{m}$.

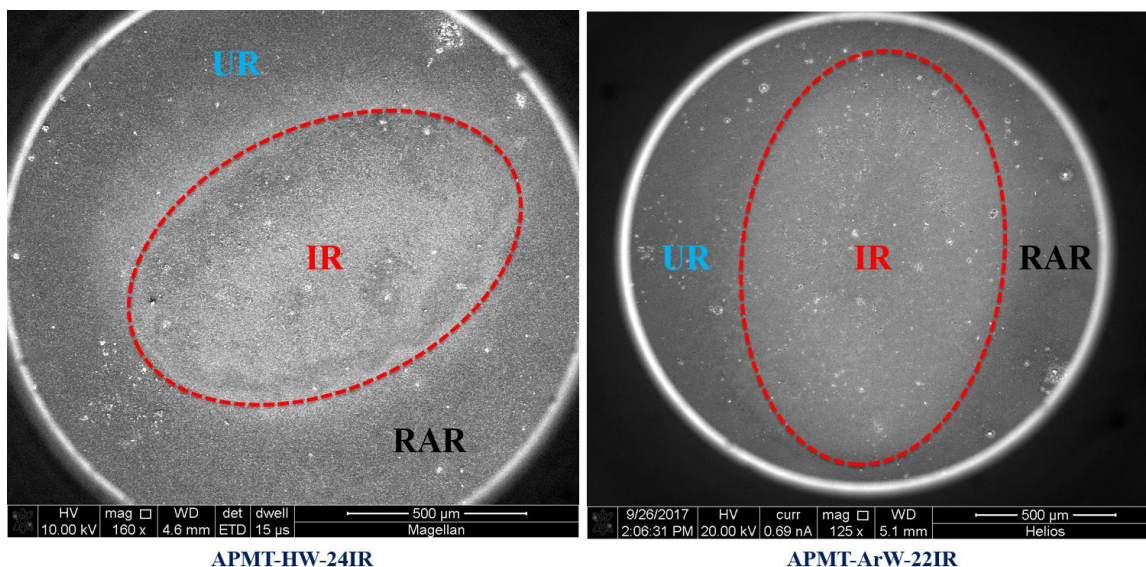


Figure C4: Post-Irradiation SEM images of electron-beam irradiated APMT sample in HW 24-hour (left) and ArW 22-hour (right). Representation of unirradiated region (UR), irradiated region (IR) and radiolysis affected region (RAR).

The high magnification SEM images in Figure C5 and Figure C6 represent the oxide particles of the three different regions (UR, IR and RAR) in the APMT Hydrogen - saturated sample and APMT Argon-saturated sample, respectively.

There are similarities in the population density of the particles in the **APMT-HW-24IR** case when comparing the regions of the different irradiating conditions; the RAR region and the UR region have very similar particles and not many crystals to form an outer oxide layer. The IR region features the most densely populated particles that form an outer oxide layer which most likely is composed of Fe_2O_3 . In the IR region, oxide particles consisted of two types, one type is less faceted crystals with a size of $\sim 0.5\ \mu\text{m}$ to $1\ \mu\text{m}$, and the other type is much smaller crystals with size of about $200\ \text{nm}$ as indicated in Figure C5. Outer oxide particle density was significantly higher in the IR region compared with RAR and UR region.

In comparison to HW, the oxide particles of the RAR and UR regions in the **APMT-ArW-22IR** case create an outer oxide layer and are densely populated. Both regions contain crystal with a size of about $0.5\ \mu\text{m}$. However, the IR region of the ArW sample contains smaller crystals with size less than $100\ \text{nm}$ and another type of crystals that are larger and grouped in clusters throughout the surface.

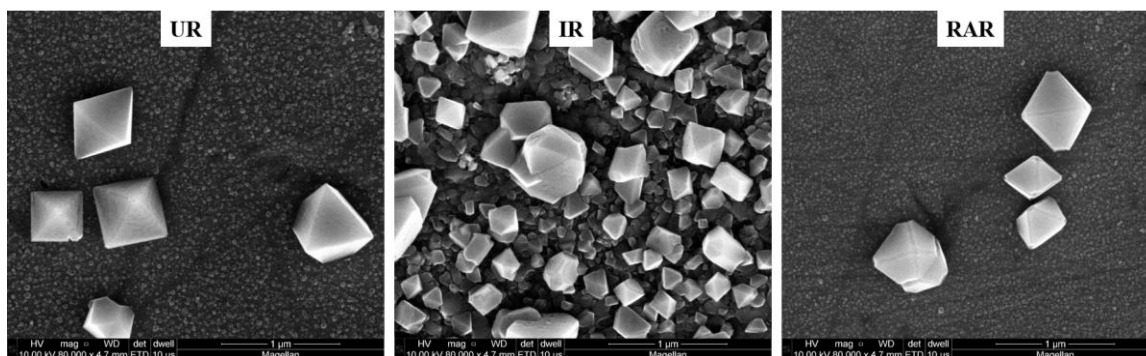


Figure C5: Post-Irradiation SEM images of 24-hour electron-beam APMT sample in HW. Representation of the three different regions, UR, IR and RAR.

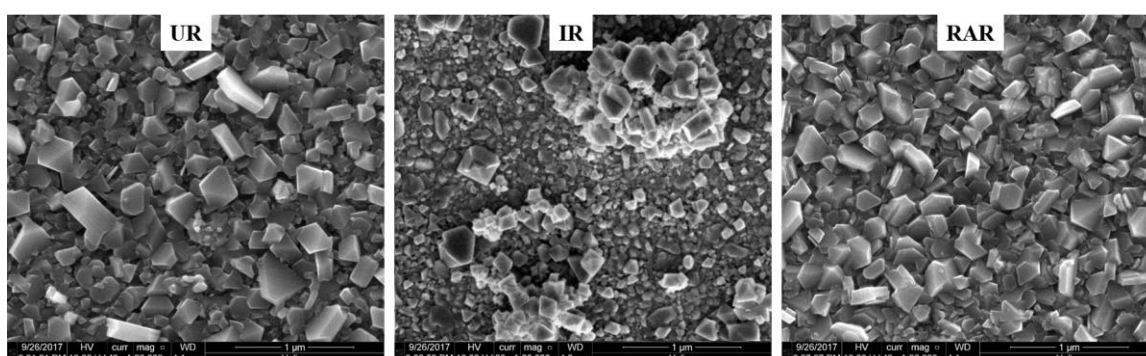


Figure C6: Post-Irradiation SEM images of 22-hour electron-beam APMT sample in ArW. Representation of the three different regions, UR, IR and RAR.

Oxide Thickness and Morphology with TEM

Focused ion beam (FIB) lift-outs from three distinctive regions (IR, RAR and UR) on the irradiated samples were prepared for transmission electron microscope (TEM) analysis of the oxide layer thickness and morphology. The FIB lift-outs were prepared using the FEI-HELIOS dual beam FIB and the samples were further investigated via high magnification TEM images and EDX line scans, performed with the Titan TEM (FEI Titan 80/30 TEM) that is equipped with an energy-dispersive X-ray system by which line profiles can be measured. Both instruments are located at the Notre Dame Integrated Imaging Facility.

The high angle annular dark field (HAADF) images were collected for oxide thickness analysis. Under such imaging conditions, the oxide would have a dark contrast compared to a light-colored metal substrate or platinum protective coating (darker gray layer on top of the oxide layer).

TEM images of the different regions (UR, IR and RAR) are presented in Figure C7 for **APMT-HW-24IR** sample. As it can be seen, the UR and RAR regions of APMT HW sample have similar features. The oxide thickness in both regions mostly comes from an inner oxide layer as the regions do not feature many precipitation particles. The inner oxide

layer appears to be very thin as the images suggest, very thin dark line at the oxide/metal interface. On the other hand, the IR region's oxide thickness mainly originates from the precipitation crystals. The dark inner oxide layer is not visible in the image as it may not be existent.

For the **APMT-ArW-22IR** sample, TEM images of the different regions (UR, IR and RAR) are presented in Figure C8. As it can be seen, all regions of APMT ArW sample have similar features among each other and are much different when compared to the APMT HW case. The oxide thickness in all regions mainly originates from the precipitation crystals. There is no boundary that is separating the inner from outer oxide layer. Average thickness measurements of both samples are presented in Table C2.

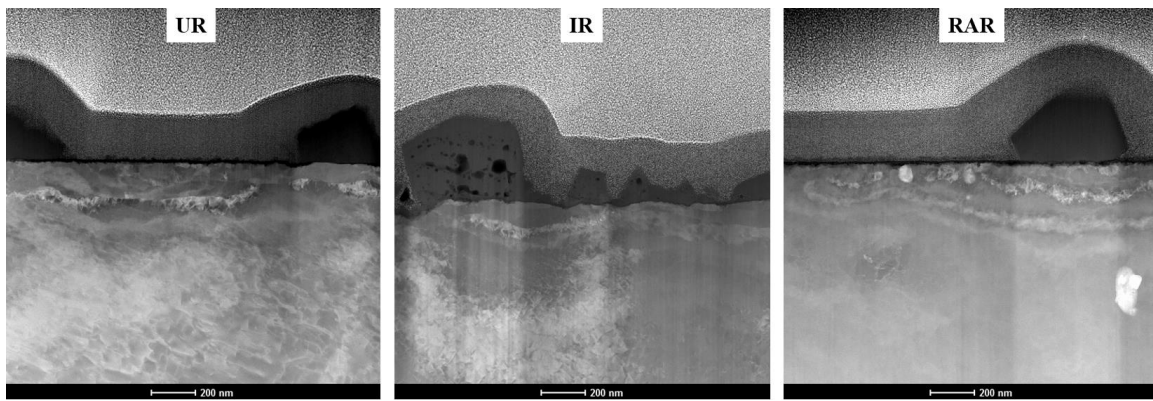


Figure C7: Post-Irradiation TEM images of 24-hour electron-beam APMT sample in Hydrogen-saturated water. Representation of the three different regions (UR, IR and RAR).

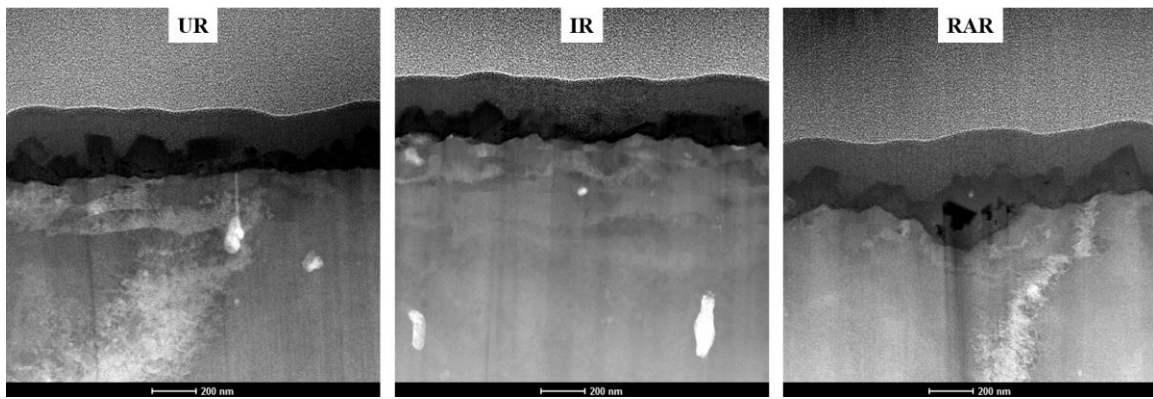


Figure C8: Post-Irradiation TEM images of 22-hour electron-beam APMT sample in Argon-saturated water. Representation of the three different regions (UR, IR and RAR).

Table C2: Oxide thickness observed on samples irradiated in both HW and ArW conditions.

Sample	Region	Total Oxide (nm)
APMT-HW-24IR	IR	170 ± 112
	RAR	67 ± 102
	UR	35 ± 56
APMT-ArW-22IR	IR	142 ± 33
	RAR	197 ± 76
	UR	108 ± 42

Oxide Composition Analysis with EDS

Energy Dispersive X-ray Spectroscopy (EDX) line scans were performed to reveal elemental distribution information about the APMT sample irradiated in HW conditions for 24 hours and the APMT sample irradiated in ArW conditions for 22 hours. The EDX spectra were collected on Titan TEM and TIA acquisition software. Similar to the University of Michigan EDX spectra, the chromium and oxygen peaks were overlapping at ~0.5 keV, which resulted in larger "oxygen" concentration in the metal region of every sample. This artifact was corrected by removing the Cr-L contribution from the EDX spectra and normalizing the oxygen concentration to the level that was typically found in the bulk metal. This correction was only done to the metal region, but not applied in the oxide region due to less contribution from the Cr-L peak in the oxide where O-K peak is significantly larger. Multiple EDX line scans were completed on each TEM sample and are shown in the figures below.

The TEM samples included in the **APMT-HW-24IR** line scans cover the precipitation oxide layer, the inner oxide layer and some of the metal region. The UR and RAR regions of this case feature a very thin inner oxide layer that is represented by some of the EDX line scans. The metal region of all HW scans contains about 70% iron, 20% chromium and 5-10% aluminum as those are very close to the percentages found in the original composition of the bulk metal.

Figure C9 shows two plots representing the line scans of the unirradiated region of the **APMT-HW-24IR** sample corresponding to the arrows in the images above them. The line scan shown in the left figure only covers the inner oxide and the metal regions. The oxide layer in this scan is rich in oxygen and chromium (both about 30-40% atomic concentration and about 20% iron, suggesting a chromium rich oxide. The line scan shown in the right figure covers part of a precipitation crystal and the metal region. The line scan suggests 60% atomic concentration of iron and about 40% atomic concentration of oxygen without any chromium or aluminum in the crystal.

Figure C10 shows two plots representing the line scans of the irradiated region of the **APMT-HW-24IR** sample corresponding to the arrows in the images above them. The oxide layer in both scans is rich in oxygen and iron, about 60% atomic concentration of oxygen and about 40% atomic concentration of iron. This suggests presence of hematite in the precipitation layer.

Figure C11 shows two plots representing the line scans of the radiolysis affected region of the **APMT-HW-24IR** sample corresponding to the arrows in the images above them. Similar to the IR region, the oxide layer in the scan that contains precipitate (right figure) is rich in oxygen and iron, about 60% atomic concentration of oxygen and about 40% atomic concentration of iron, which suggests presence of hematite in the precipitation layer. The scan covering the inner oxide alone (left figure) contains a bit more oxygen (~65% atomic concentration) and less iron (~35% atomic concentration) than the precipitation layer in the figure to the right.

EDX of APMT-HW-24IR e-beam - UR

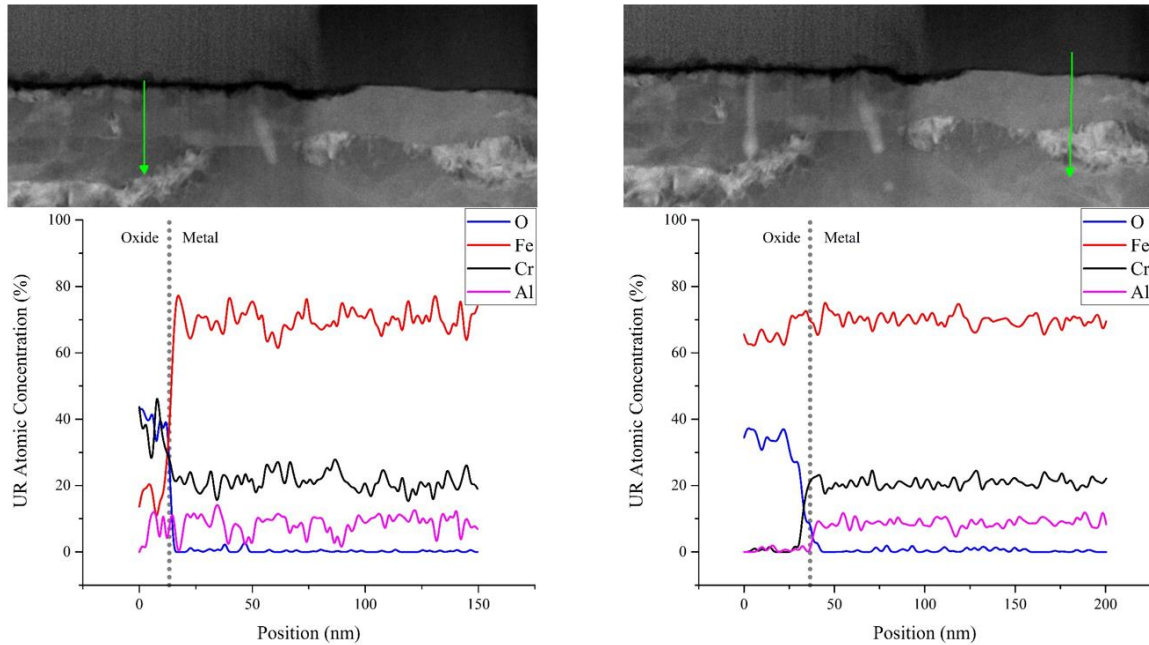


Figure C9: Bottom: STEM EDX line scans results for UR section of the 24-hour electron-beam irradiated APMT sample in Hydrogen-saturated water. Representation of oxide and metal regions of scan showing atomic concentration vs. position . Top: HRTEM images of UR region (the thin arrows show the EDX line scan direction).

EDX of APMT-HW-24IR e-beam - IR

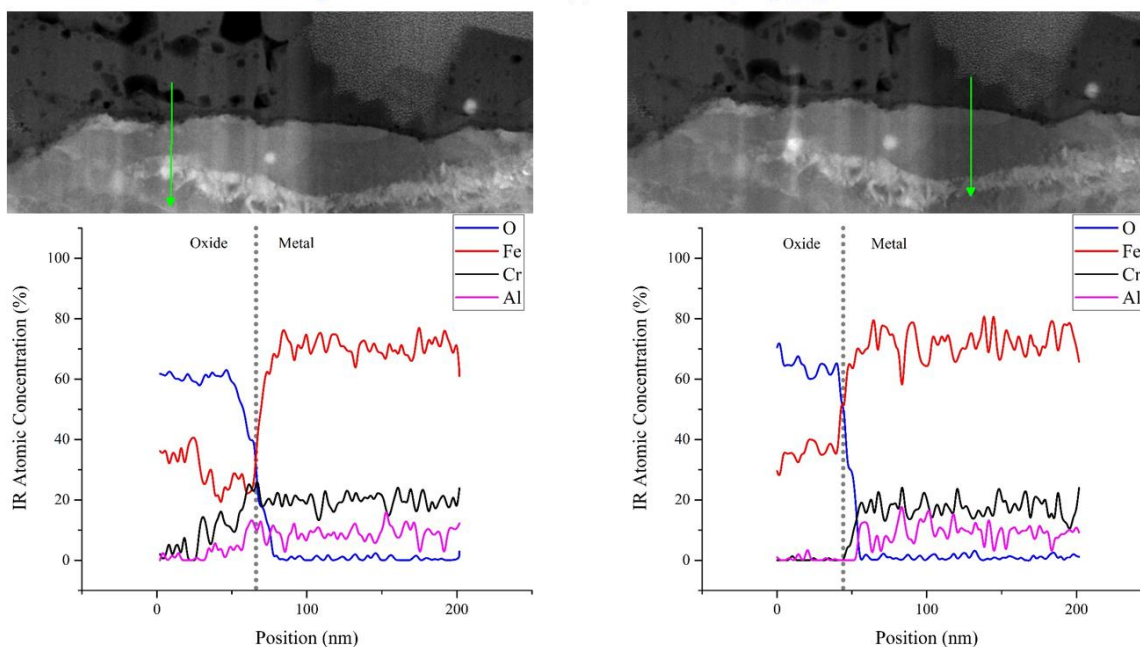


Figure C10: Bottom: STEM EDX line scan results for the 24-hour electron-beam irradiated APMT sample in Hydrogen-saturated water. IR region showing atomic concentration vs. position, in the oxide and metal region of the scan. Top: HRTEM images of IR region (the thin arrows show the EDX line scan direction).

EDX of APMT-HW-24IR e-beam - RAR

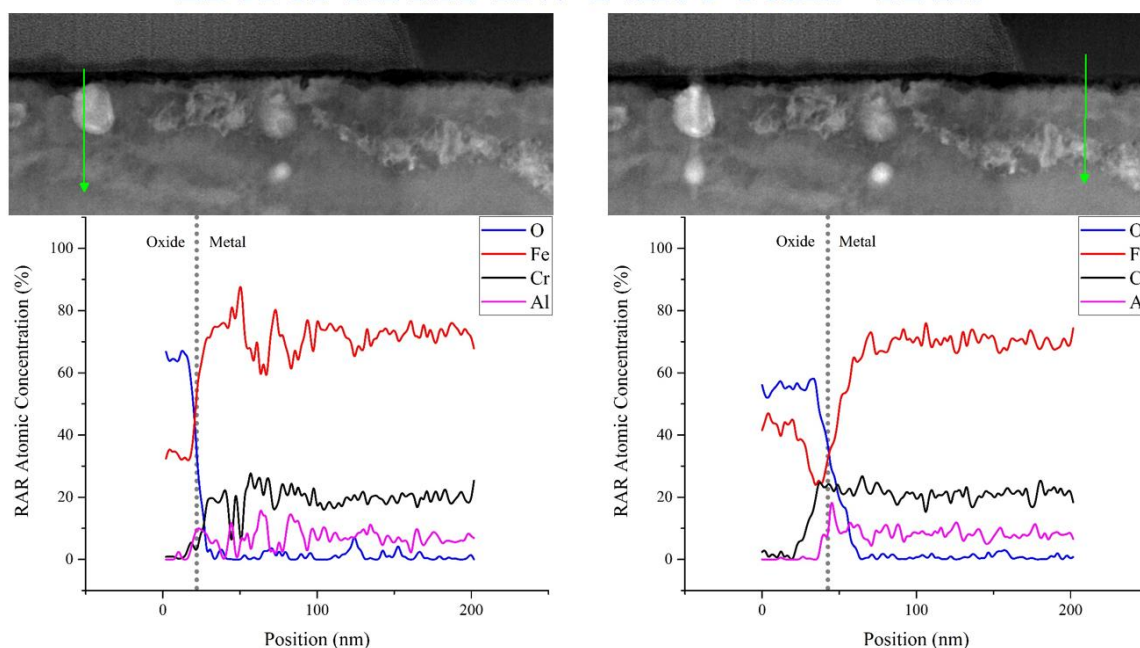


Figure C11: Bottom: STEM EDX line scans results for the 24-hour electron-beam irradiated APMT sample in Hydrogen-saturated water. RAR section showing atomic concentration vs. position, crossing the oxide and metal region.. Top: HRTEM images of RAR region (the thin arrows show the EDX line scan direction).

The TEM samples included in the **APMT-ArW-22IR** line scans cover the precipitation oxide layer, the inner oxide layer and some of the metal region. The boundary between the precipitation oxide layer and an inner oxide layer in all ArW scans is not easily distinguished. The metal region of all ArW line scans contains about 70% iron, 20% chromium and 5-10% aluminum as those are very close to the percentages found in the original composition of the bulk metal.

Figure C12 shows two plots representing the line scans of the unirradiated region of the **APMT-ArW-22IR** sample corresponding to the arrows in the images above them and the scan direction. The oxide layer in both scans is rich in oxygen and iron (both about 40-50% atomic concentration).

Figure C13 shows two plots representing the line scans of the irradiated region of the **APMT-ArW-22IR** sample corresponding to the arrows in the images above them. The oxide layer in both scans is rich in oxygen and iron, about 70% atomic concentration of oxygen and about 30% atomic concentration of iron.

Figure C14 shows two plots representing the line scans of the radiolysis affected region of the **APMT-ArW-22IR** sample corresponding to the arrows in the images above them. The oxide layer in both scans consists of precipitation layer that is rich in oxygen and iron, about 75% atomic concentration of oxygen and about 25% atomic concentration of iron.

EDX of APMT-ArW-22IR e-beam - UR

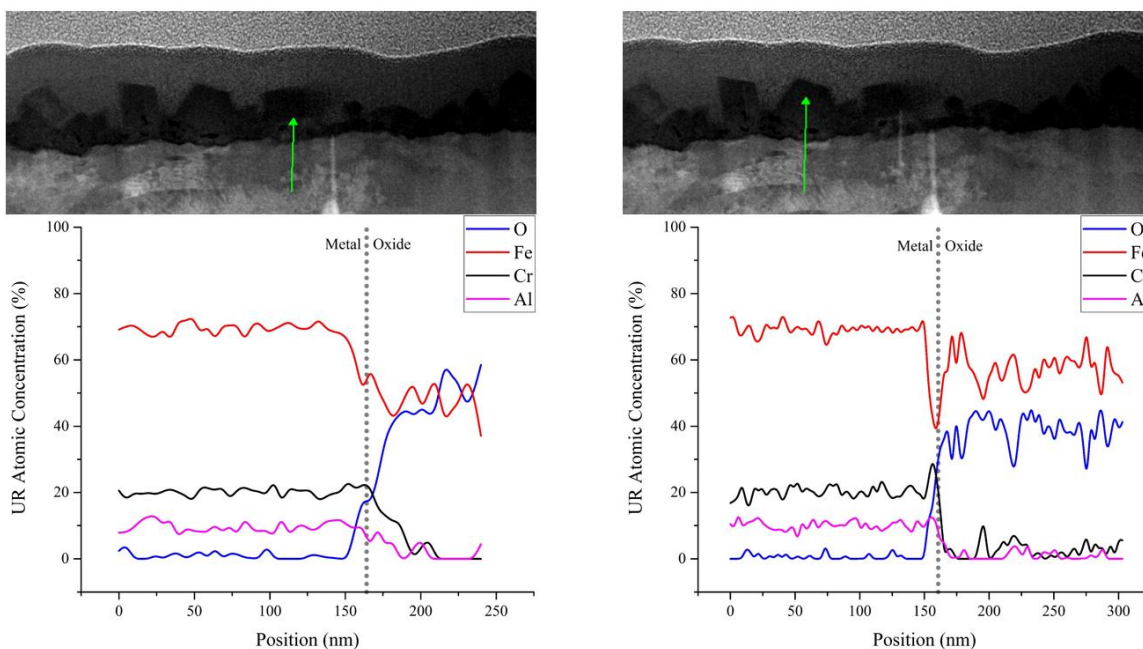


Figure C12: Bottom: STEM EDX line scans results for the 22-hour electron-beam irradiated APMT sample in Argon-saturated water. UR section, showing atomic concentration vs. position, in the oxide and metal regions of the scan. Top: HRTEM images of UR region (the thin arrows show the EDX line scan direction).

EDX of APMT-ArW-22IR e-beam - IR

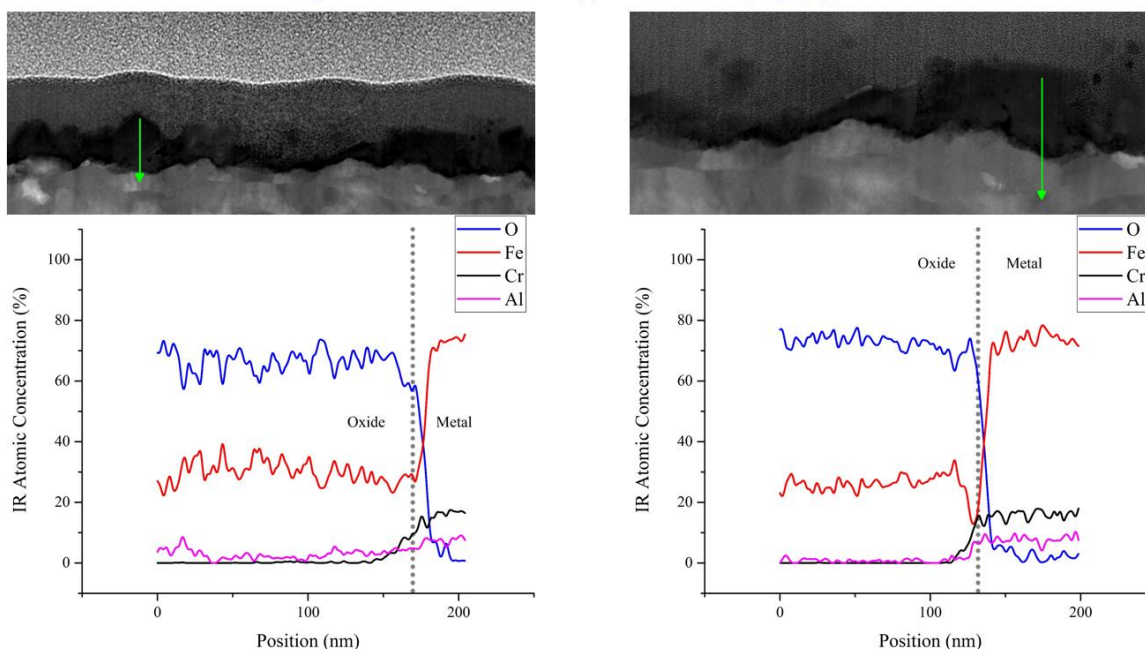


Figure C13: Bottom: STEM EDX line scans result for the 22-hour electron-beam irradiated APMT sample in Argon-saturated water. IR section, showing atomic concentration vs. position, for the oxide and metal region of the scan. Top: HRTEM images of IR region (the thin arrows show the EDX line scan direction).

EDX of APMT-ArW-22IR e-beam - RAR

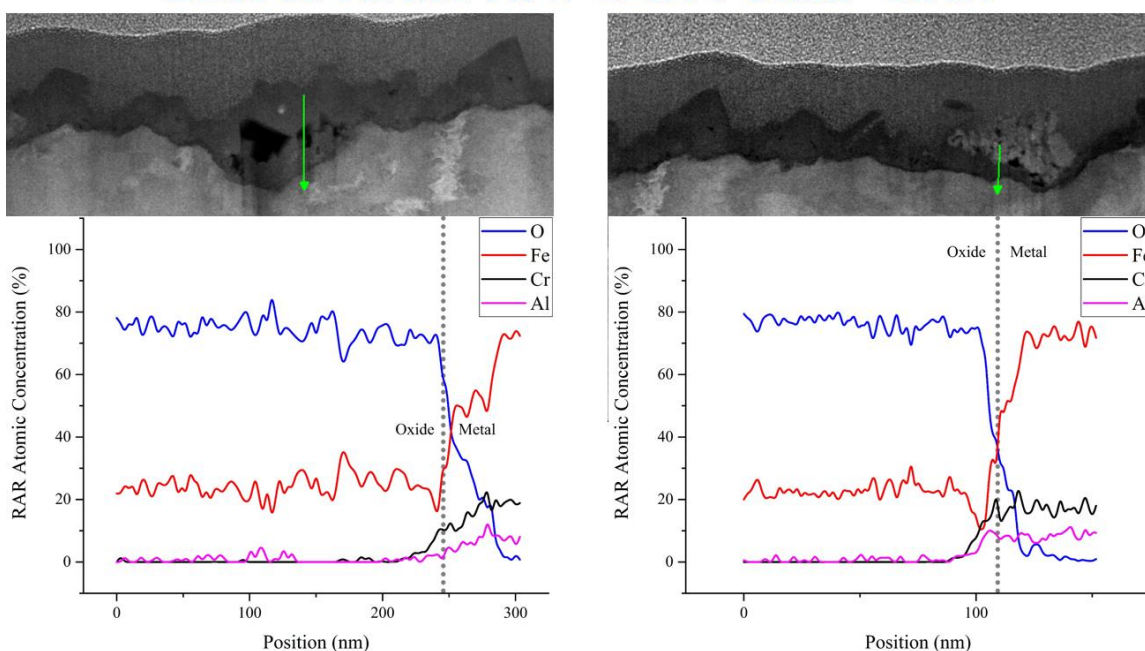


Figure C14: Bottom: STEM EDX line scan results for the 22-hour electron-beam irradiated APMT sample in Argon-saturated water. RAR section atomic concentration vs. position, showing oxide and metal region of the scan. Top: HRTEM images of RAR region (the thin arrows show the EDX line scan direction).

Oxide Phase Analysis with Raman Spectroscopy

Raman spectroscopy was used to identify the oxides formed on the surface of the irradiated sample. Spectra were recorded using a Micro-Raman Spectrometer (NRS-5100, Jasco). The spectra were collected using a 532 nm wavelength green laser, at a typical laser power of 50 mW, during a total of 200s of exposure time.

Three regions on the irradiated sample were measured using Raman spectroscopy, irradiated region (IR), radiolysis affected region (RAR) and unirradiated region (UR). Three individual spectra were also taken in each region for data consistency check.

Raman analysis of corroded steels usually features corrosion products that are composed of a mixture of iron oxides (maghemite, hematite, magnetite). It is assumed the Raman signal is primarily due to a precipitation oxide layer. The formation of hematite is associated with a high corrosion potential, and is generally present in the IR region of the samples, but sometimes it appears in the other regions.

Raman spectra of the UR, RAR and IR region of the APMT-HW-24IR sample in the Hydrogen-saturated water and APMT-ArW-22IR sample in Argon-saturated water are presented in Figure C15 and C16, respectively. In both of the present experiments, there is presence of the typical Raman peaks related to iron oxides, specifically hematite and magnetite.

In the **APMT-HW-24IR** case (Figure C15), the IR region is rich in hematite peaks, which suggests high corrosion potential. It also contains the magnetite peak, which suggests that the inner layer may consist of magnetite phase or a spinel with iron chromite composition. The UR and RAR regions lack the presence of outer oxide precipitation layer. The typical 665 cm^{-1} peak which is related to magnetite and is usually present in the UR and RAR regions, in this case is slightly shifted to a higher wavenumber, closer to the 678 cm^{-1} peak for FeCr_2O_4 . This suggests presence of iron chromite.

In the **APMT-ArW-22IR** case (Figure C16), the UR and RAR regions contain the typical hematite peaks, most likely present in the dense precipitation layer, and some magnetite peaks which suggests presence of magnetite phase or iron chromite composition in the inner layer. In comparison, the IR region features peaks rich in chromium and nickel and some hematite peaks. Nickel is a part of the ND corrosion cell (made of hastelloy 276C) and is released when the cell is exposed to normal water chemistry and lower temperature (250 to 290°C) rather than 325°C. The nickel-chromium-oxide layer that we encountered in the past by exposing the sample to normal water chemistry, deteriorated our EDX results as the full precipitation layer consisted of nickel-rich oxide. To lower the nickel content deposition in the IR region, we have switched from using oxygen saturated water to argon saturated water. This has helped us avoid the densely populated nickel-rich layer, but still gives rise to sparse appearance of nickel particles.

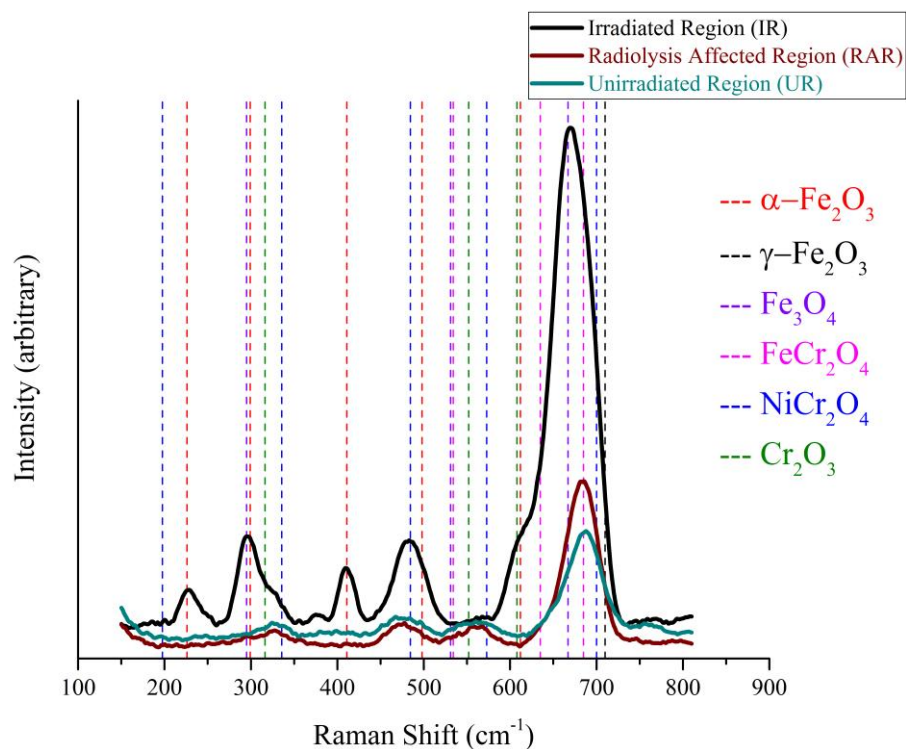


Figure C15: Post-irradiation Raman spectra collected from the 24-hour electron-beam irradiated APMT sample in Hydrogen-saturated water. Representation of the three different regions (IR, RAR and UR) and associated Raman peaks.

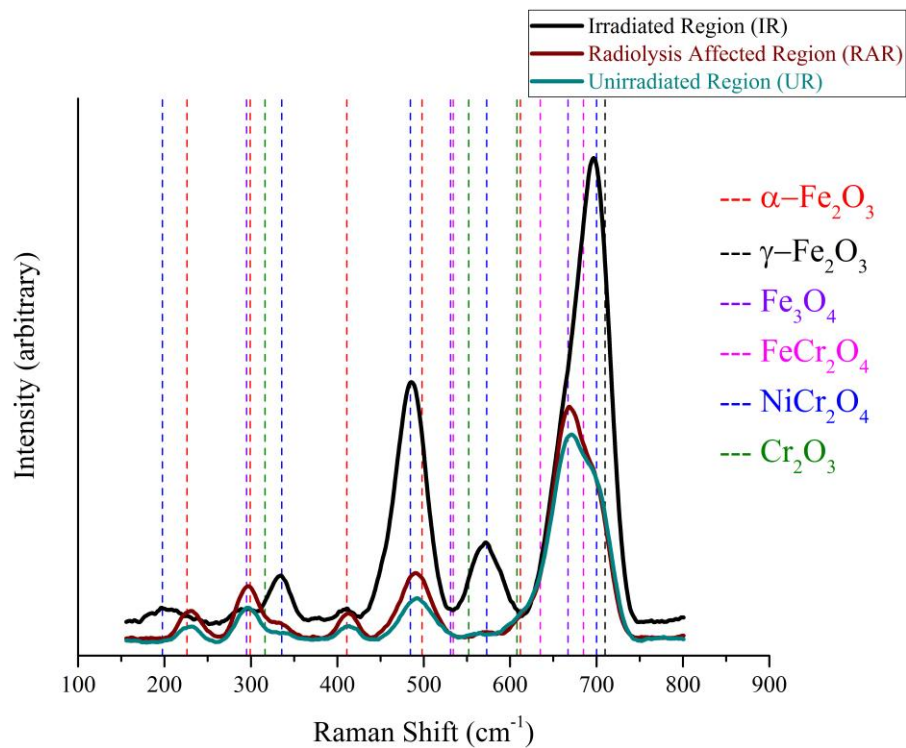


Figure C16: Post-irradiation Raman spectra collected from the 22-hour electron-beam irradiated APMT sample in Argon-saturated water. Representation of the three different regions (IR, RAR and UR) and associated Raman peaks.

Electron Post Irradiation Characterization Summary

The oxide species found on irradiated samples under different conditions were analyzed using EDX and Raman and the findings are summarized in Table C3.

Table C4: Summary of the oxide species found on APMT in HW and NWC conditions under proton irradiation.

Samples	Regions	Outer Oxide/Inner Oxide	
		ArW 288°C, Argon-sat	HW 320°C, 3 ppm H ₂
APMT	IR	α -Fe ₂ O ₃ NiCr ₂ O ₄	α -Fe ₂ O ₃ FeCr ₂ O ₄ Fe ₃ O ₄
	RAR	α -Fe ₂ O ₃ Fe ₃ O ₄	FeCr ₂ O ₄
	UR	FeCr ₂ O ₄	