U.S. DEPARTMENT OF ENERGY
Nuclear Energy

Advanced surface plasma nitriding for development of corrosion resistant and accident tolerant fuel cladding

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Advanced surface plasma nitriding for development of corrosion resistant and accident tolerant fuel cladding

Purpose:

This project aims to develop an advanced nitriding technique for surface modification of fuel cladding materials or in-core components, driven by the needs to increase corrosion resistance, wear resistance and accident tolerance.

Logical Path:

Materials modifications: Surface plasma nitridation under various conditions
→Ion Irradiation: Temperature and dpa dependence
→Structural characterization: TEM, SEM
→Mechanical testing: fracture toughness and hardness
→Corrosion testing: corrosion resistance with or without nitridation
→Optimize plasma nitridation process for alloys of DOE interest

Towards accident tolerant fuel cladding

Thin ceramic coating is attractive to provide a **protective layer** for Zr alloys under normal operating conditions & off normal condition (BDBA Beyond design-basis accident condition)

→ Reduce oxidation
Reduce hydrogen pick up

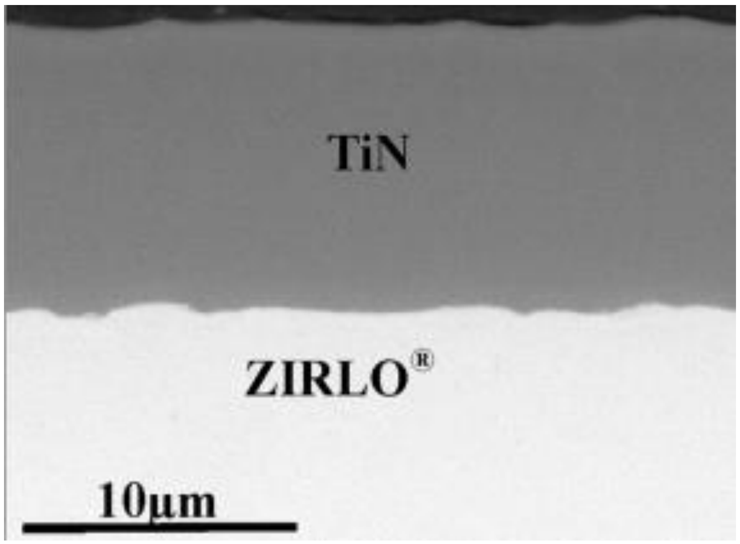
Fukushima Daiichi accident

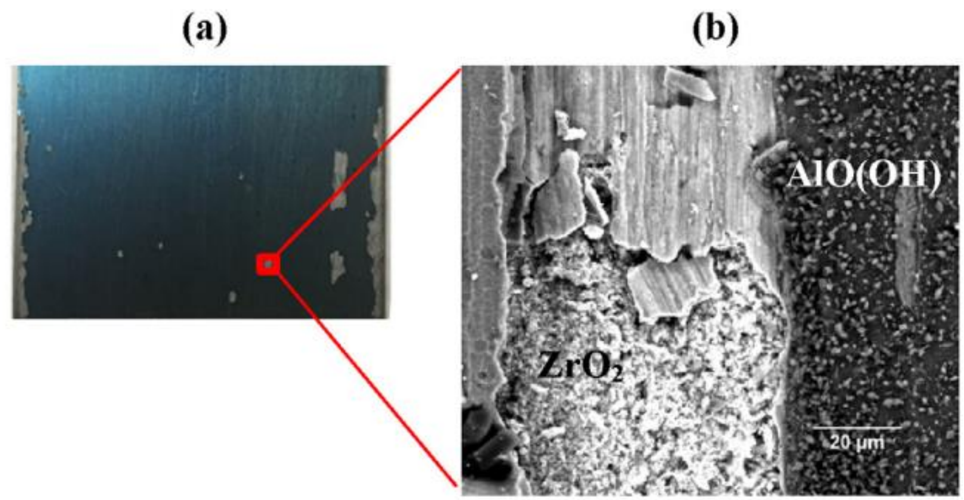
However, **challenges** exist for achieving

- good thermal conductivity,
- excellent radiation tolerance
- satisfactory mechanical property
- no debonding under BDBA conditions

Example of debonding issue

Vapor deposition of TiN layer





Debonding after autoclave testing for 33 days, in 360°C water
JNM 478, 236 (2016)

➡ Instead of **coating**, we need a technique which is **converting** the original materials into a ceramic layer

Various industry nitriding techniques

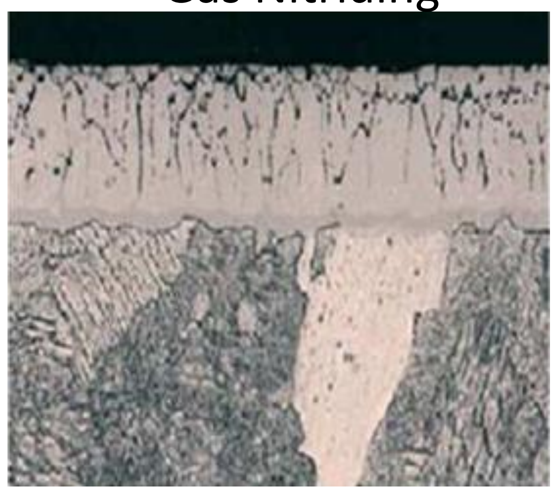
Salt Bath Nitriding

Gas Nitriding

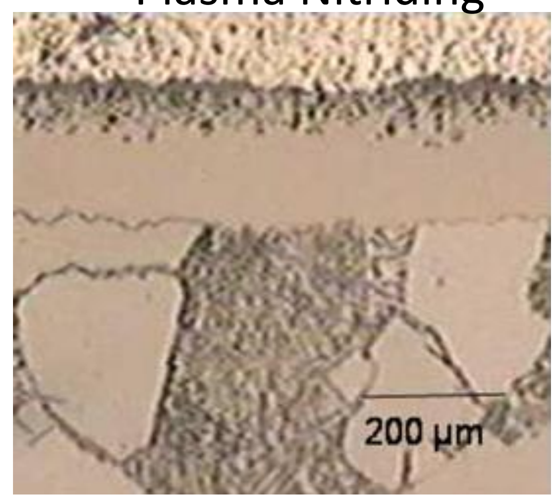
Plasma Nitriding

Salt Bath Nitriding

Gas Nitriding



Plasma Nitriding



High friction due to rough porous zone
Post polishing necessary
Very good corrosion resistance

Low friction due to smooth zone
No post polishing needed
Good corrosion resistance

History of nitriding

Nitriding process was first developed in the early 1900s by Adolph Machlet as a method to increase materials' hardness, via annealing in Ammonia. He also invented the technique of using hydrogen to dilute the amount of nascent N.

In parallel to Machlet's works, Adolph Fry also noticed the benefit of N addition and invented a similar technique by using Ammonia, but without H as a dilutant gas. His studies focused more on substrate alloying engineering, after the discovery that certain elements in steels such as Cr, Mo, Al, Va and W are beneficial as nitride stabilizer. The studies led to commercial steels known as "Nitralloy".

Shortly after gas nitriding, salt bath nitriding and ion/plasma nitriding were invented. Bernhardt Berghaus invented the "glow discharge" method of nitriding in 1932. General Electronic Company started the further development of ion nitriding units and commercialization in 1950s, followed by the acceptance by US Navy.

Advantages of plasma nitriding

Plasma nitriding has the following advantages:

(1) Nitride formation occurs over **a wide range of temperatures**, allowing **low temperature process** without phase transformation of materials;

(2) Hardening is controllable **with or without** nitride compound layer formation;

(3) Both **hardness and fatigue strength** can be enhanced;

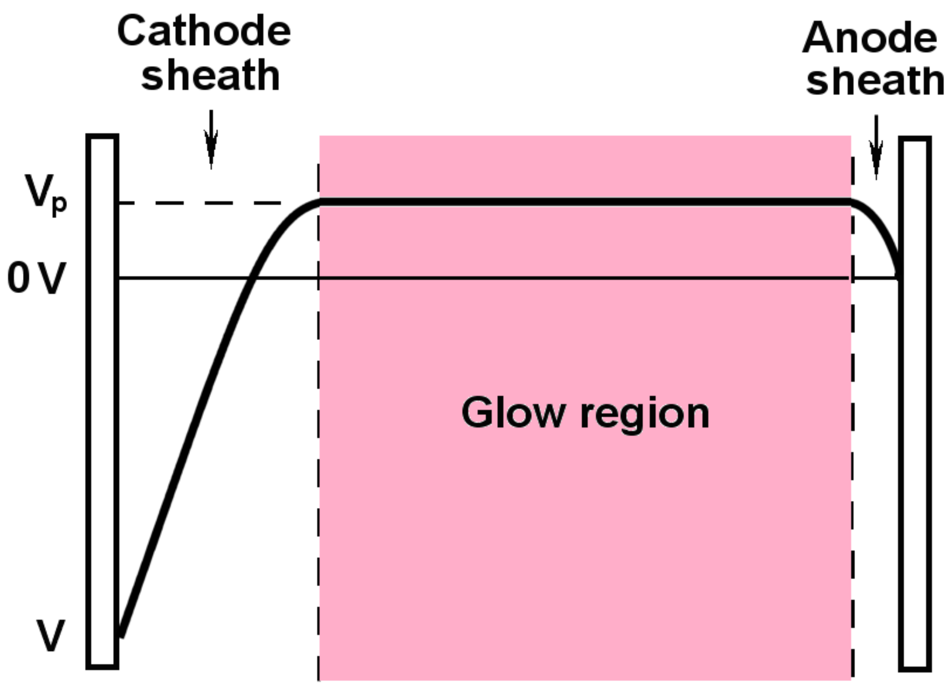
(4) Surface is **porosity-free** and there is no need for additional polishing;

(5) The technique can be combined with other processing, such as post-nitriding oxidation or simultaneous nitriding and carburizing to further improve mechanical properties or corrosion resistance.

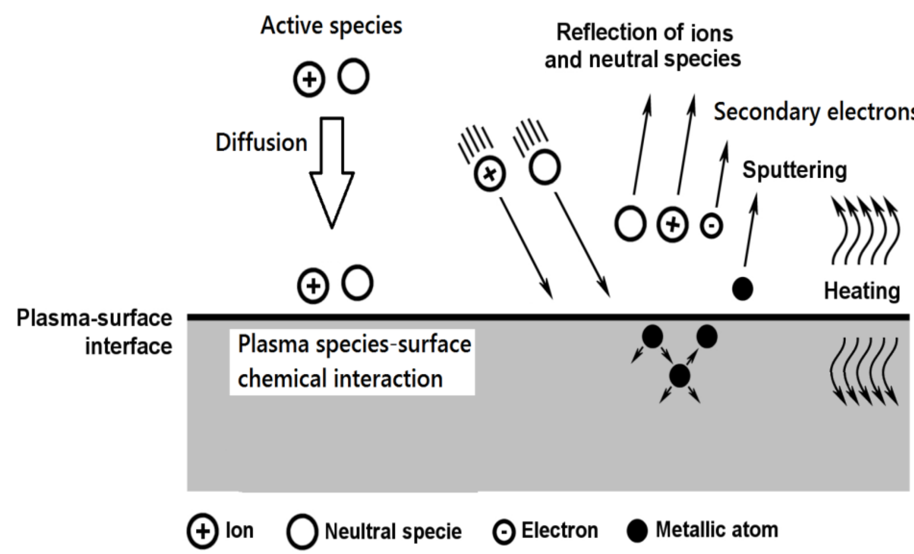
Industry plasma nitriding

High voltage processing equipment, www.ivicorp.com

Principles of surface plasma nitriding

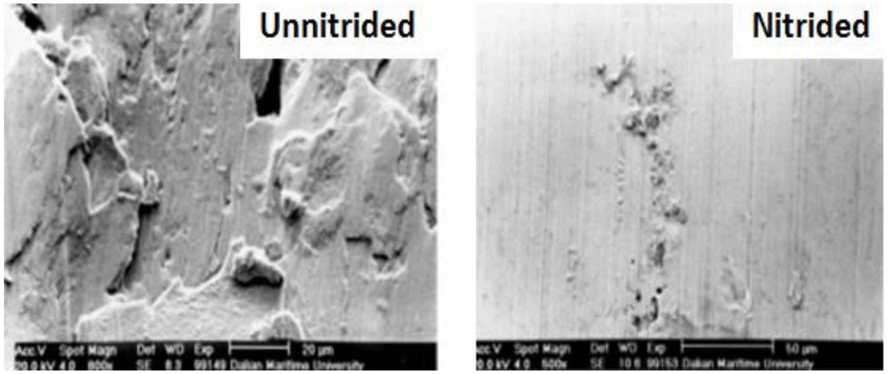


300–1000 V and 1–10 Torr

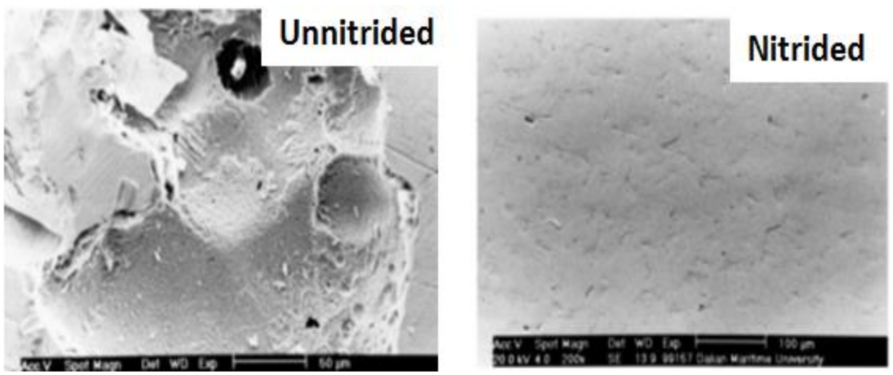


DOI: 10.5772/61989, Ch. 5

Benefits of surface nitride layers



304 steels after disc wear testing



304 steels after corrosion testing in NaCl solution

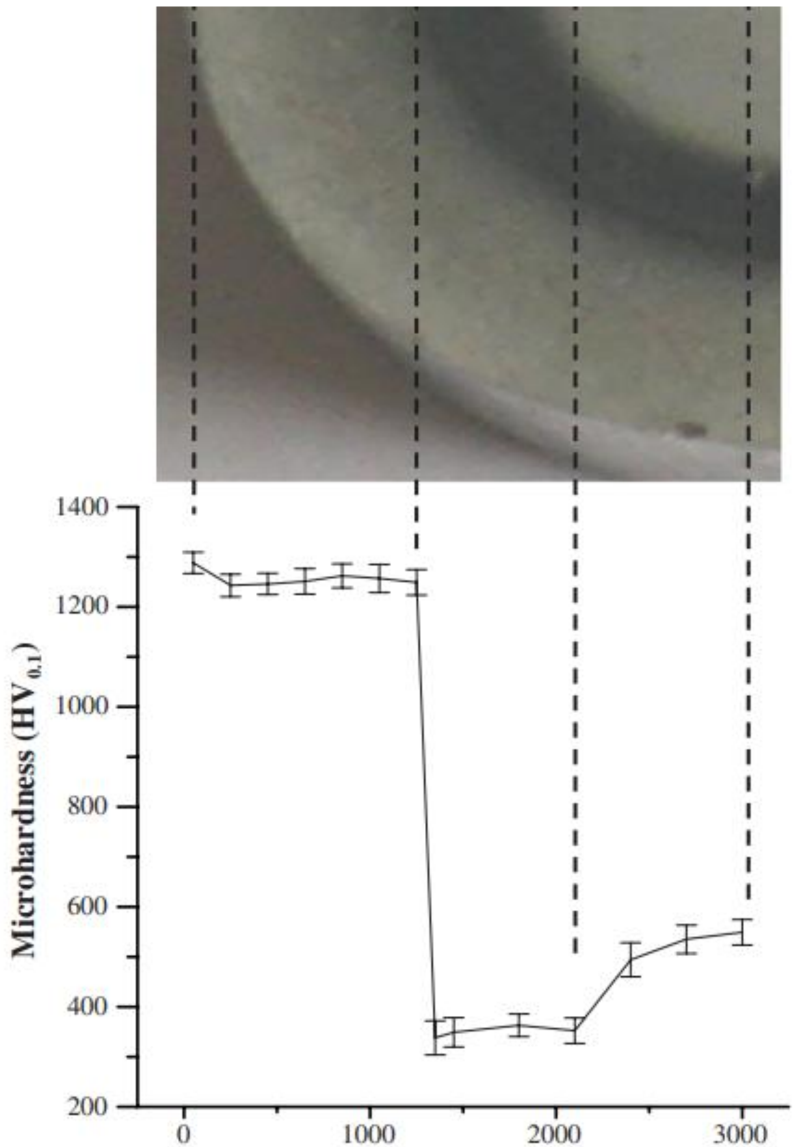
Advantages of plasma nitriding

- Enhanced hardness
- Enhanced wear resistance
- Enhanced corrosion resistance
- Strong bonding
- Low temperature process (much lower than tempering temperature)
- Reduced oxidation under off-normal condition

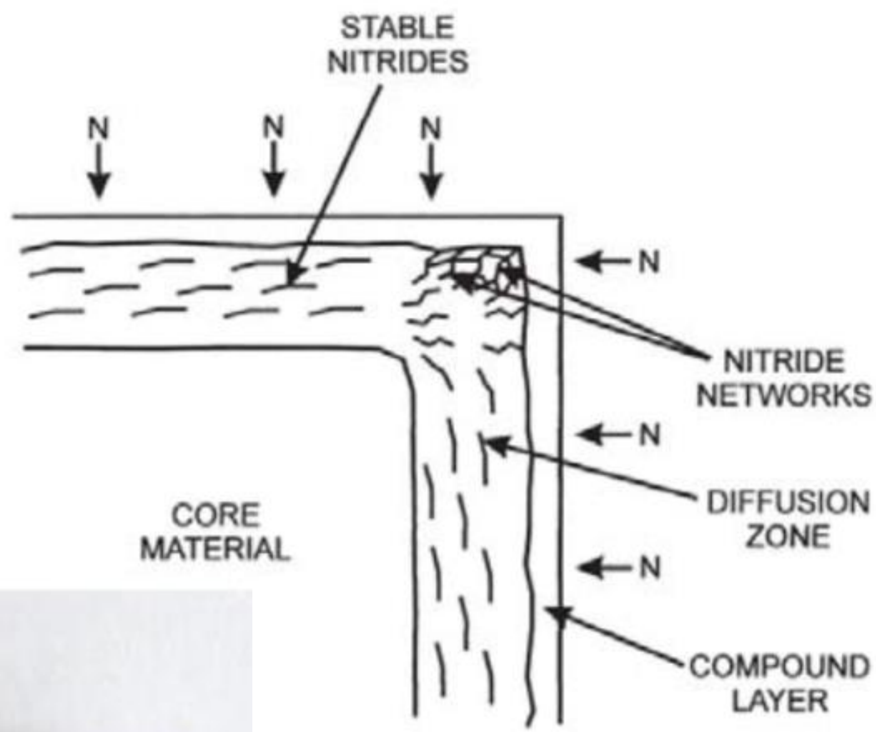
→ Enhanced accident tolerance

Liang, Bin, Zhiwei, Yaqin, Surf. and Coat. Tech. 130, 304(2000)

General issues of popular plasma nitriding technique

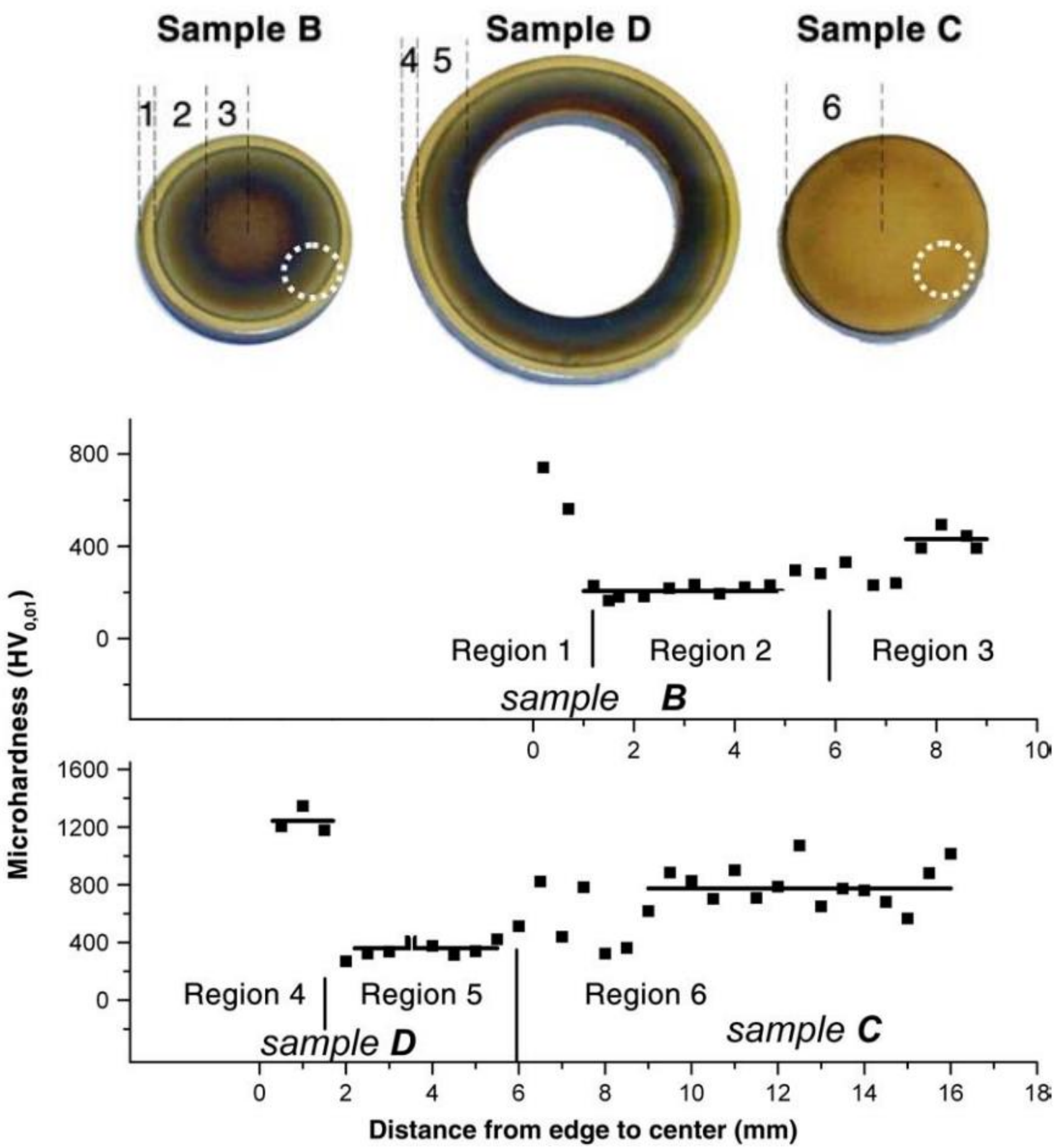


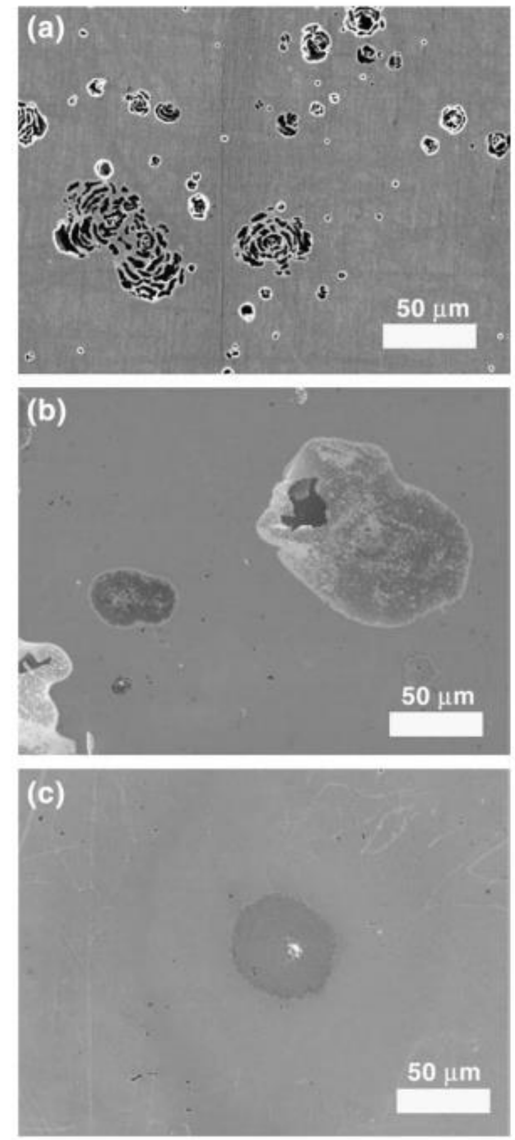
Edge effects cause **non-uniformity**



Surface and Coatings Technology 201, 2450-2454 (2006)

Non-uniformity issue

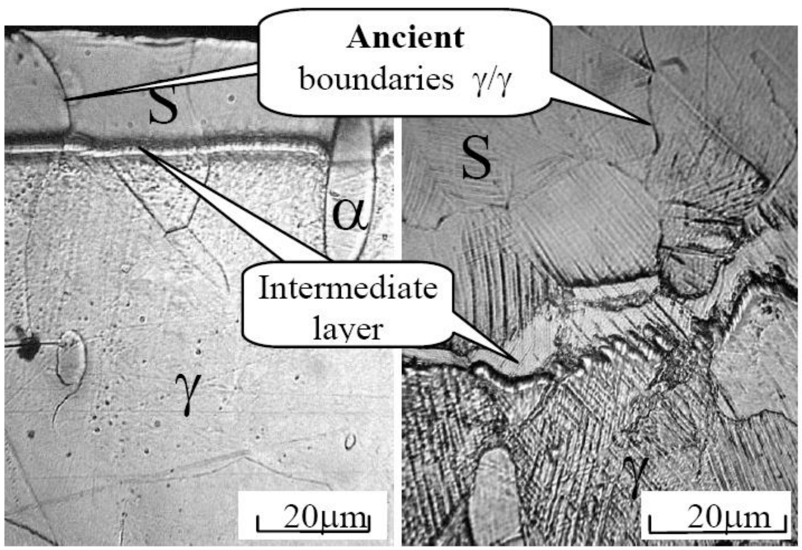




M. Olzon-Dionysio et al. / Surface & Coatings Technology 204 (2010) 3623

#2 issue: No systematic study on NE relevant materials

316/304	Cr	Zircaloy	HT-9/T91
Below 430°C Increased corrosion resistance/hardness Formation of S layer Above 430°C Precipitates of CrN start to form	No report	No report	No report



316 SS after nitriding at 420°C

- 316 SS forms a surface nitride layer (S-phase)
- At S- and original γ- phases, a thin intermediate layer forms.
- Within S-phase, the original ferrite grain boundaries are sustained.
- S-phase has lattice parameters different from Fe_4N, suggesting that alloying elements such as Cr and Ni play a role.
- No clear understanding of Fe_4N to S transition.

Toshkov et al. J. Achiev. Mater. Manuf. Tech. 25, 71 (2007)

Our approach: Cage Plasma Nitriding

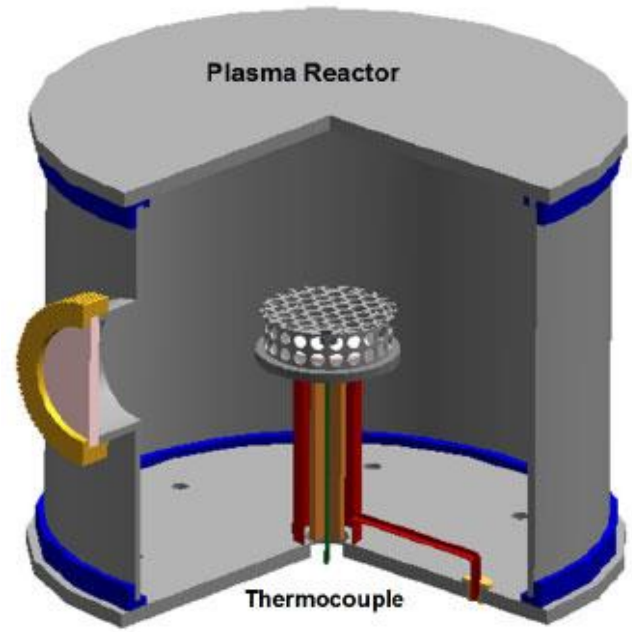
Different from the conventional plasma nitriding process, we will employ the technique of Cathodic Cage Plasma Nitriding (CCPN).

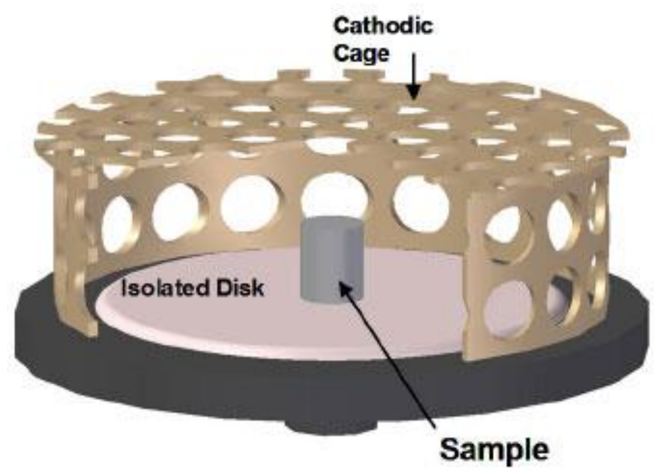
Key design

A nitriding cage is introduced to create the hollow cathode effects which result in an optimal pressure depending on the size of the holes of the cage.

Advantages

Minimize edge effects
Increase temperature uniformity
Reduce arcing.
Facilitate complex geometry.





Participants

Organization	Investigator	Role	Facilities
Texas A&M University (Lead Institution)	Lin Shao (Nucl. Eng.)	Lead investigator, plasma nitridation and ion irradiation	Investigator 1 directs an Ion Accelerator Lab equipped with multiple high energy ion accelerators
	Frank Garner (Nucl. Eng.)	Microstructural characterization	Investigator 2 is a seasoned scientist for atomic scale structural characterization using FIB, TEM, and APT.
Oklahoma State University	Don Lucca (Mech. Eng.)	Mechanical property characterization	Investigator 3 directs a surface mechanical property testing lab equipped with various indentation instrument
Massachusetts Institute of Technology	Michael Short (Nucl. Eng.)	Corrosion testing in water loop and sodium loop	Investigator 4 directs a corrosion testing lab equipped with multiple water, steam and liquid sodium coolant loops

Our approach: Cage Plasma Nitriding

Numerous problems have been identified and solved:

- severe arching when igniting plasma,
- metallic sputtering and deposition on inner ceramic insulators which cause electrical shortage and
- inconsistent nitriding results.

Solutions:
- anode is redesigned for stable electrical grounding,
- multiple shielded sample holders are used to replace single isolation disk,
- additional shields are used to isolate thermocouple feedthrough.

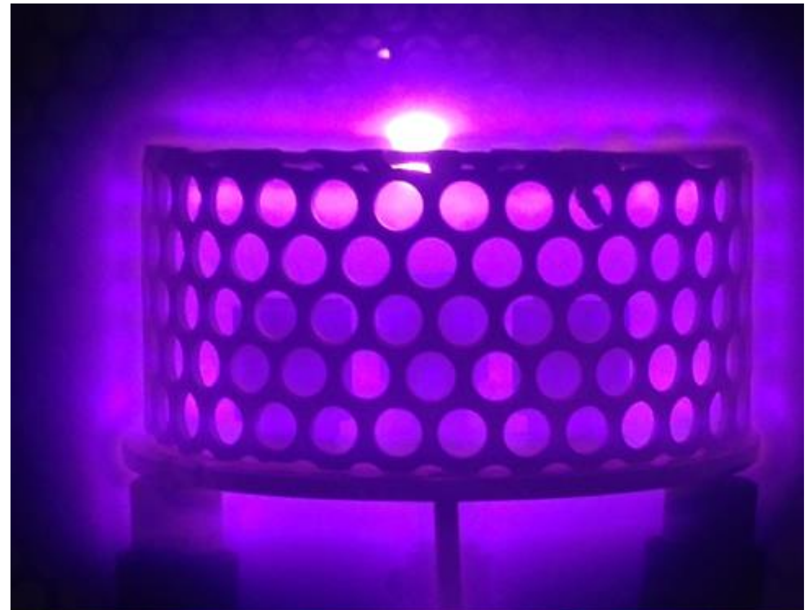
The device built in the PI’s lab

Examples of technological issue

One problem is a single hollow cathode effect on the cage.

This resulted in a hot spot on the cage causing an unknown temperature distribution that was constantly changing.

We adjust pressure (reduced), voltage bias (reduced), and hole sizes (increased), to avoid the single hollow cathode effect.



Testing matrix

Gas: N_2/H_2 (90%/10%)

316L	HT9	T91	Zircaloy4	Fe

×

Pressure	Temperature (°C)								
	400			450			525		
750	1h	2h	4h	30m	1h	2h	30m	1h	2h
1000	1h	2h	4h	30m	1h	2h	30m	1h	2h
1500	1h	2h	4h	30m	1h	2h	30m	1h	2h

×

316 cage	Ti cage	No cage

×

Samples are floated	Samples are biased

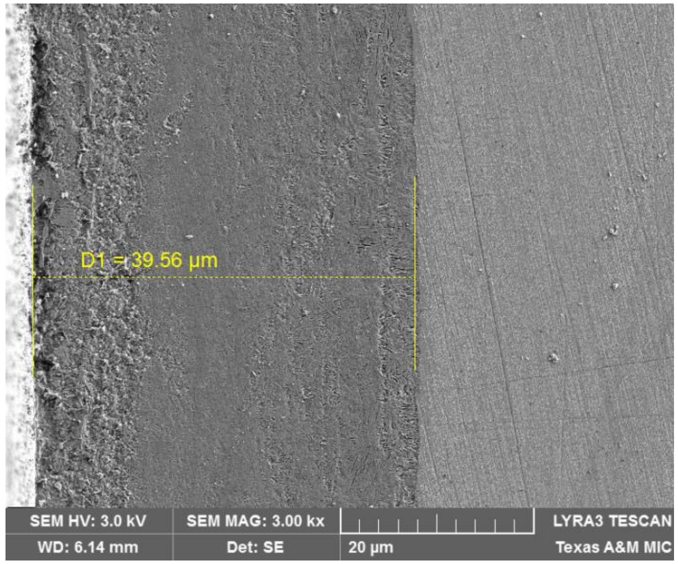
×

Different locations within the cage

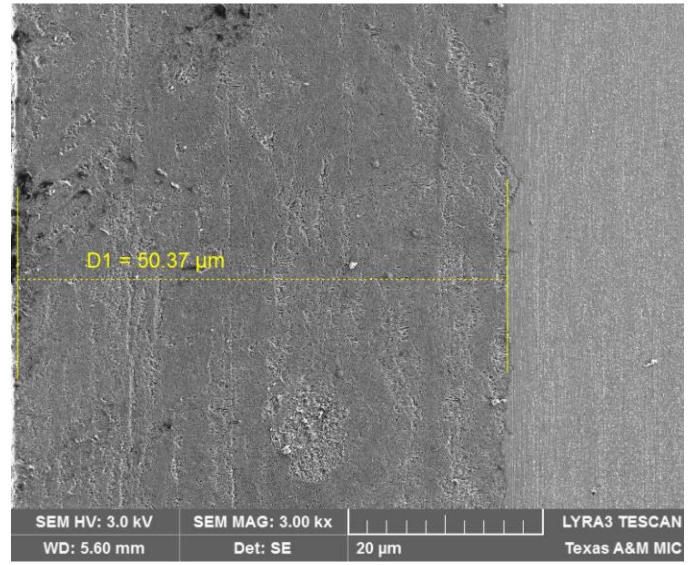
Case #1: Nitridation of 316L temperature and pressure dependence

316L: 525°C, 1.5 Torr

Plasma direction

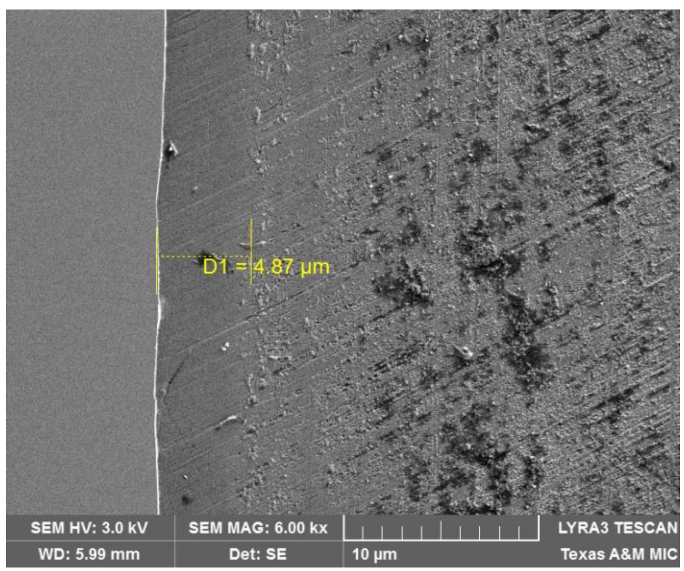


1 Hour

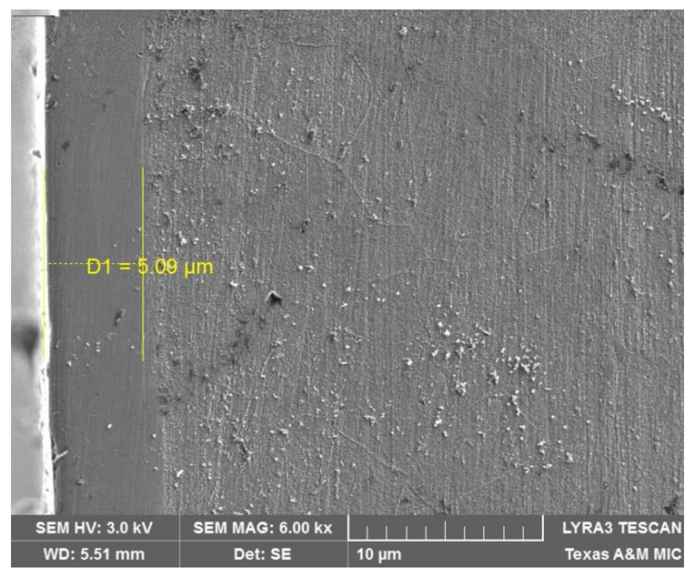


2 Hour

316L: 400°C, 2 Hours

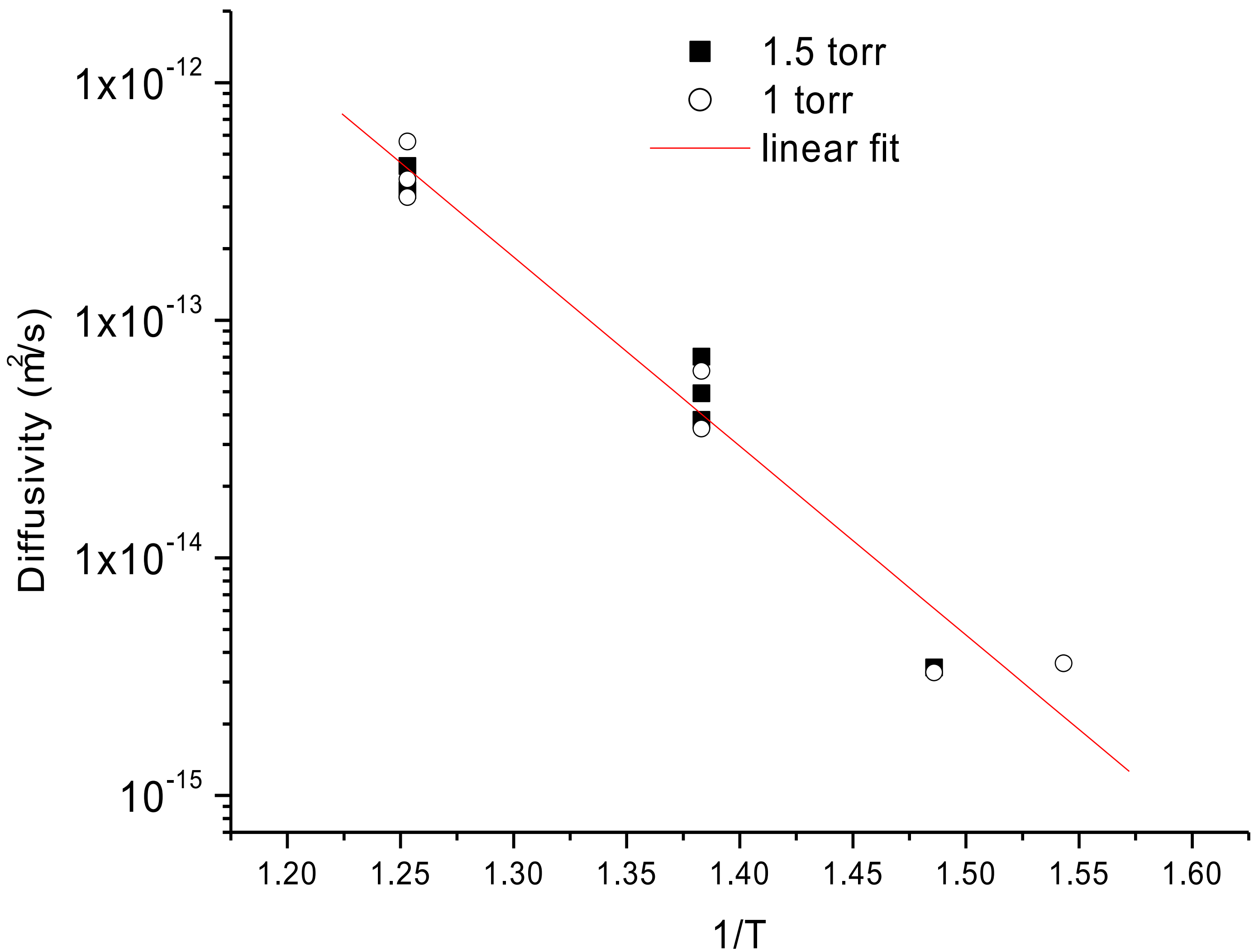


1 Torr



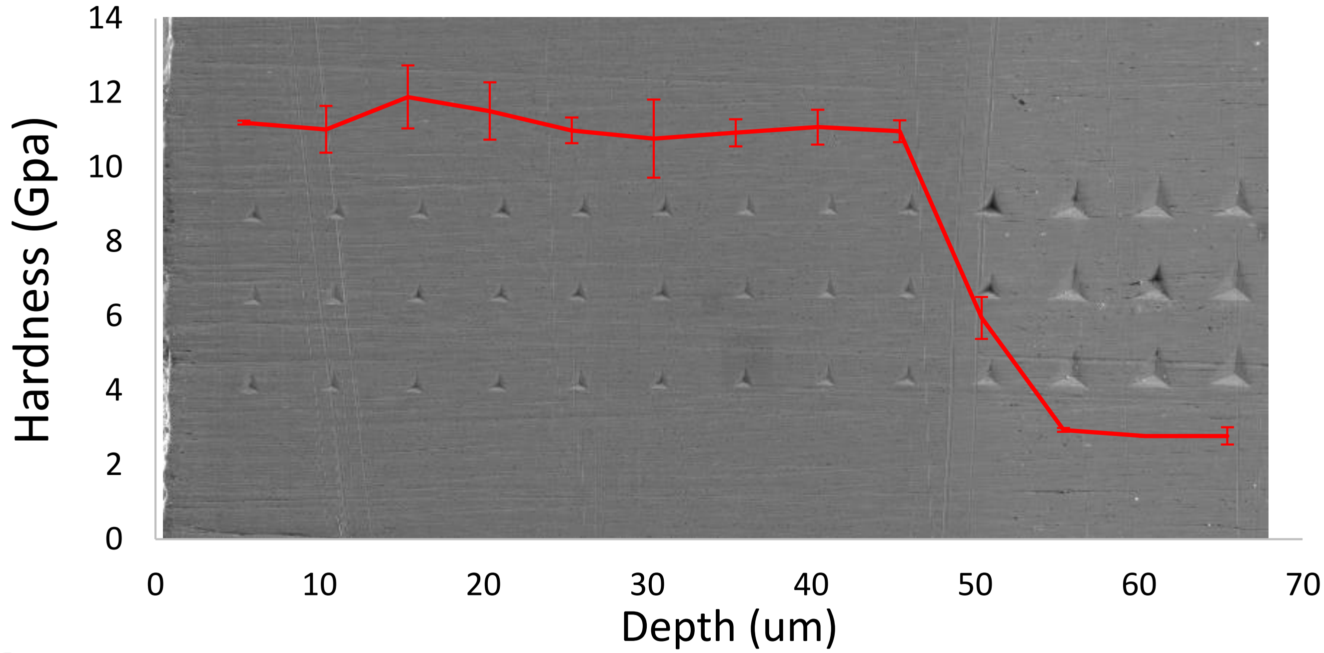
2 Torr

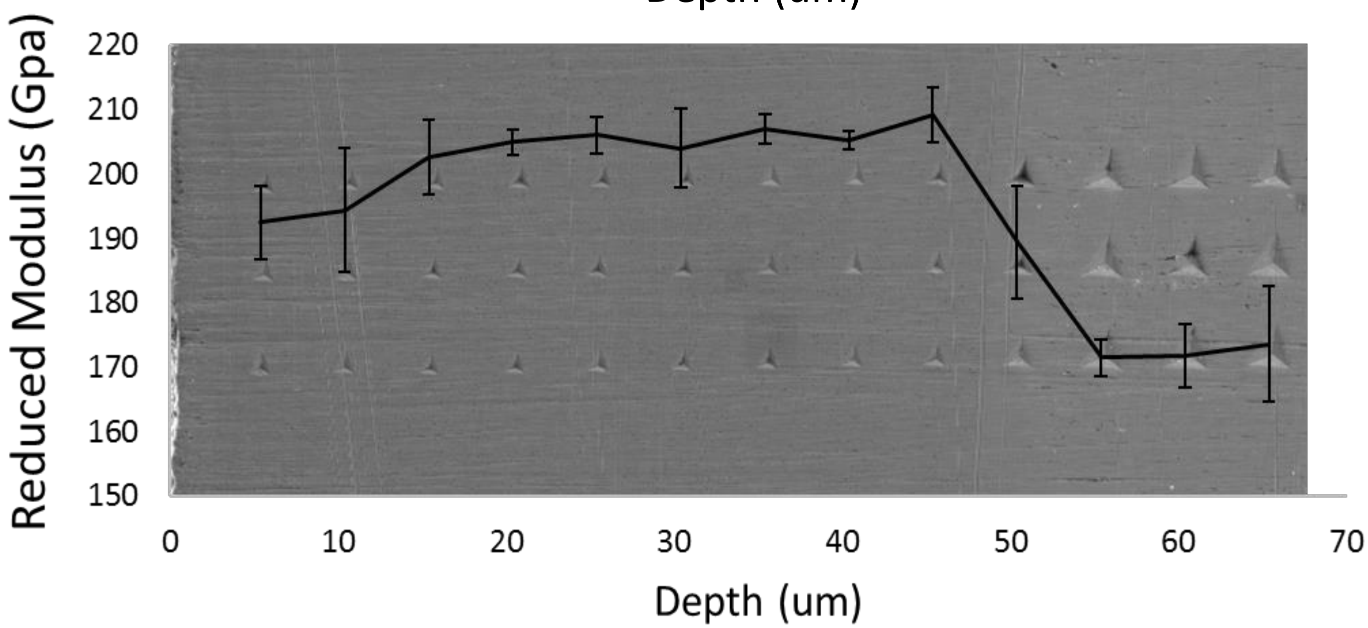
Nitridation of 316L: nitridation kinetics



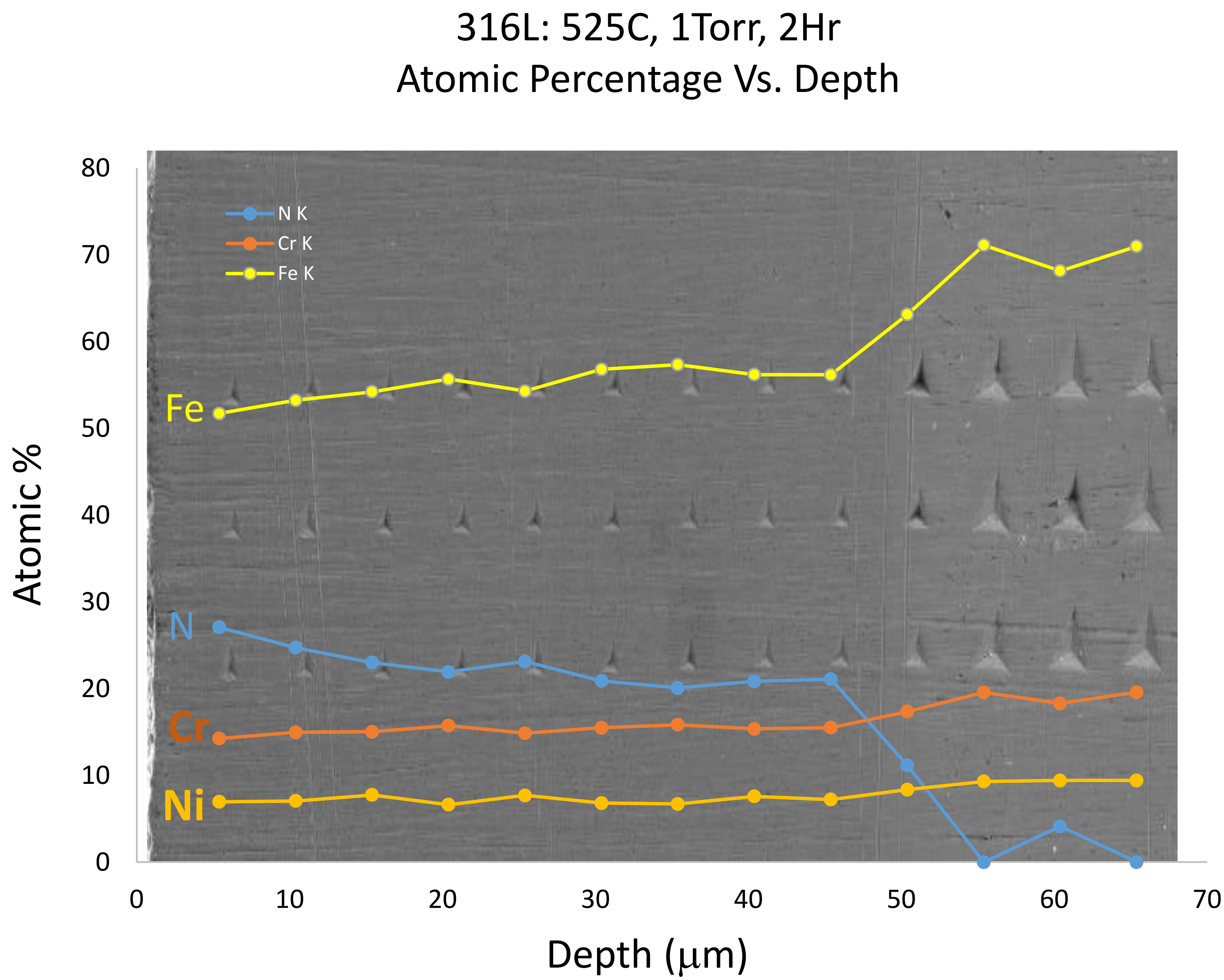
Nitridation of 316L: mechanical property

316L: 525°C, 1Torr, 2Hr, Hardness Vs. Depth

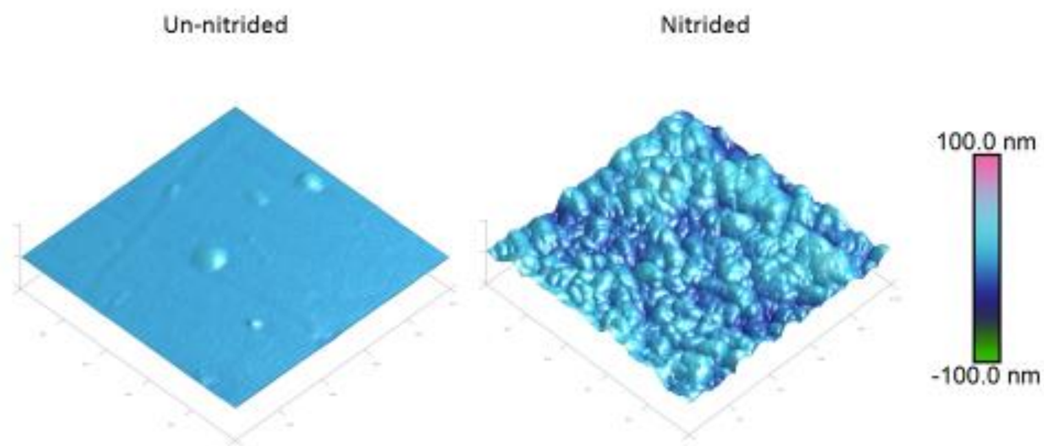




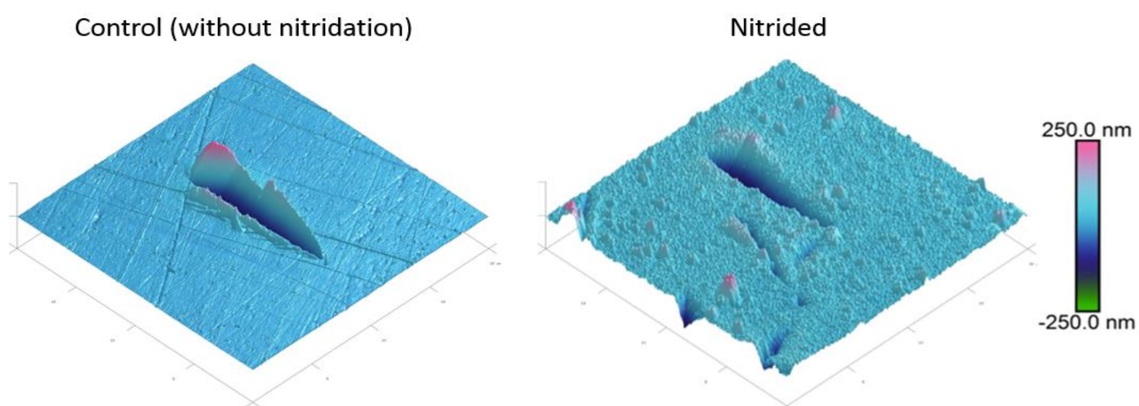
Nitridation of 316L: composition analysis



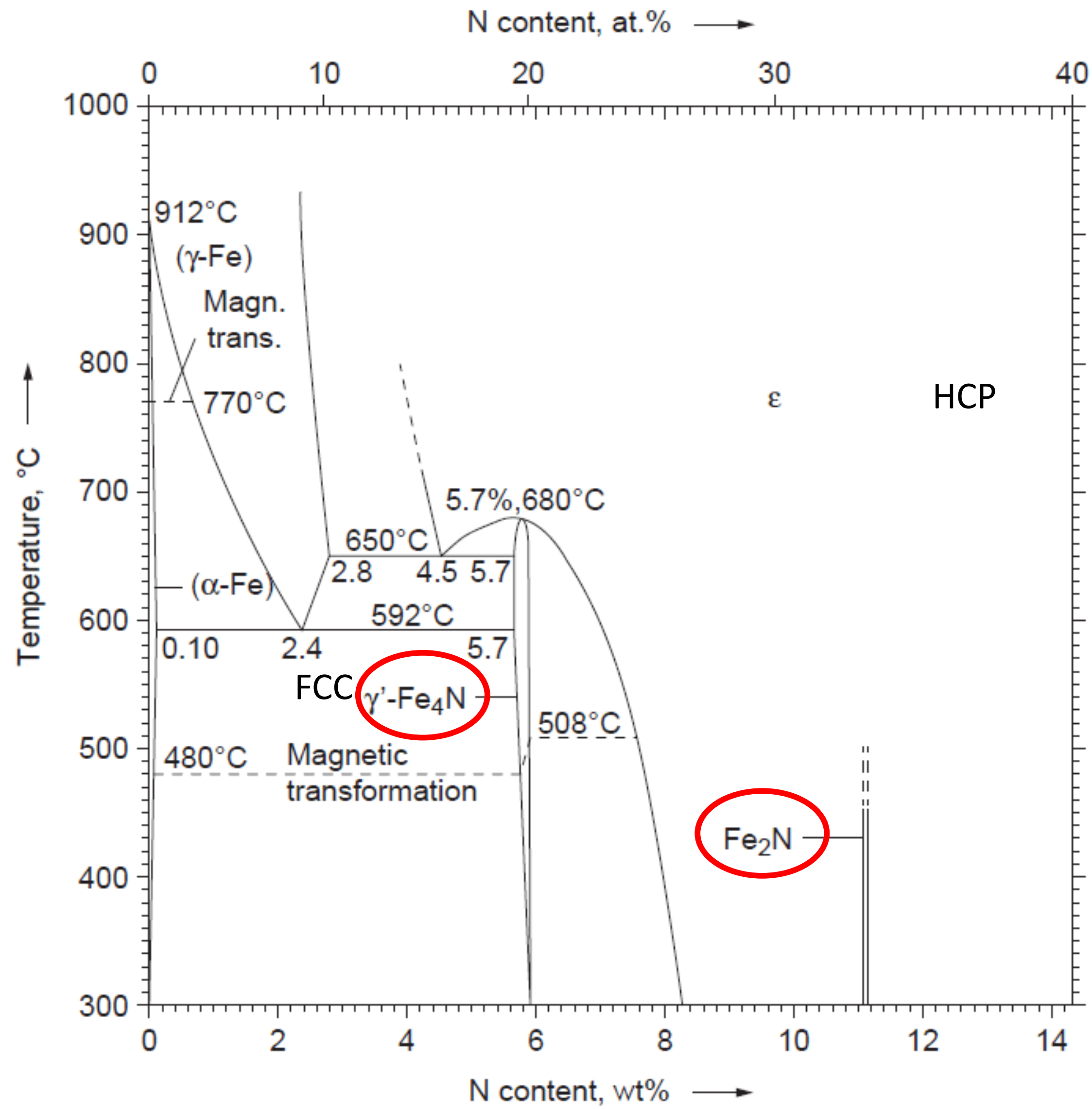
Nitridation of 316L: scratching tests



	Roughness Rq (nm)		
	Ave.	Max.	Min.
Un-nitrided	1.2	2.1	0.5
Nitrided	11.8	14.3	10.7

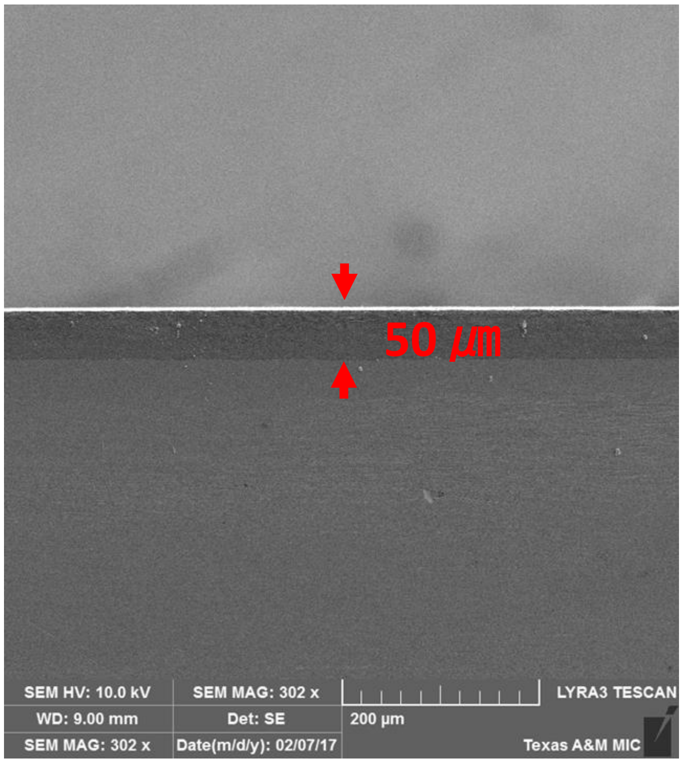


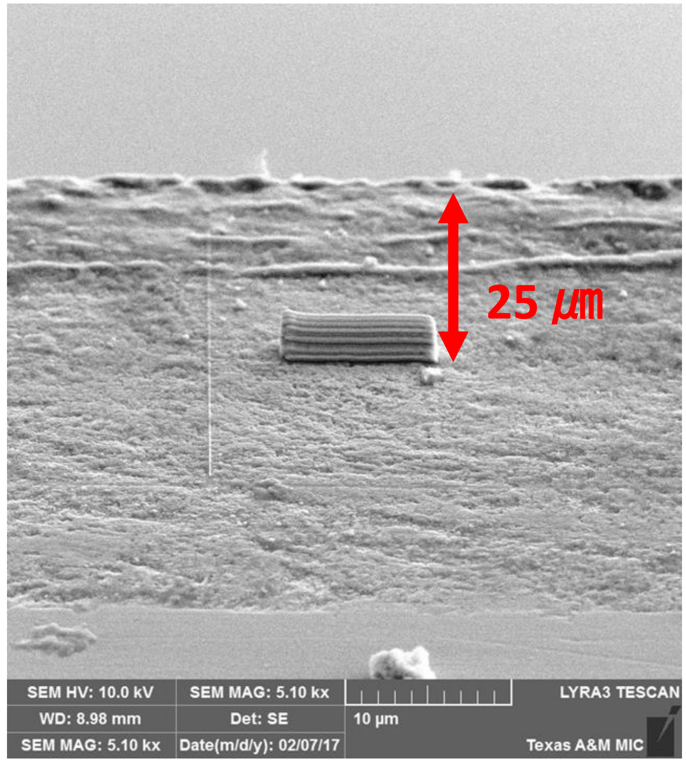
Nitridation of 316L: phase diagram

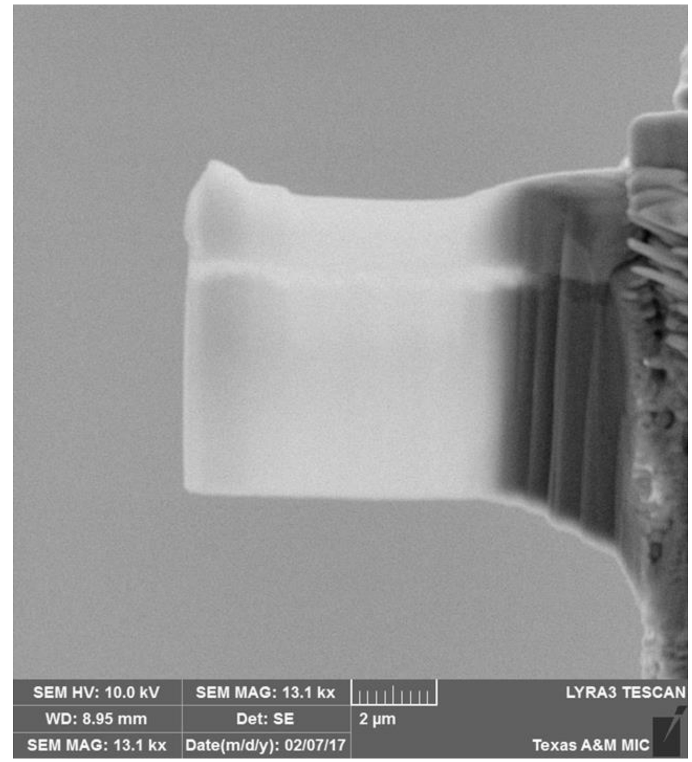


Nitridation of 316L: Structural characterization (FIB)

316L, 525℃, 2 hr, 1.5T

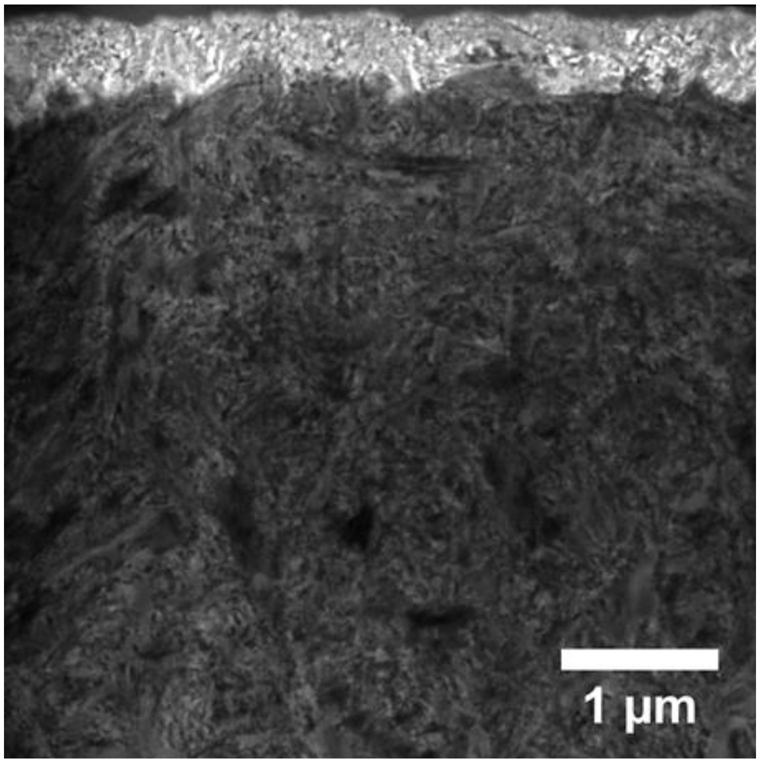


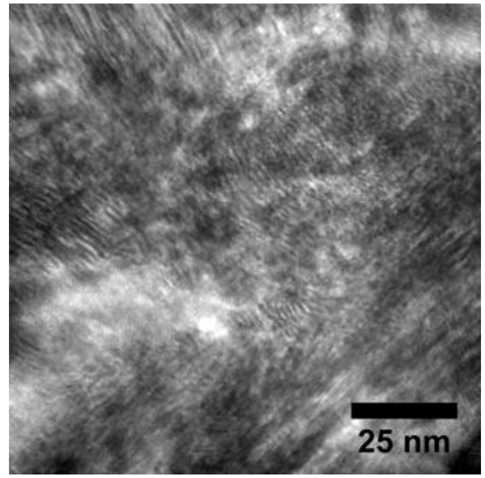


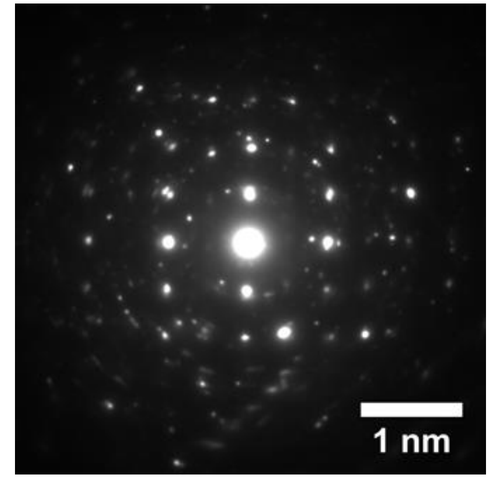


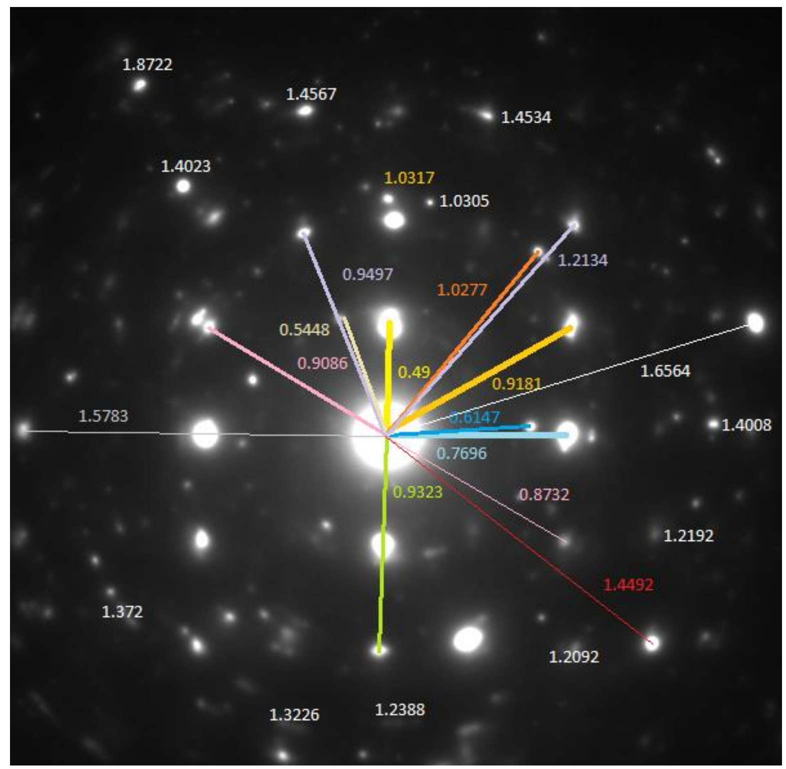
- Thickness of nitride layer is 50 ㎛.
- Cross section was obtained from 25 ㎛ depth of the nitride surface.

Nitridation of 316L: Structural characterization (TEM)









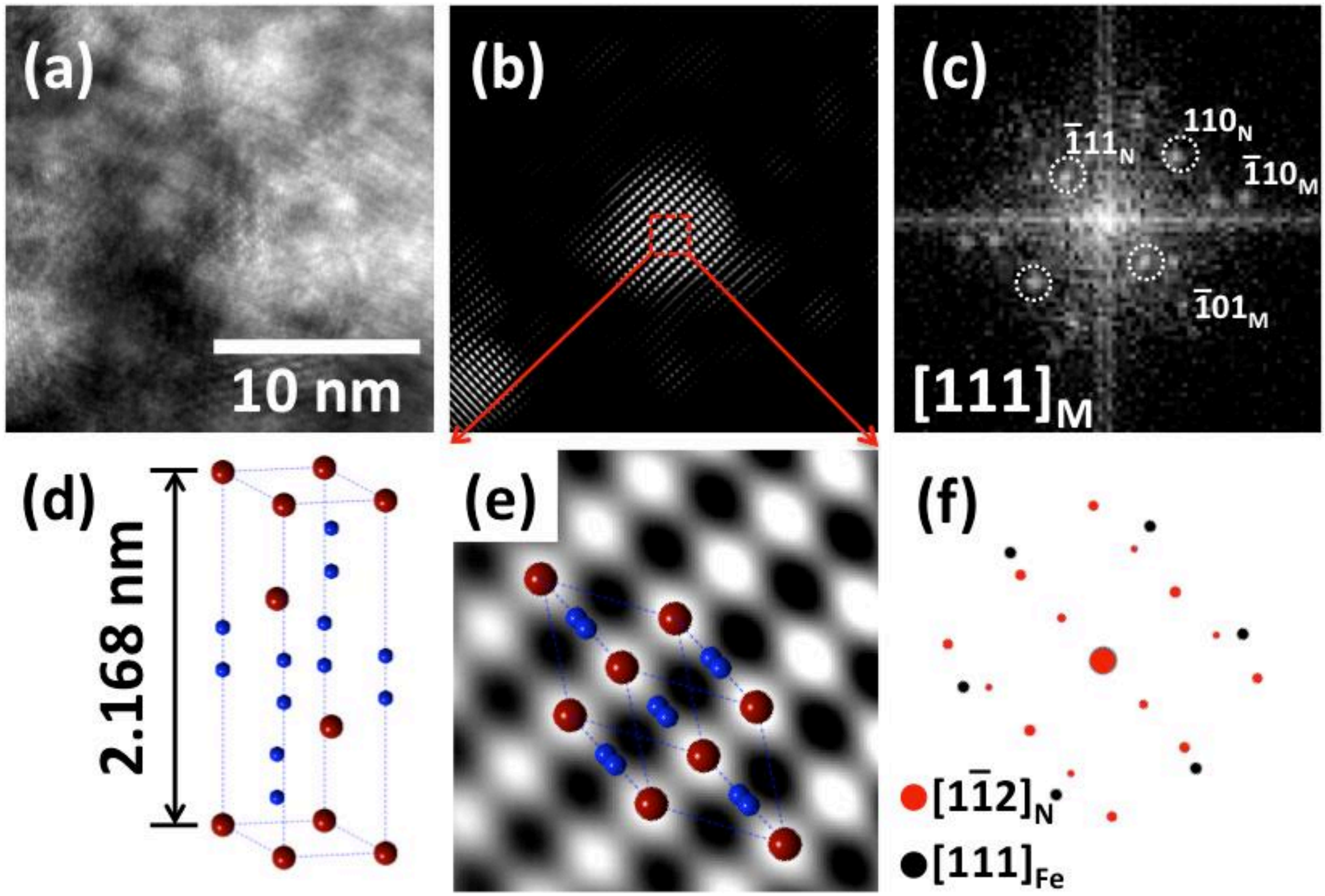
Measured reciprocal spacing [1/Å]

Indexed with Fe_2N

Indexed d-spacing is slightly different from measured value but other unindexed peripheral dot spacings match pretty well with known Fe_2N spacings.

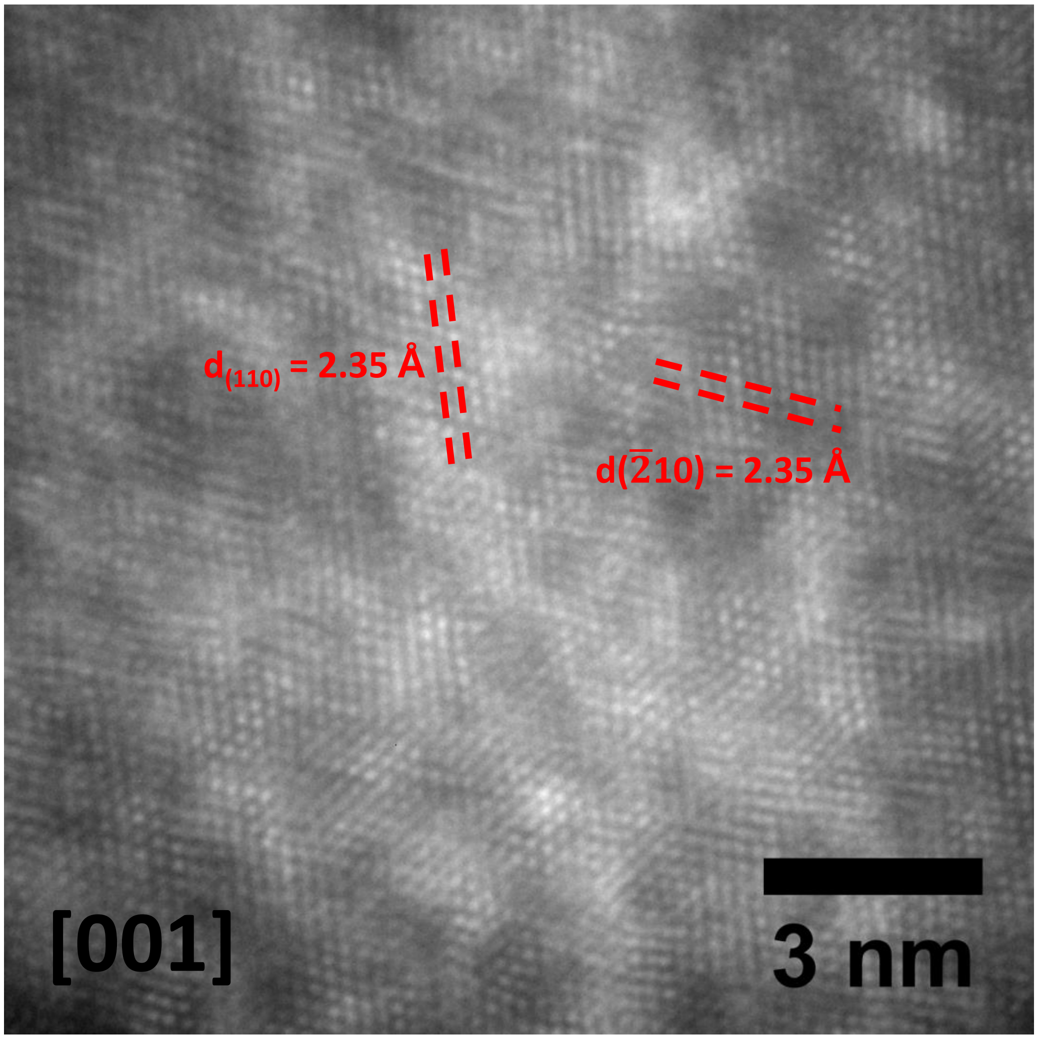
N-implanted Fe: Structural characterization (TEM)

FeN_2 Phase confirmation

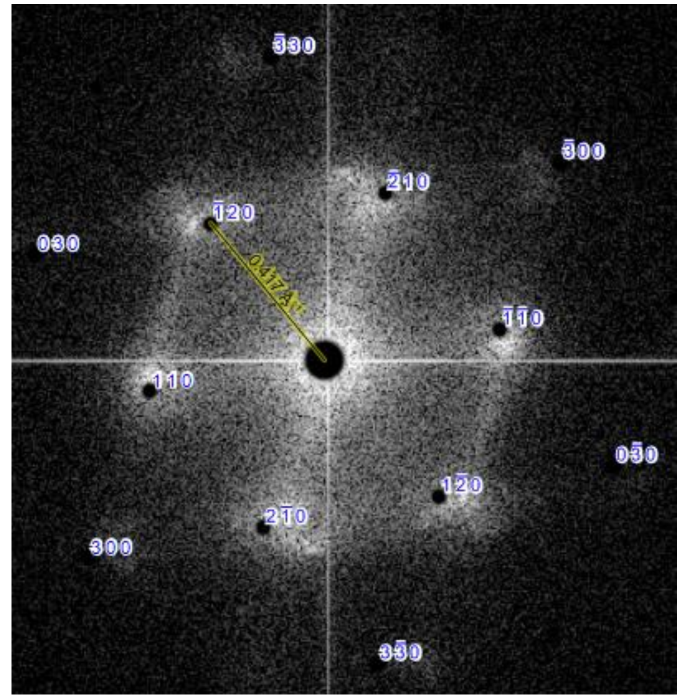


Nitridation of 316L: Structural characterization (TEM)

High resolution image of bottom matrix

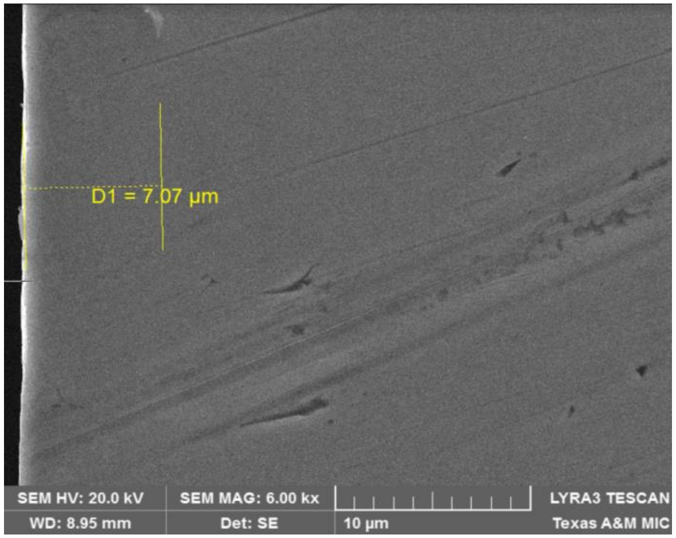


FFT

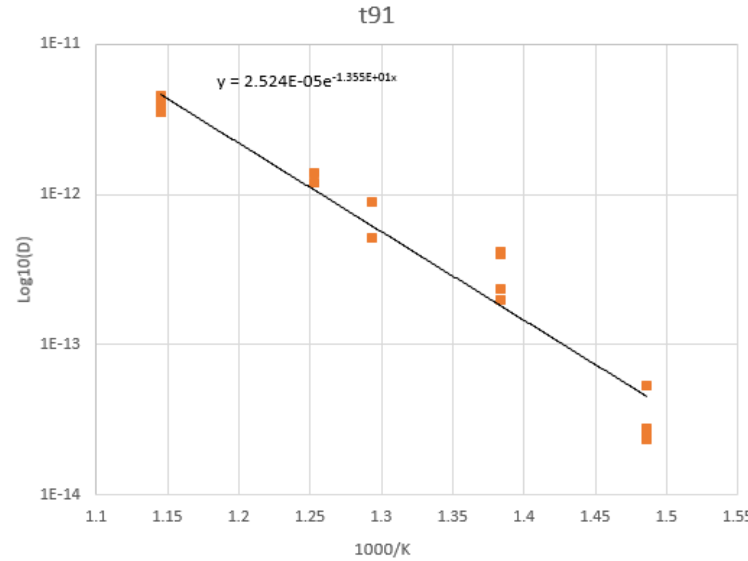


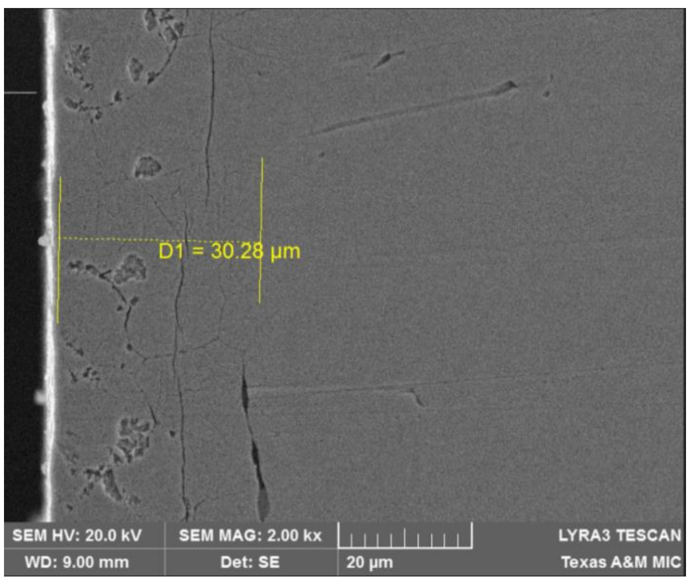
HRTEM provides additional evidence for Fe_2N formation. The interplanar spacings from the FFT of the image only satisfy one nitride compound: Fe_2N.

Case #2: Nitridation of T91

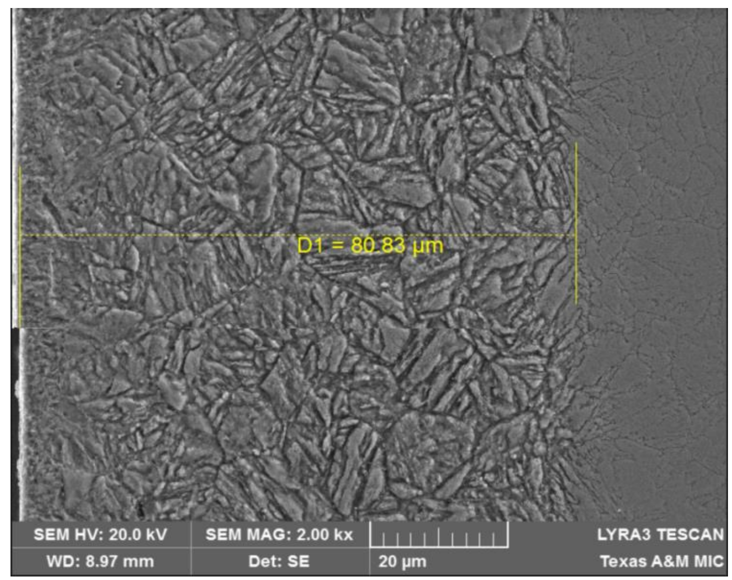


400°C for 30 minutes



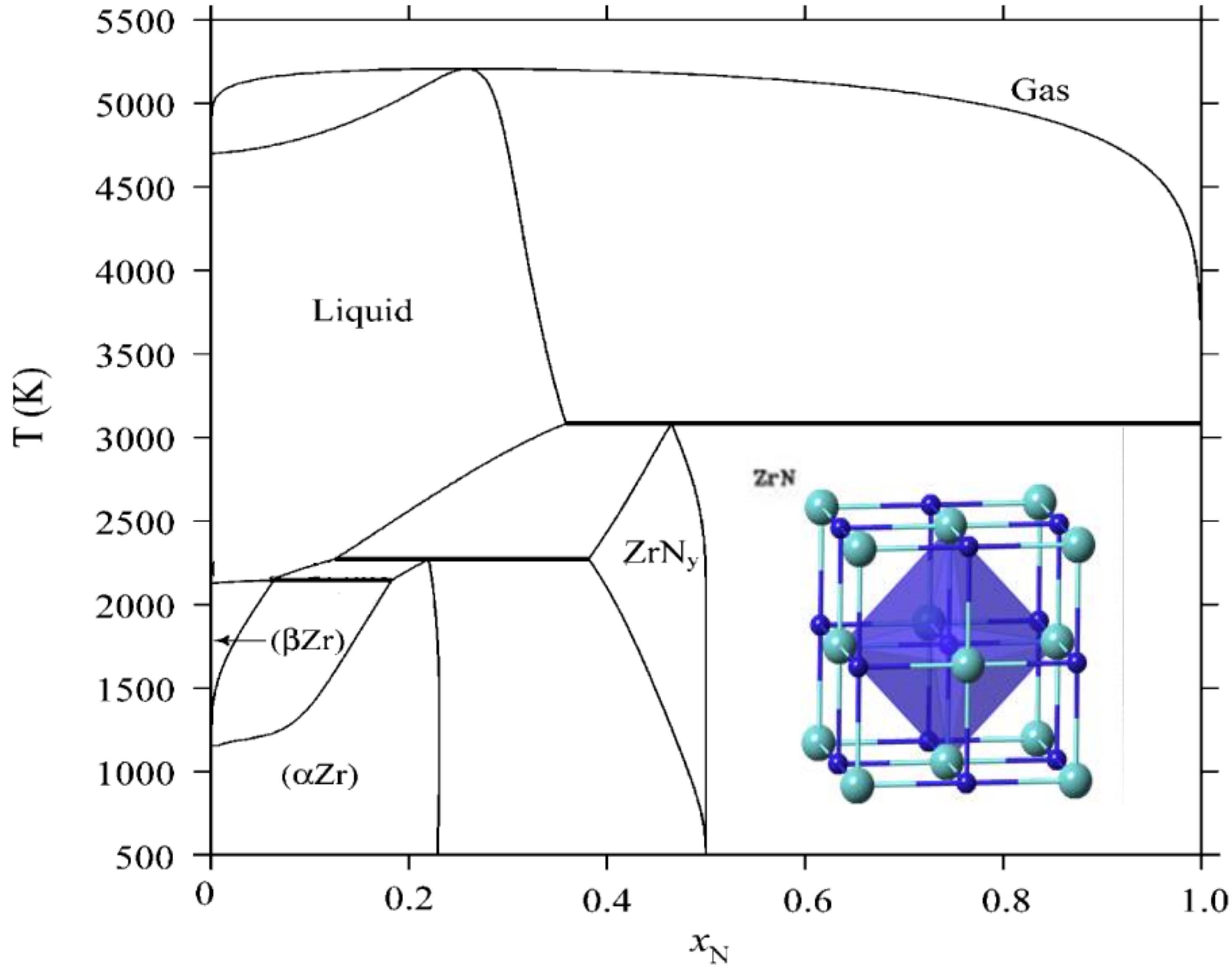


500°C for 30 minutes

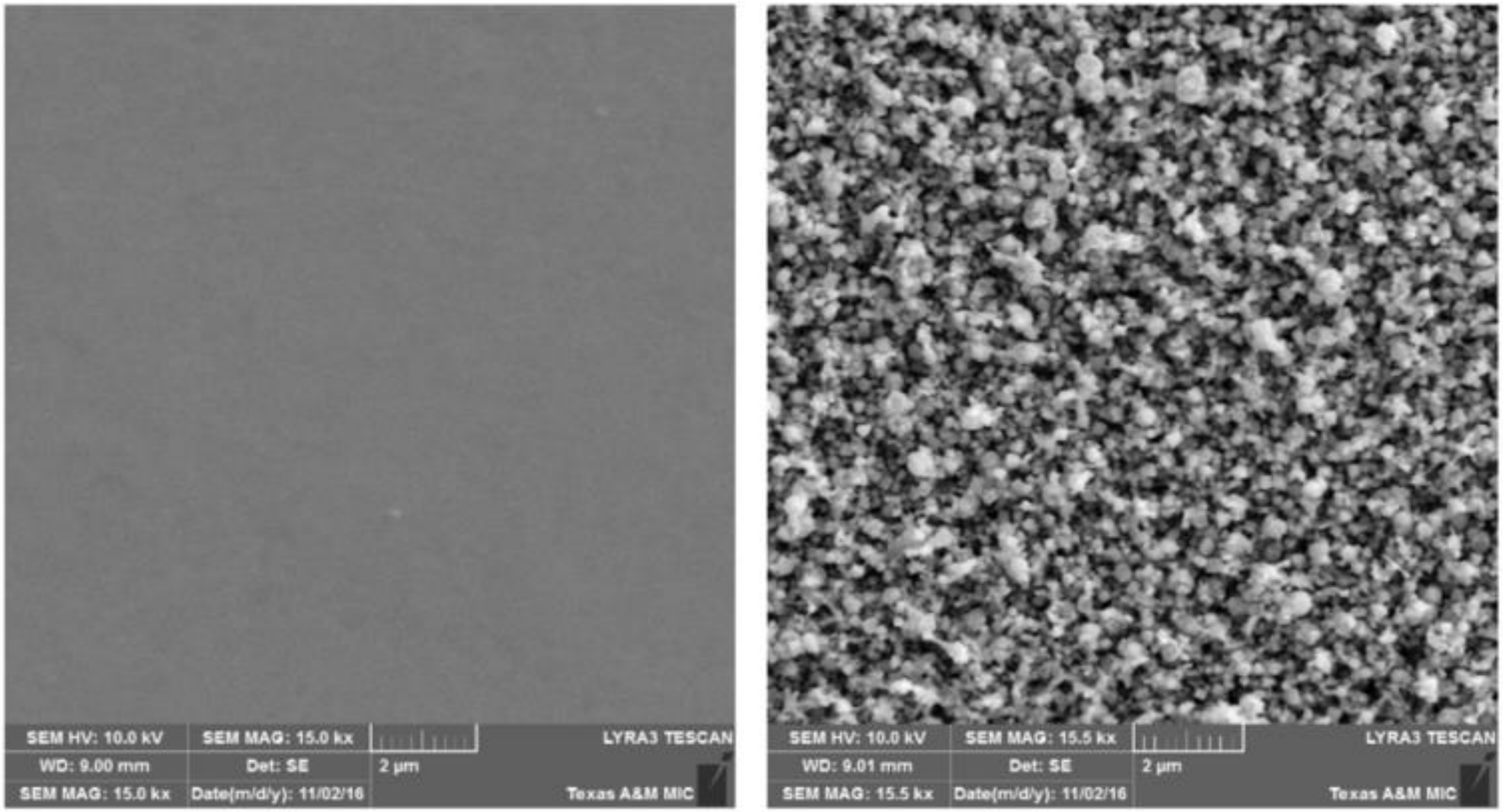


600°C for 30 minutes

Case #3: Nitridation of Zircaloy-4



Nitridation of Zircaloy-4

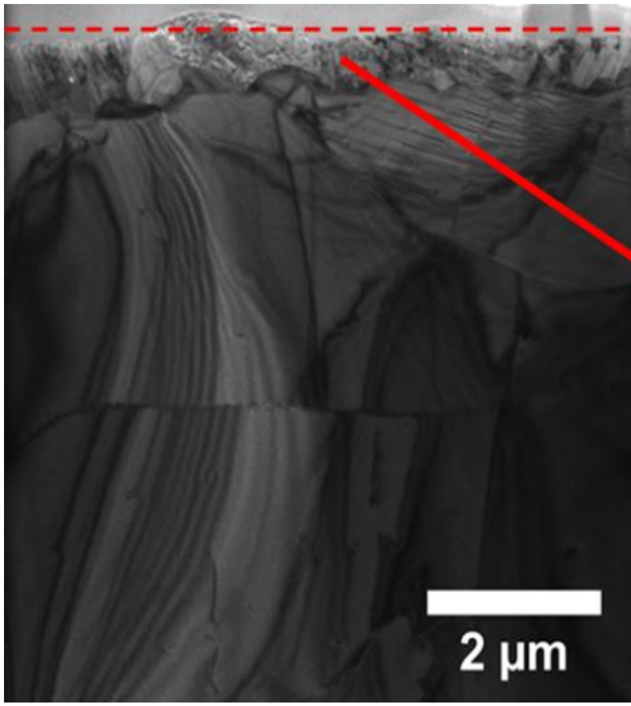


Reference　　　　Nitrided Zr4

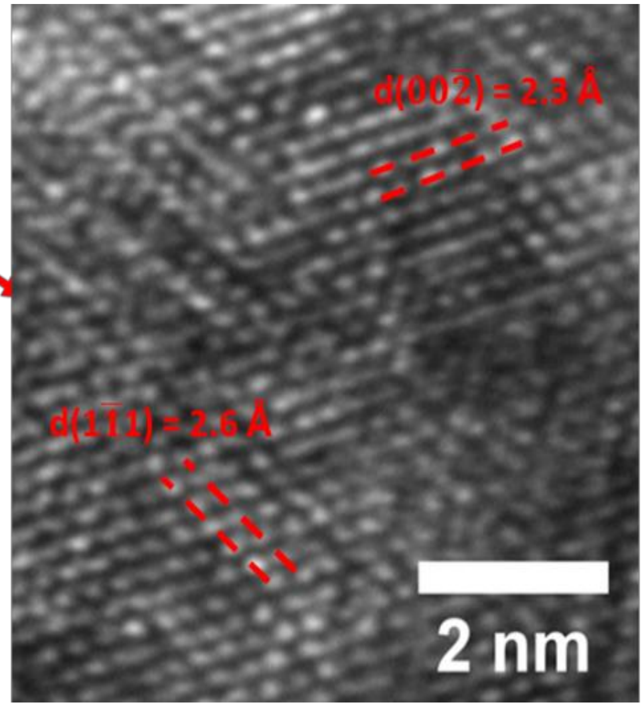
SEM surface images of control Zircaloy-4 (left) and nitrided Zircaloy-4 (right).

Nitridation of Zircaloy-4

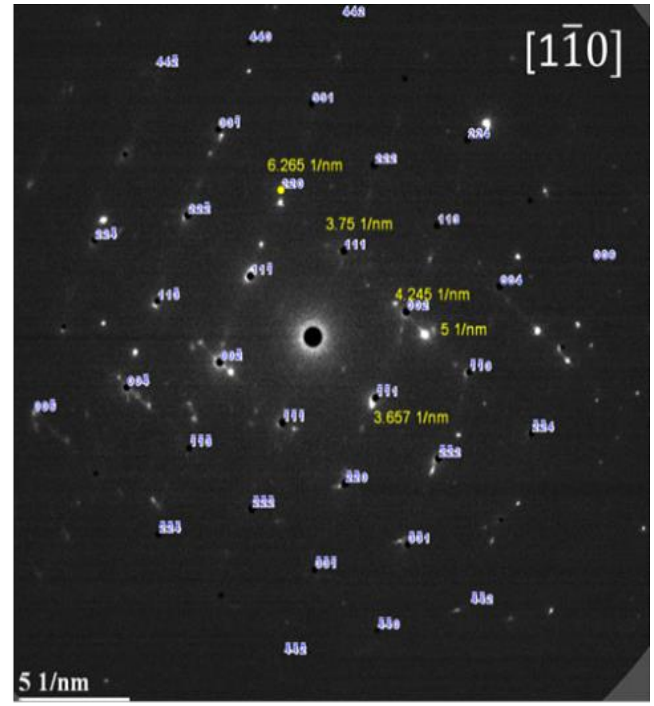
Confirmation of ZrN phase



Cross sectional TEM



high resolution TEM

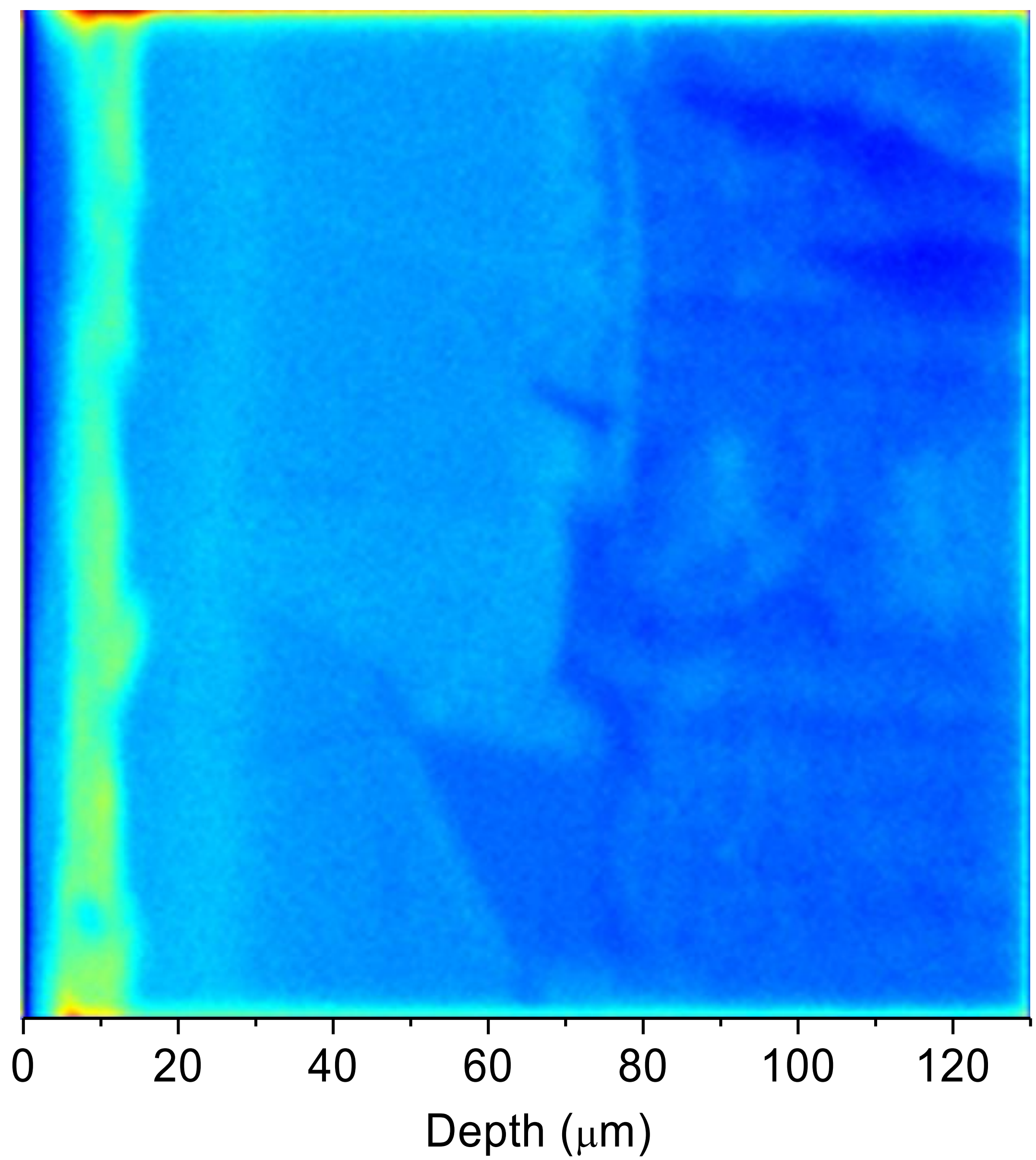


localized diffraction

The interplanar spacing, d(00$\bar{2}$)=2.3A and d(1$\bar{1}$1)=2.6A, match well with that of cubic ZrN phase. Diffraction patterns show the agreement of lattice distances with [111], [220] and [131] of cubic ZrN phase

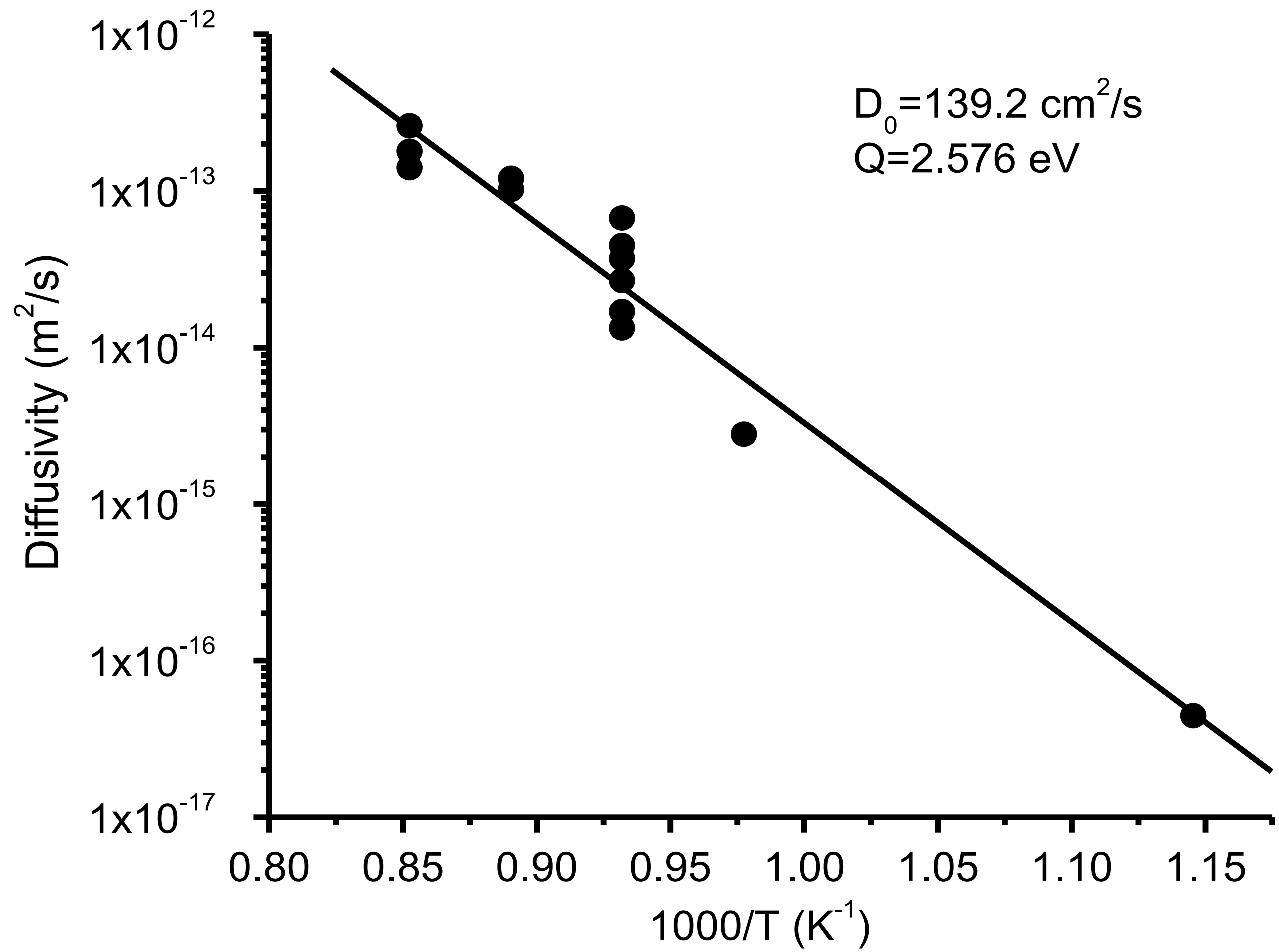
Nitridation of Zircaloy-4

Nitrogen mapping over cross section of nitride sample (FIB-based Nano SIMS)



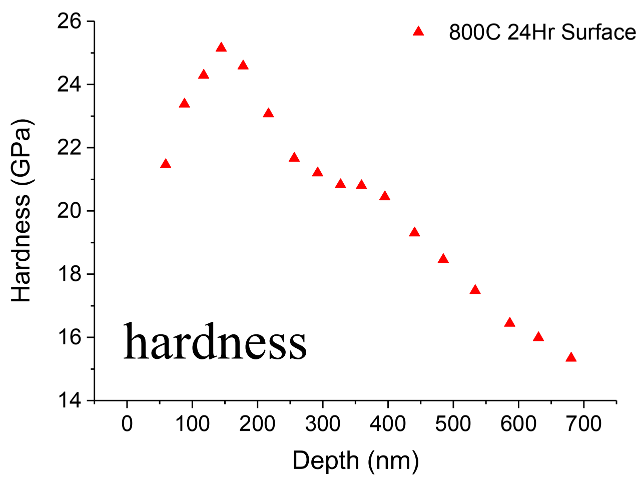
Nitridation of Zircaloy-4

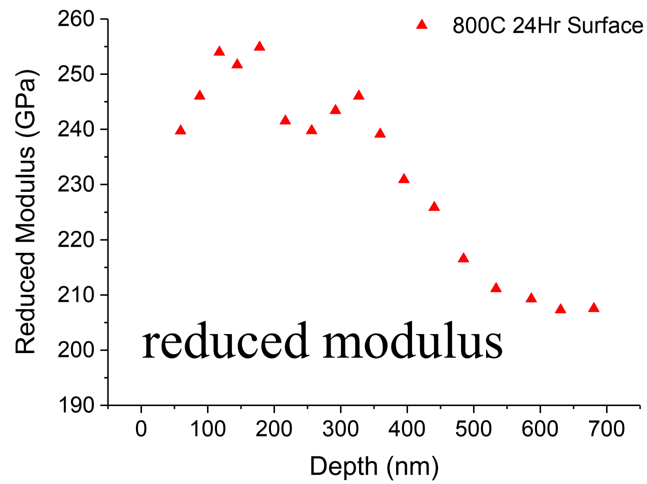
Diffusion Kinetics

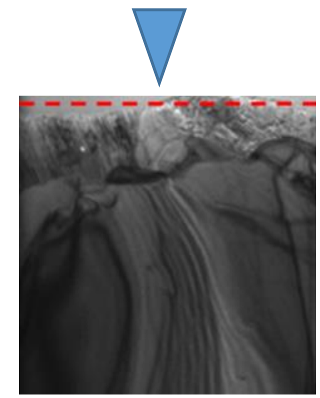


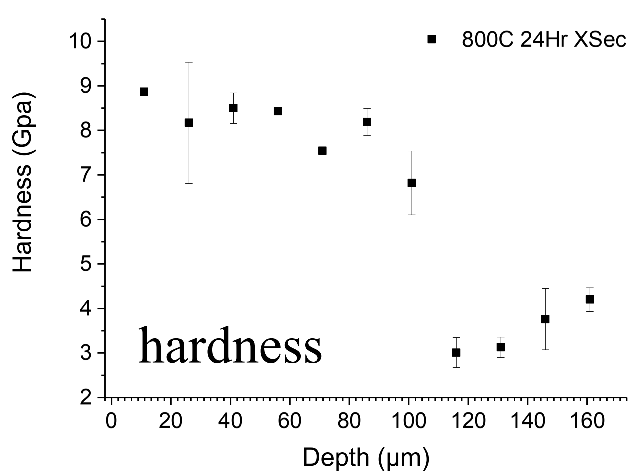
Nitrogen diffusion in Zircaloy-4 after plasma nitriding at floating potential.

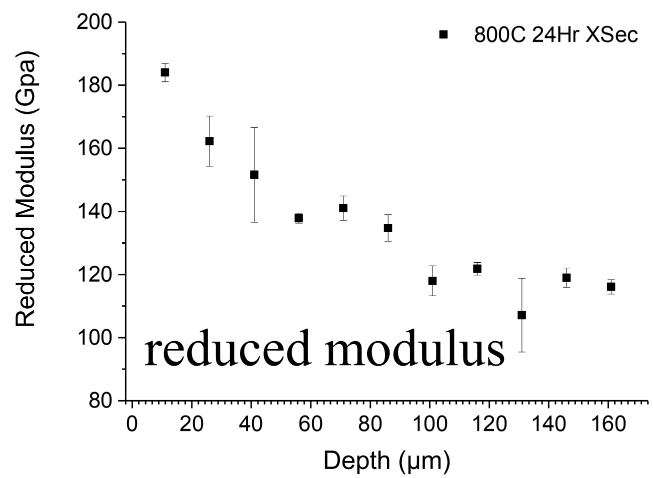
Nitridation of Zircaloy-4: Indentation tests

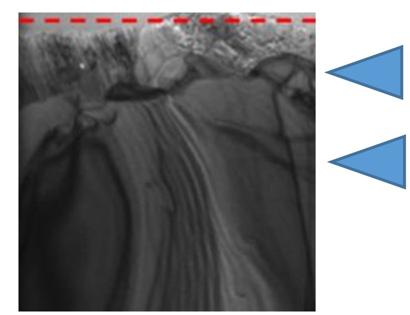




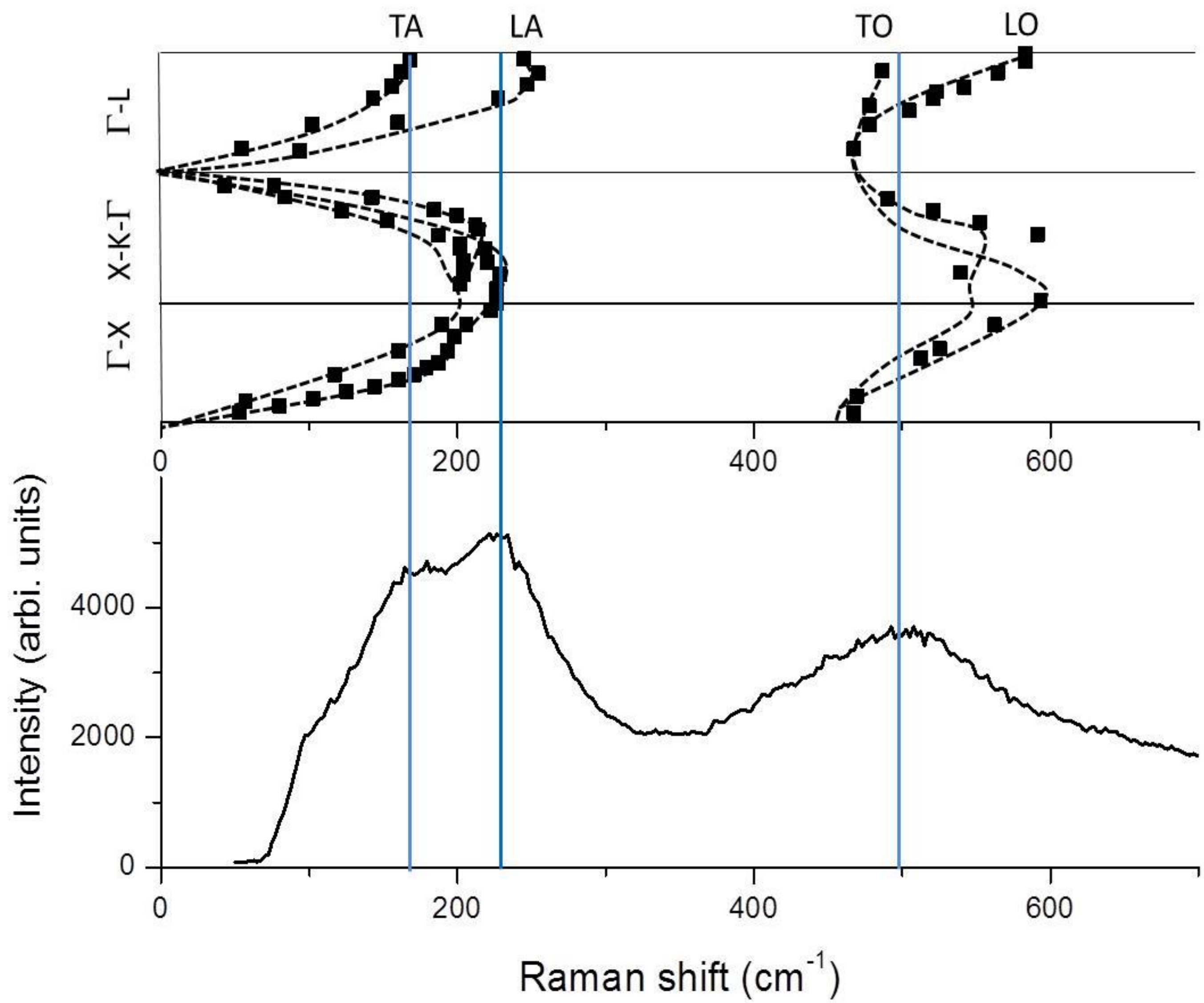






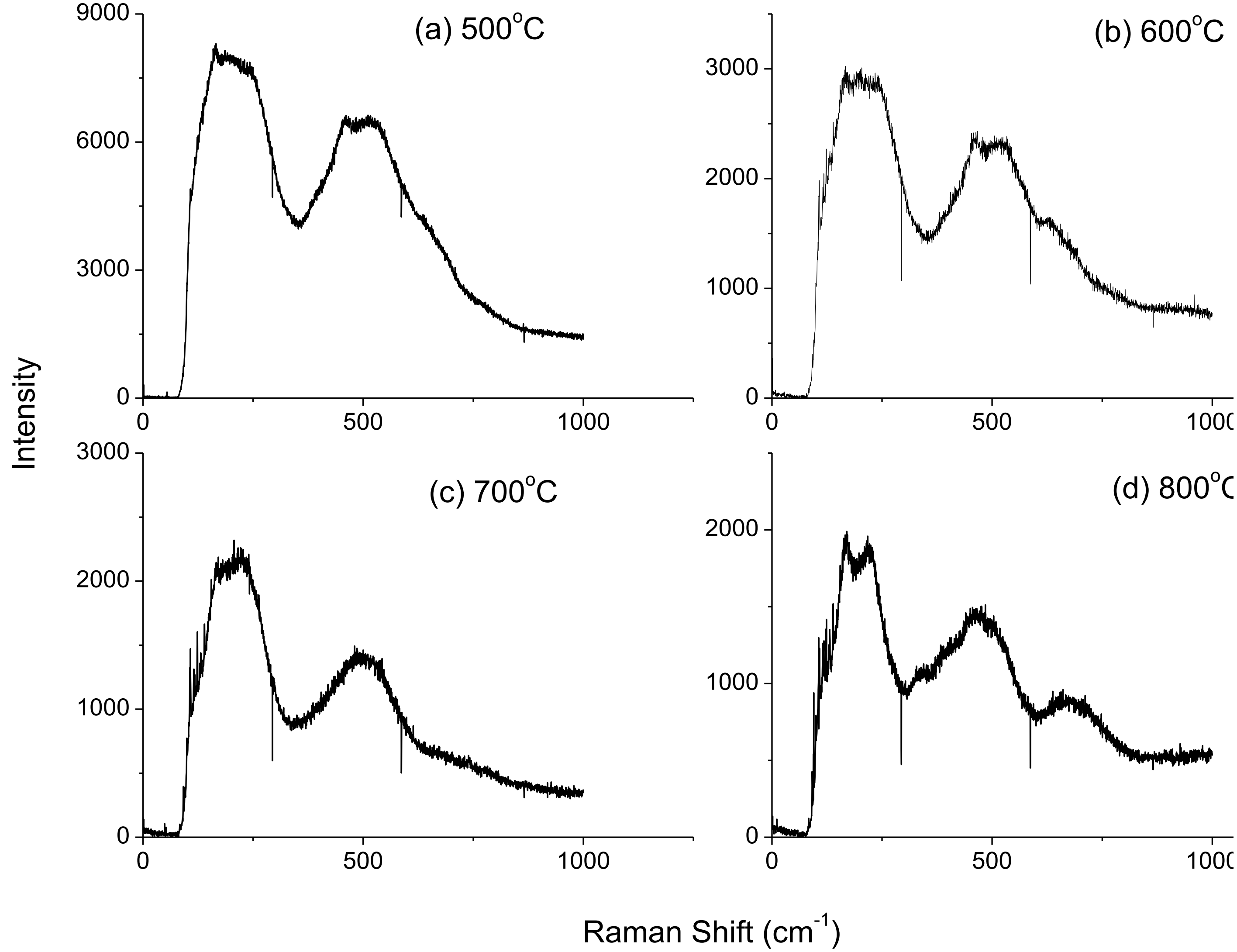


Raman spectrum of ZrN

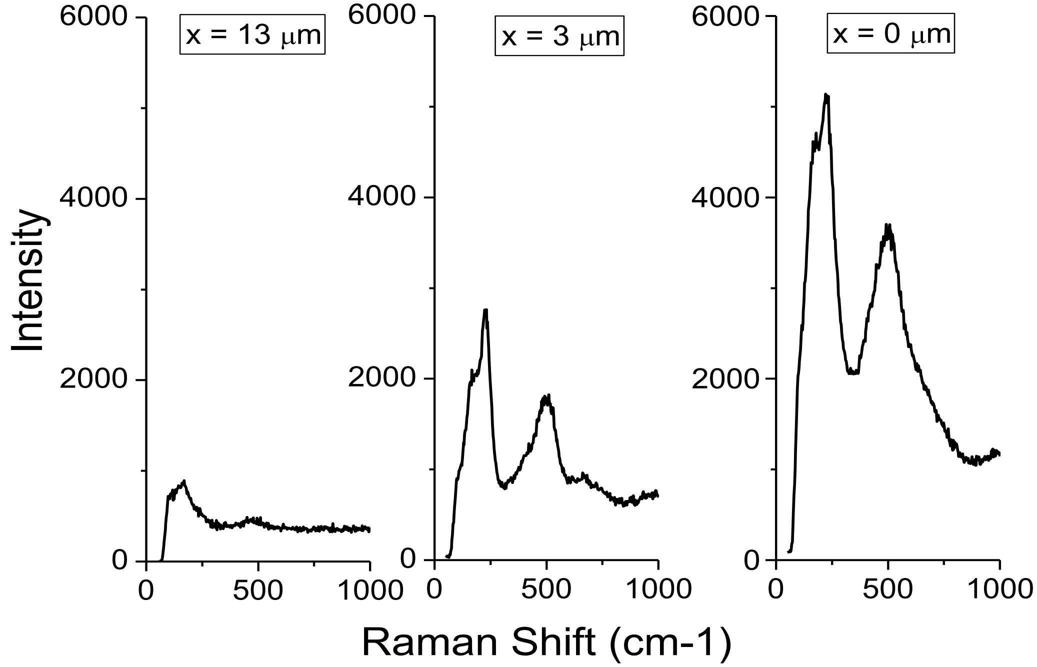


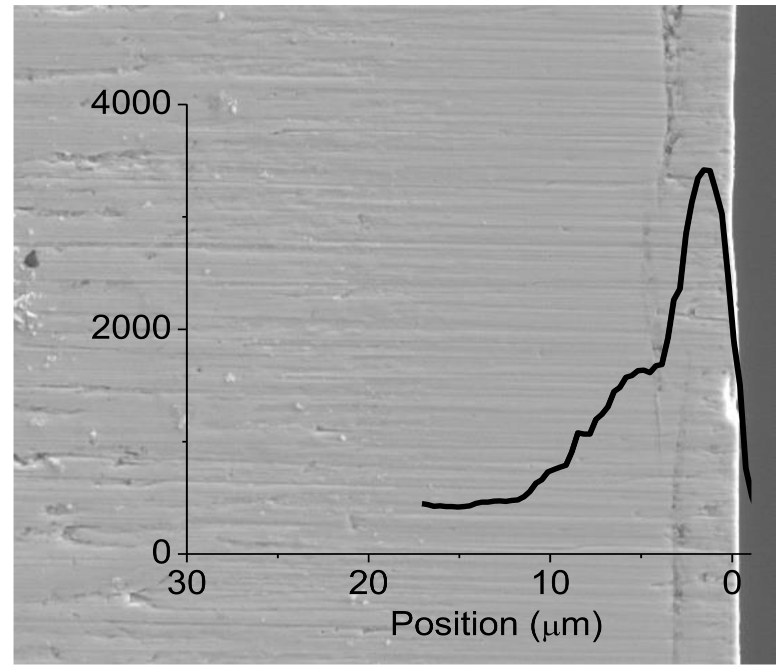
Nitridation of Zircaloy-4: Raman analysis

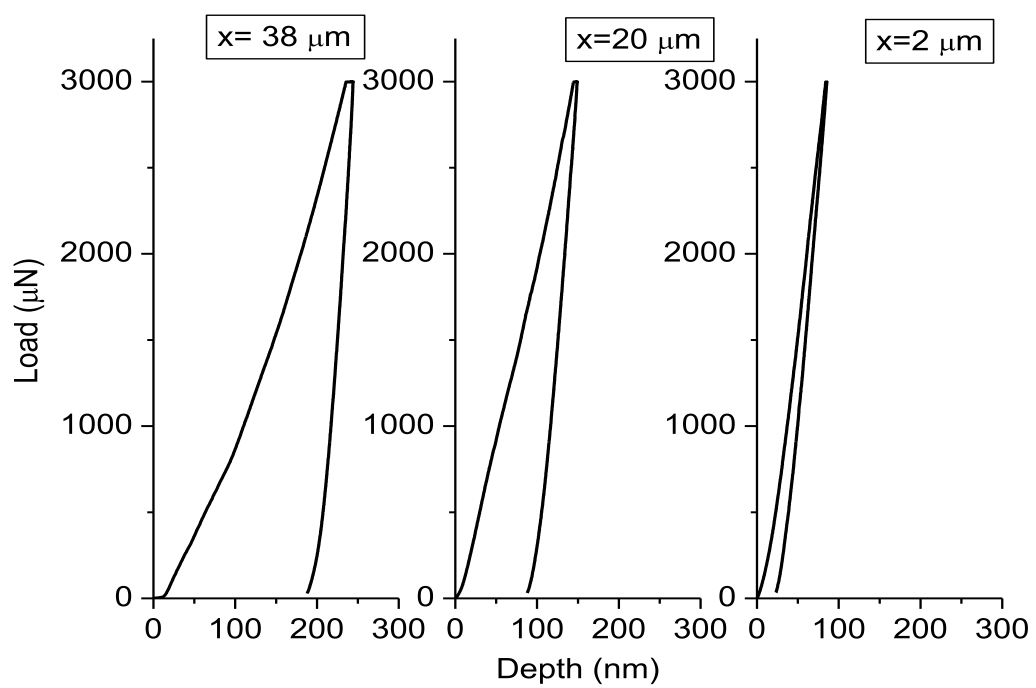
Temperature dependence studies

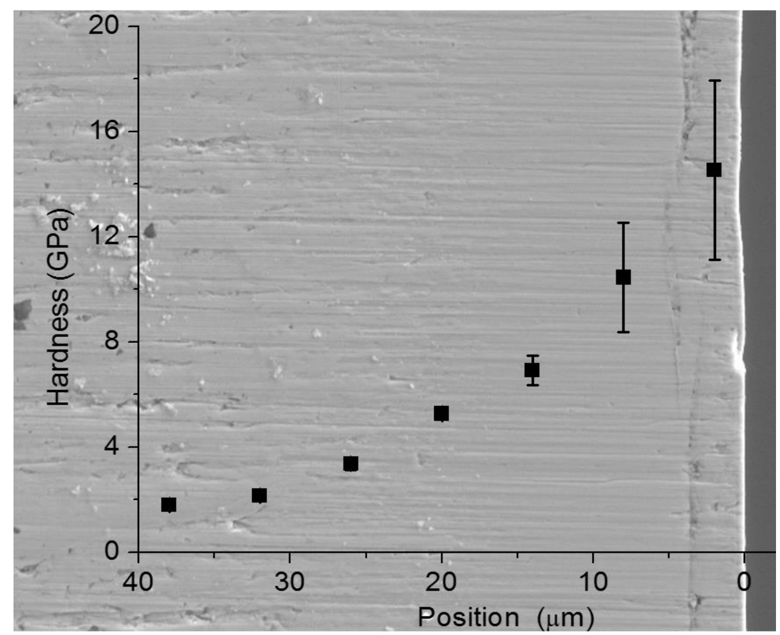


Nitridation of Zircaloy-4 (at 700°C)

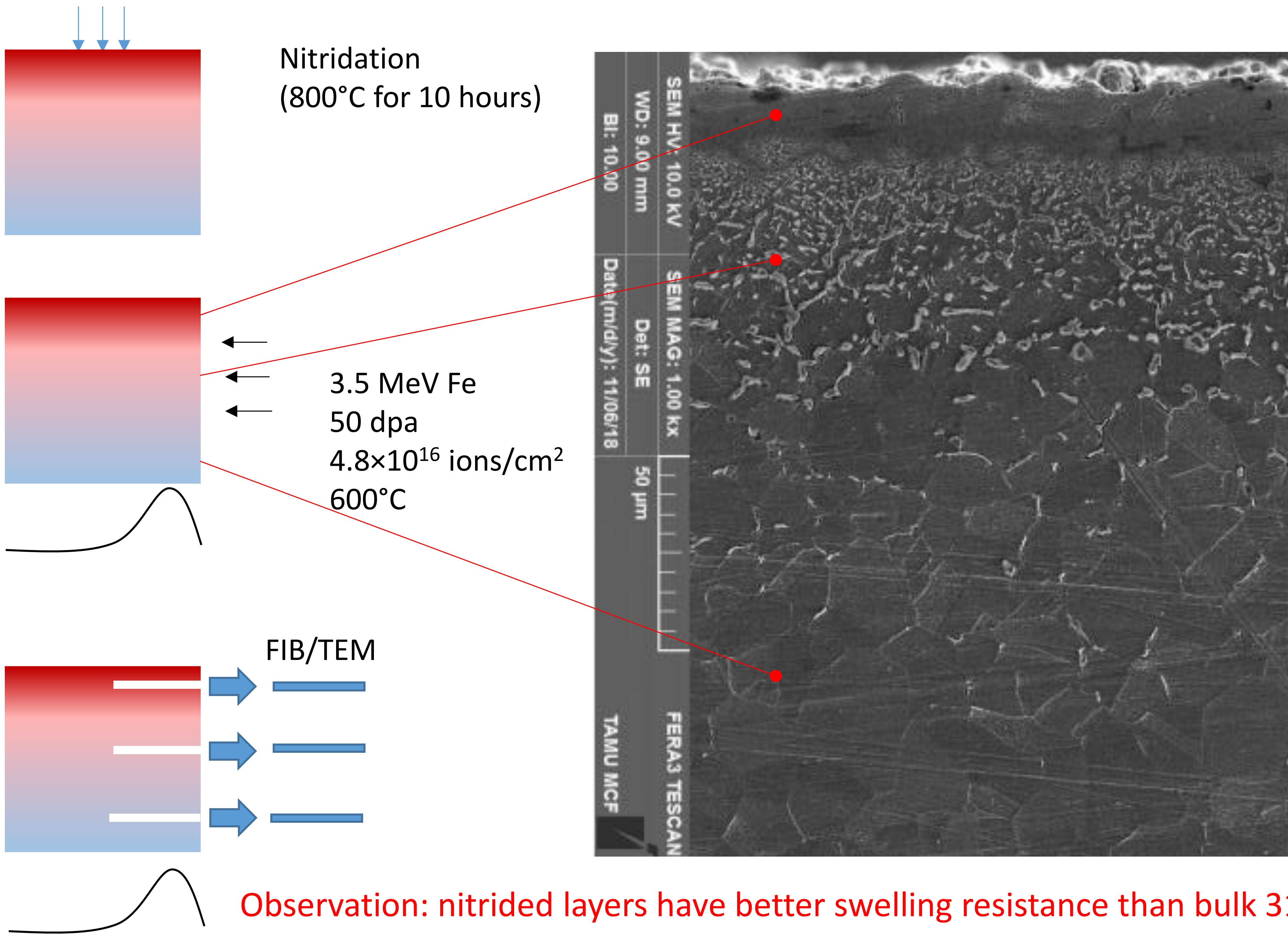






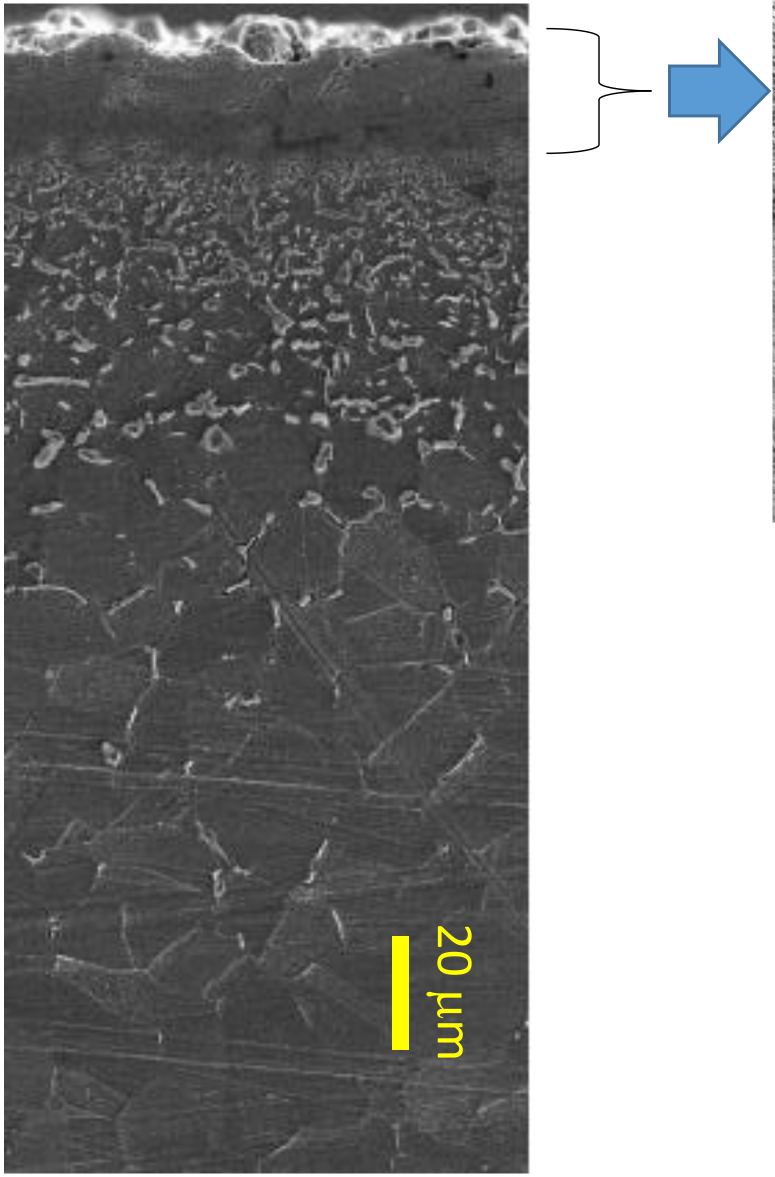


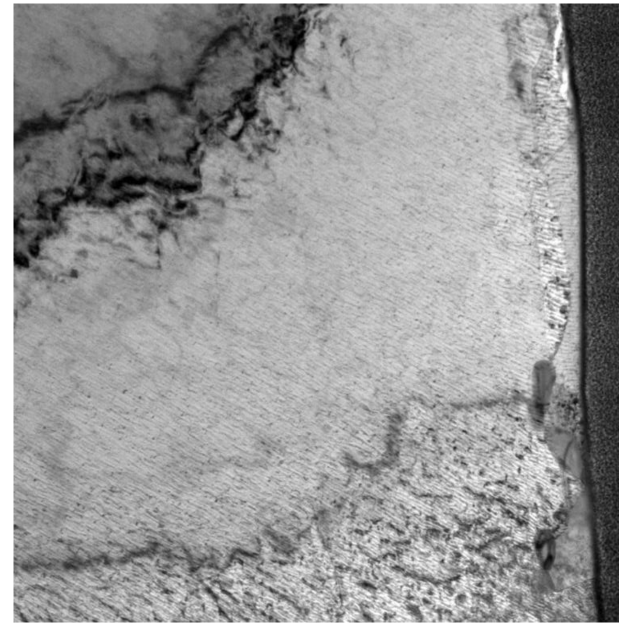
Irradiation testing of nitrided samples: 316L

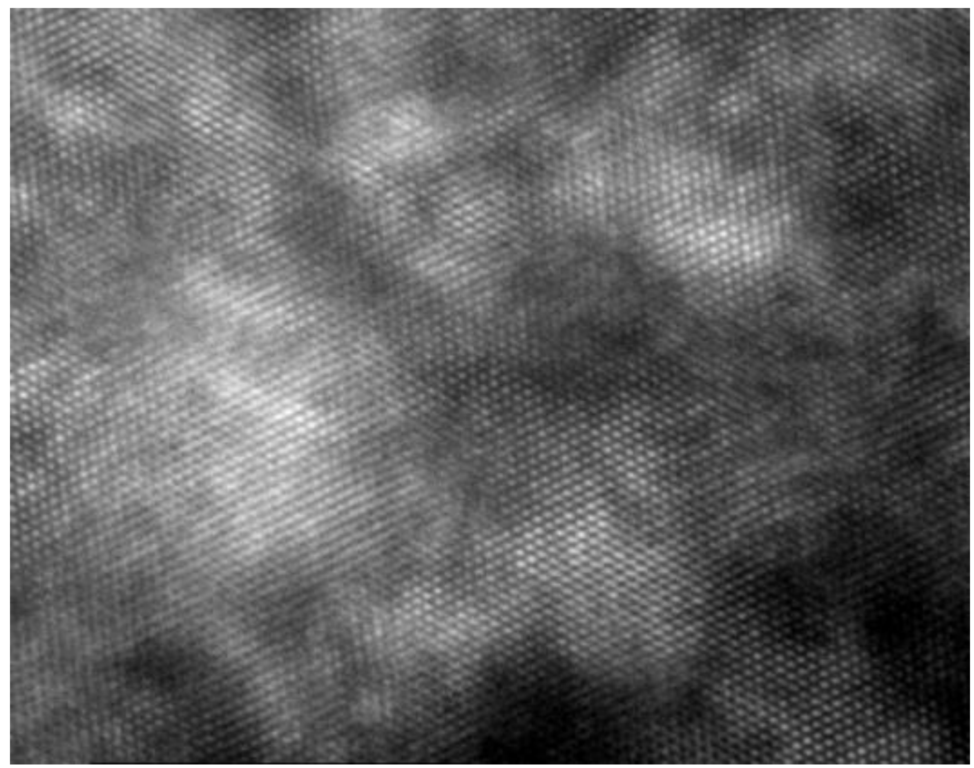


Observation: nitrided layers have better swelling resistance than bulk 316L

Nitride layer (top layer) of 316L after 50 dpa irradiation

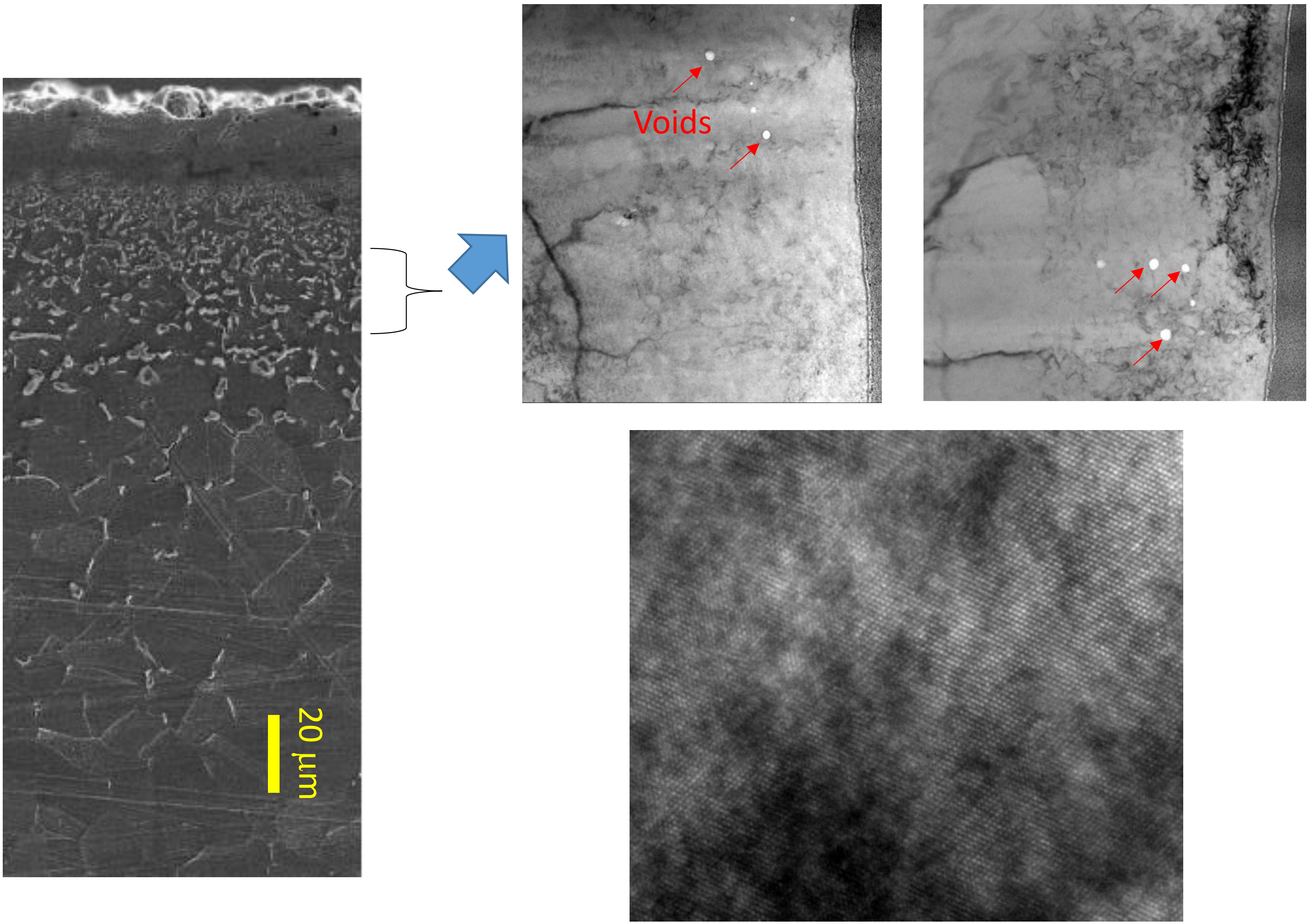




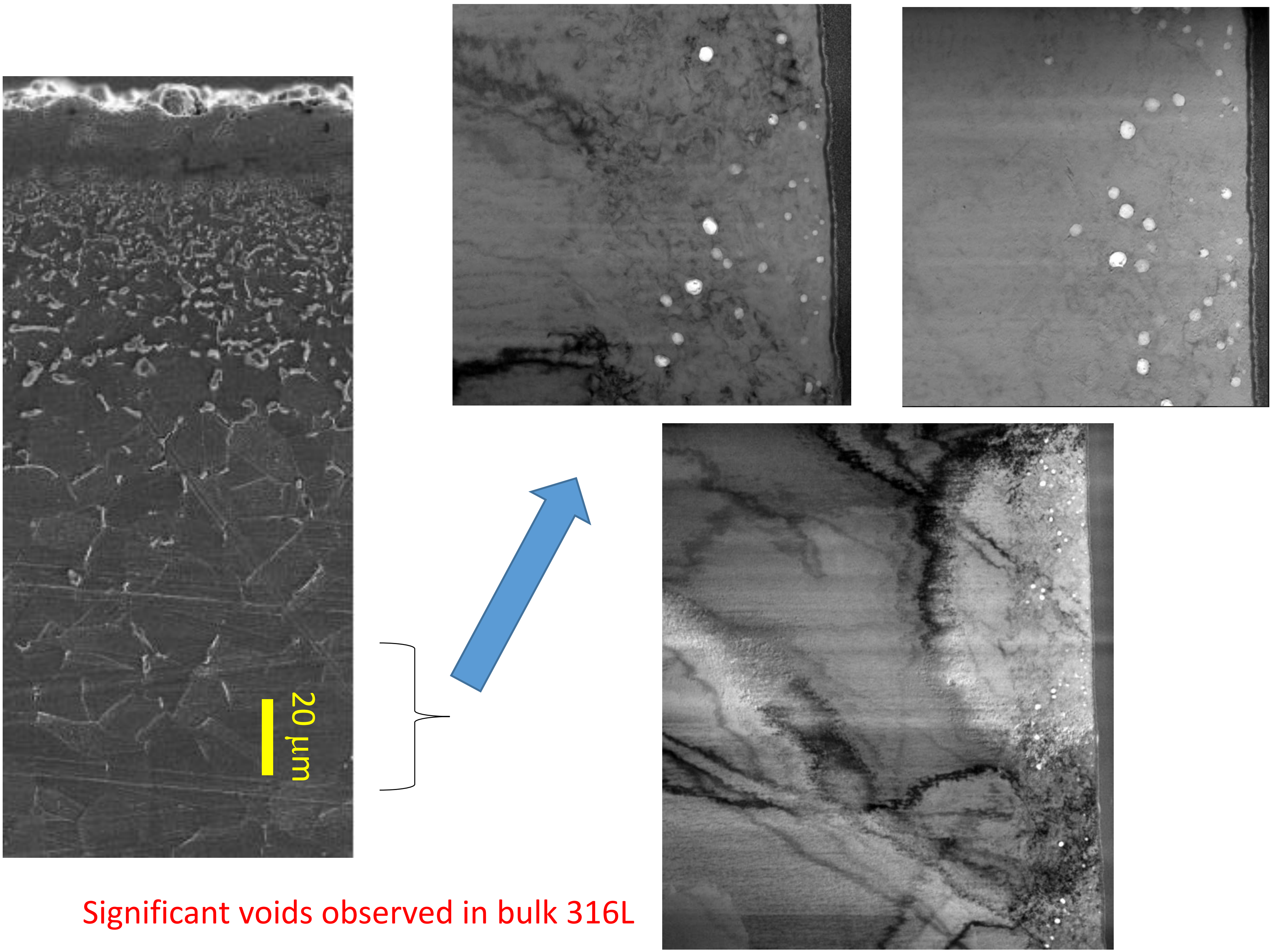


No voids observed
No amorphization observed

N Diffusion layer (middle layer) of 316L after 50 dpa irradiation



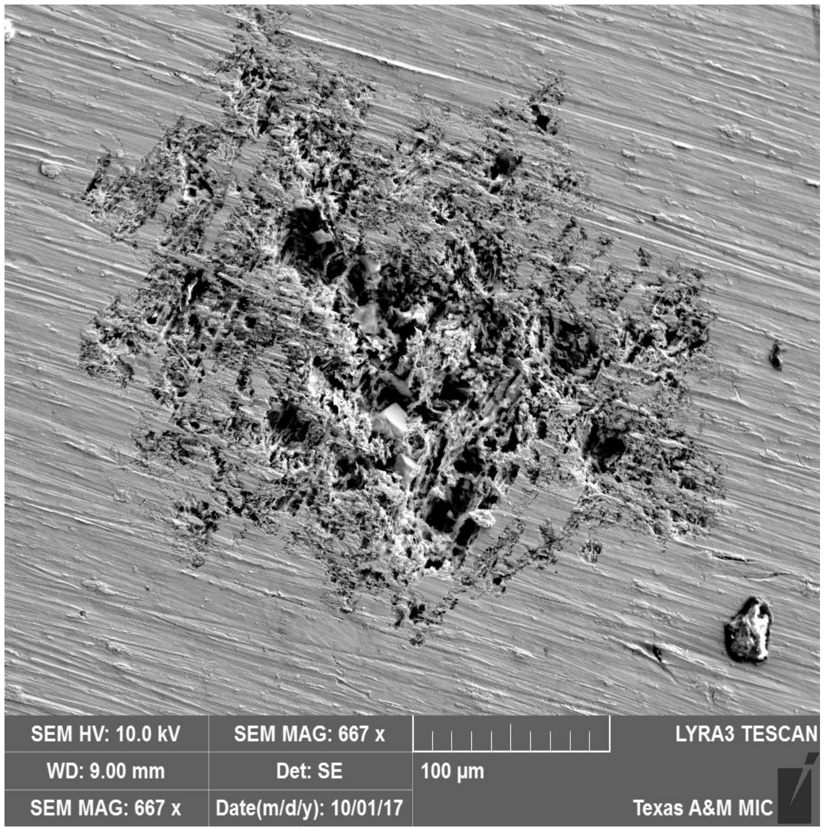
Bulk (bottom layer) of 316L after 50 dpa irradiation



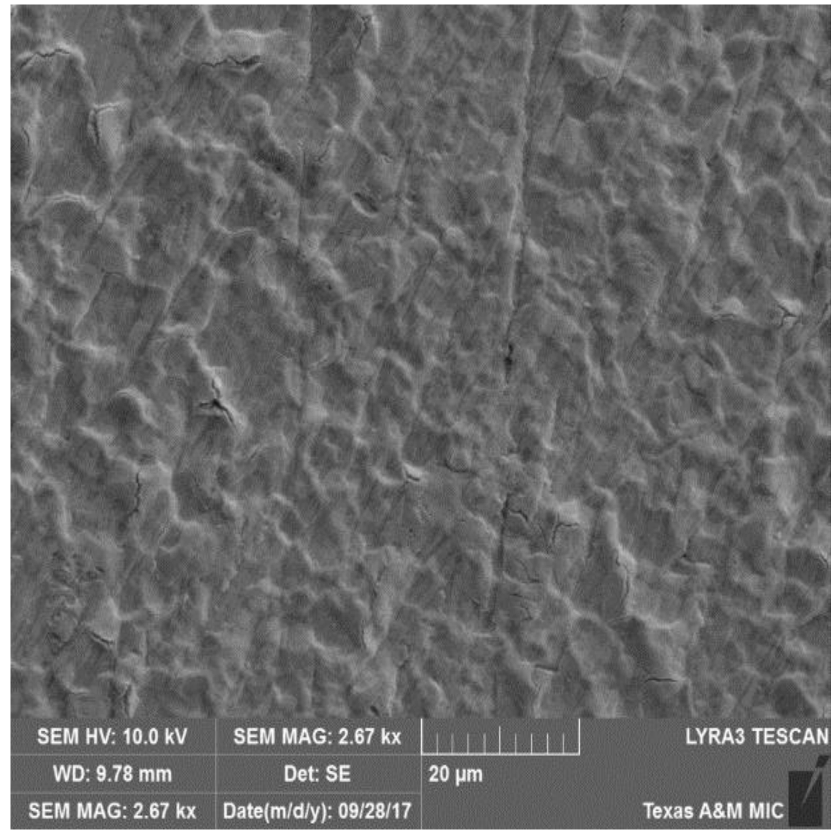
Significant voids observed in bulk 316L

Nitridation of Zircaloy-4: Corrosion Test

Reference sample without nitridation

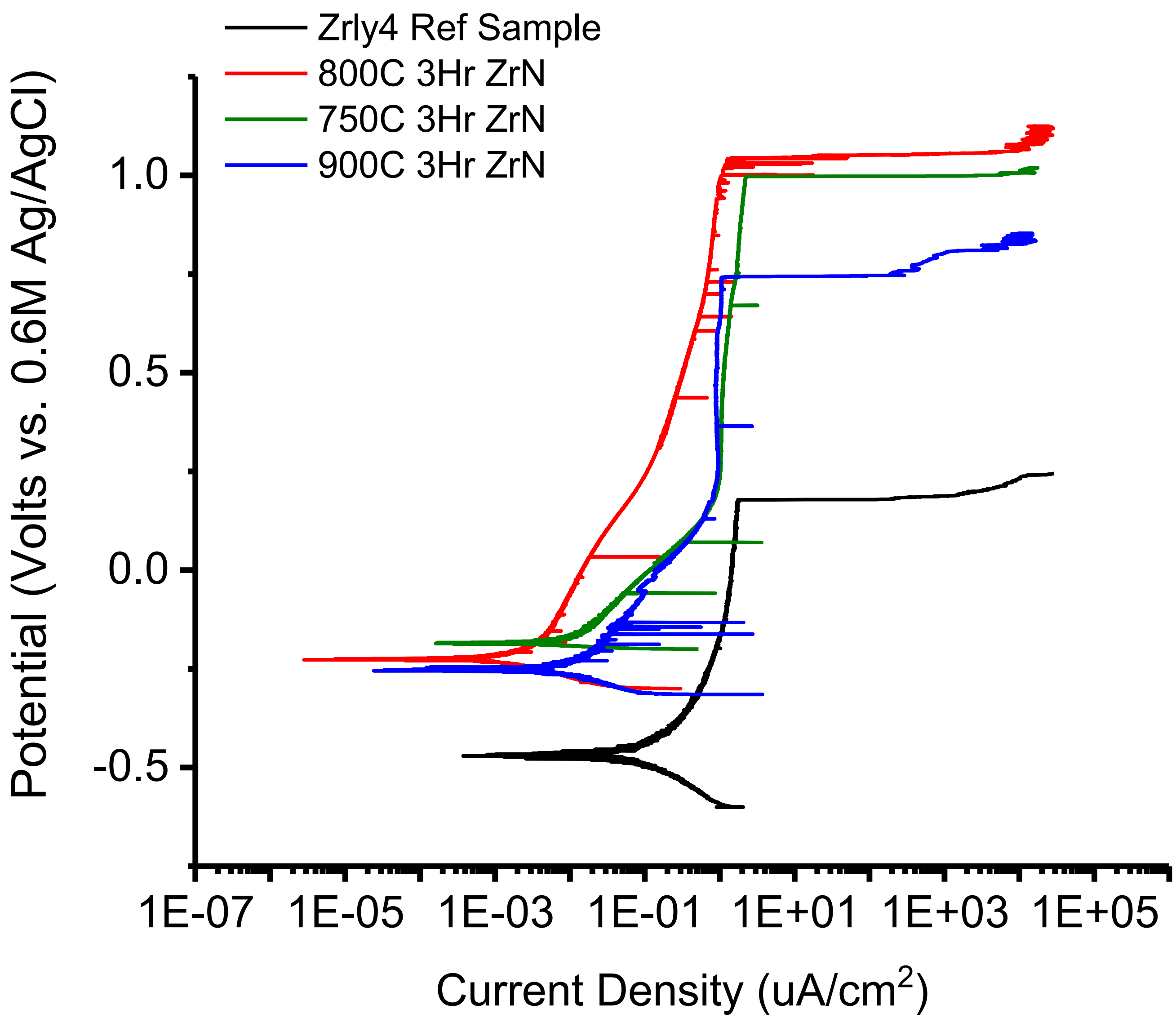


Nitrided sample



Surface morphologies of the tested Zircaloy-4 with or without surface nitridation

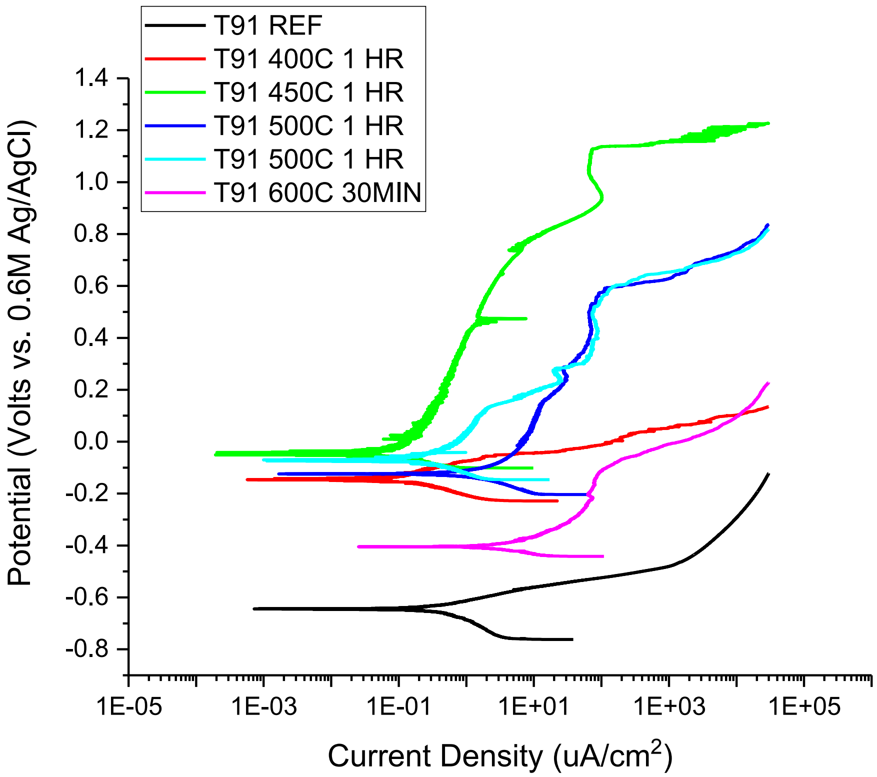
Nitridation of Zircaloy-4: Corrosion Test



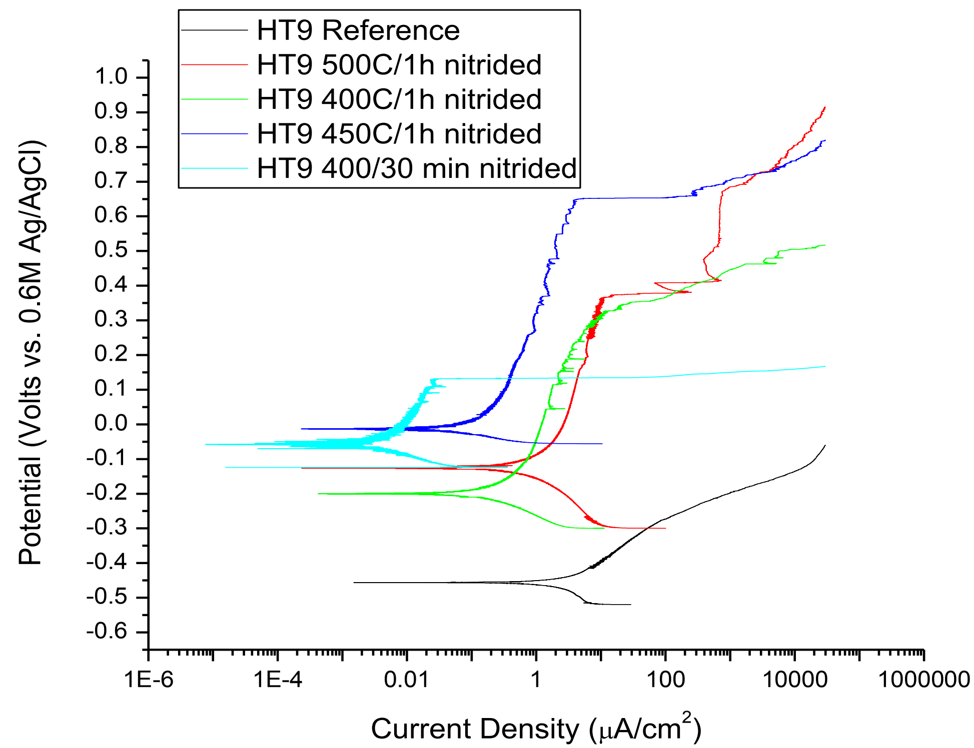
General observations:

- The value of the corrosion potential (also called Open Circuit potential) is higher for the nitrided samples.
- The corrosion current densities around the OCP potential are a few orders of magnitude lower for the nitrided samples compared to the bare sample.
- The breakdown potential is increased in the nitride samples.

Corrosion Test of Other Alloys



T91

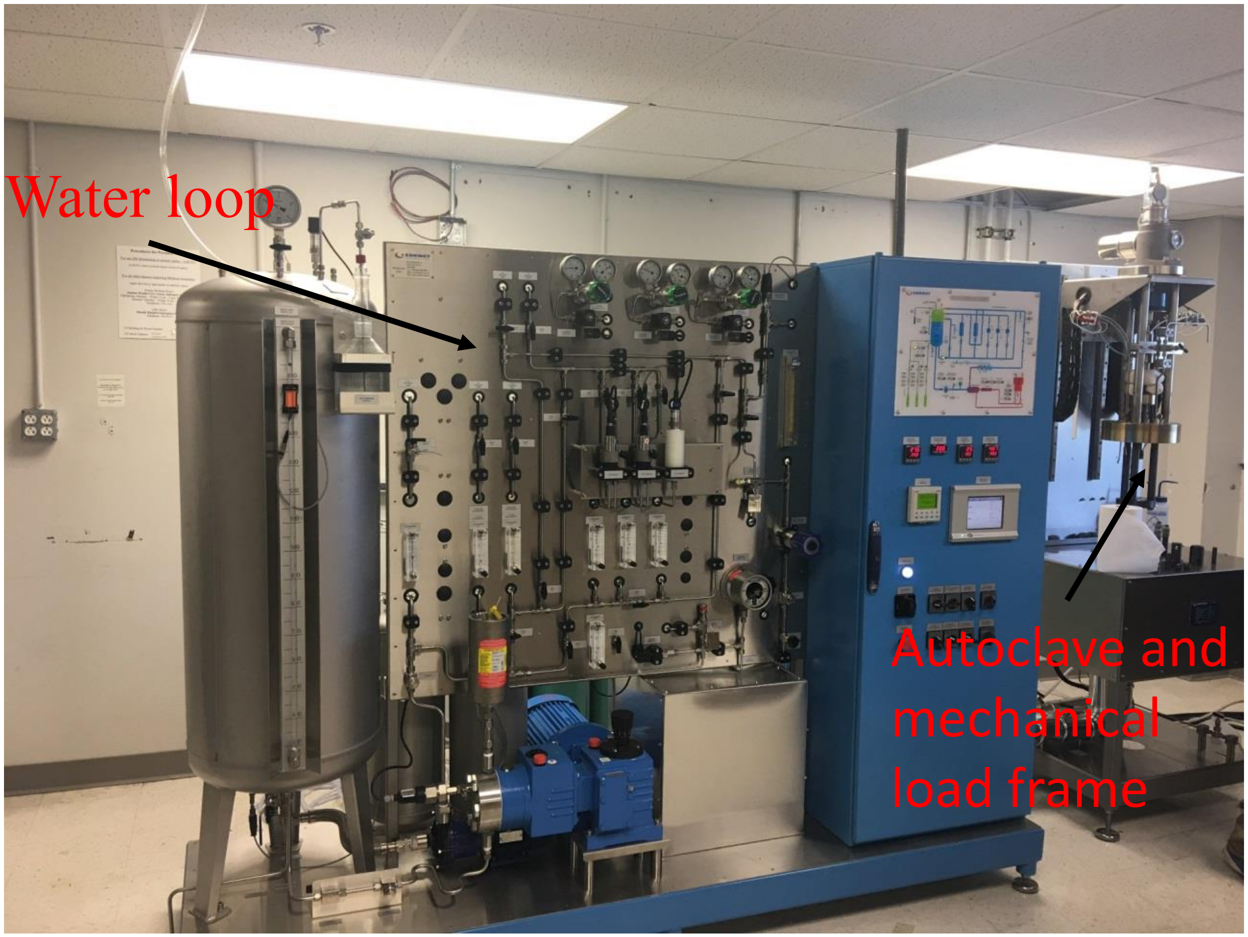


HT-9

The main conclusion:

In all samples, surface nitridation can improve corrosion resistance.

Additional and " true" corrosion tests in PWR-like coolant are still on-going (samples will be released on Dec. 25, 2018)

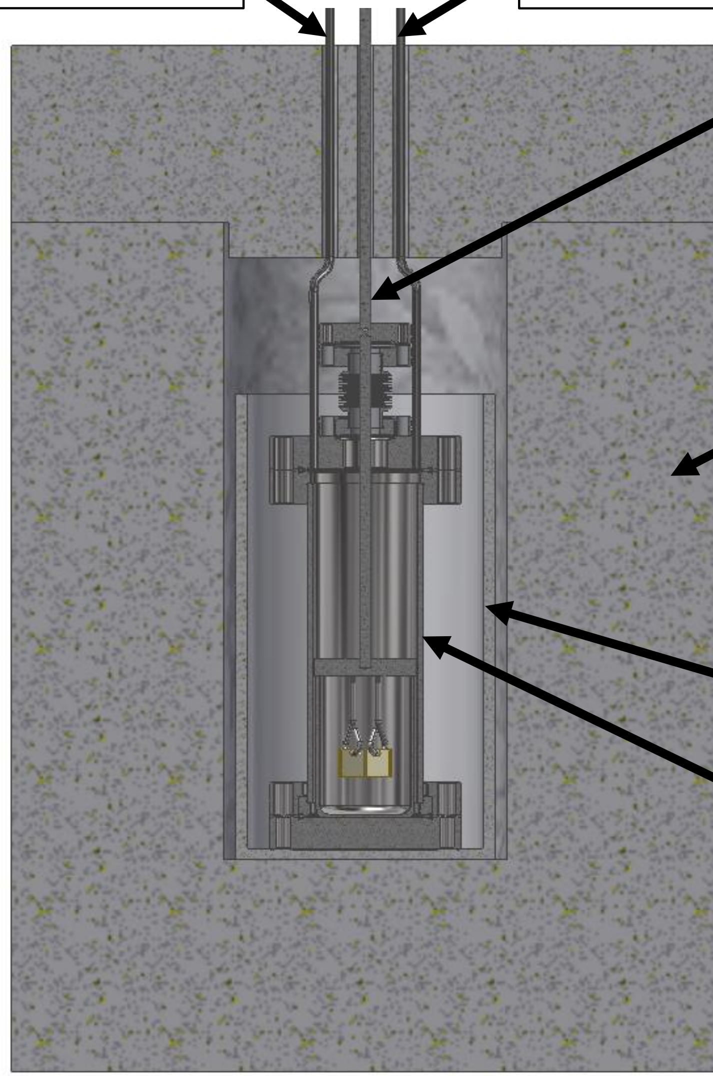


Specifications:

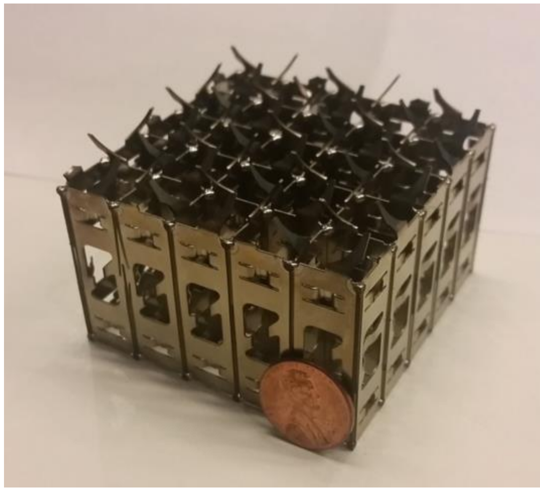
- Recirculation loop with a 4-liters autoclave for a 360ºC and 20 MPa water condition
- Dissolved hydrogen measurement and control
- Dissolved oxygen measurement and control

Additional and “ true” corrosion tests in Liquid Sodium are still on-going (samples will be released on Dec. 15, 2018)

- Liquid Sodium Corrosion Setup
- Temperature: 600 °C
- Atmosphere: High purity argon or high purity argon plus a desired concentration oxygen.
- All the materials in contact with the liquid sodium are either the samples or stainless steel 316.
- The difference with the molten salt one is that this setup has a closed system inside of the glove box. The molten salt one is sharing atmosphere with the glove box.

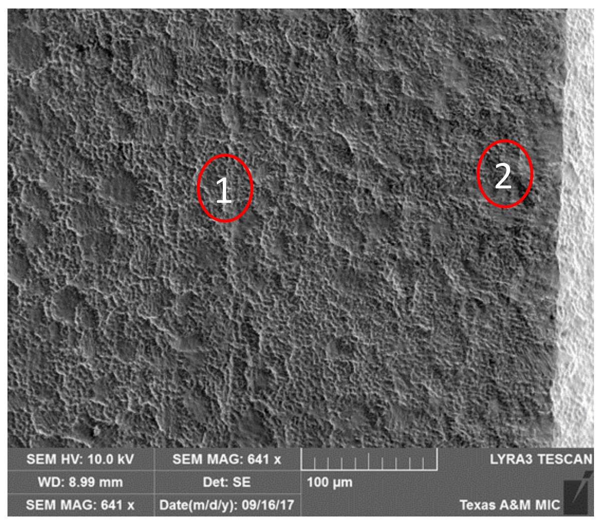


Nitridation of Westinghouse Zircaloy-4 spacer



EDS Measurement at Grid Edge

- Location 1   44% Nitrogen
- Location 2   40% Nitrogen



Thanks!

lshao@tamu.edu

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