
Influence of Surface Modifications on the Adsorption and Absorption of Tritium into Stainless-Steel 316

Introduction

High concentrations of tritium develop on stainless-steel (SS) surfaces exposed to a tritium atmosphere.¹ These high concentrations are attributed to tritium dissolution within the adsorbed water layers present on all metal surfaces.¹⁻⁴ Tritium dissolved within these layers contributes $\geq 20\%$ to the total inventory absorbed by SS.¹ Additionally, these water layers govern the migration of the isotope during an exposure to a tritium atmosphere, as well as during a storage period following the exposure. Because such a large fraction of the tritium inventory resides in the water layers, altering these layers by altering the metal surface can significantly affect the total quantity of tritium absorbed by SS.

In the present study, the effect of altering the metal surface on the migration and total absorption of tritium into SS 316 was investigated by preparing SS samples with a variety of surface modifications, which included mechanical polishing, electropolishing (EP),^{5,6} gold plating, nitric-acid treatments, and Fe or Cr oxidation.⁷ The migration and total absorption of tritium in the various SS samples was measured using plasma-induced ion sputtering⁸ and thermal desorption.⁹

A quantitative tritium migration model (QTRIMM) based on Fickian diffusion through composite media is used to describe the measured total tritium inventories and migration rates. The composite medium treated in this model is the adsorbed water layer(s)/metal-lattice system. This model accounts for the high concentrations of tritium on the surfaces of SS by relating the tritium concentrations on the surface and in the metal lattice at the surface/metal-lattice interface.⁸

Modeling

QTRIMM is based on a numeric solution to the diffusion equation¹⁰ and can be used to calculate the tritium concentration profiles in a metal substrate.⁸ The boundary conditions used in this model are based on several fundamental assumptions. The first assumption is that a rapid equilibrium occurs between tritium in the gas phase and tritium dissolved in the adsorbed surface water. The second assumption is that all iso-

tope exchange reactions have equal probability; consequently, there will be equal tritium mole fractions in the gas phase and on the surface. Equal reaction probabilities are not likely because the formation of double-isotope species, such as T_2O , is not as probable as the formation of a single-isotope species, such as HTO. The consequence of making this limiting assumption will be discussed later.

$$\chi_{\text{surf}} = \chi_{\text{gas}}, \quad (1)$$

where χ_{surf} and χ_{gas} are the mole fractions of tritium in the adsorbed water layers and gas phase, respectively. The assumption of equal mole fractions leads to an equation for the quantity of adsorbed tritium (A_{surf}) on a stainless-steel surface during exposure to tritium gas:

$$A_{\text{surf}} = \lambda * \chi_{\text{gas}} * SA * Q * \frac{2\text{-mol H}}{1\text{-mol H}_2\text{O}}, \quad (2)$$

where λ is the tritium decay constant (Bq), SA is the surface area of the metal (m^2), and Q is the surface concentration of adsorbed water ($\text{mol H}_2\text{O}/m^2$).

Once tritium adsorbs onto the metal surface, it can diffuse into the metal lattice. To determine the flux of tritium across the surface-water layer/metal-lattice interface, the tritium concentrations at the interface are related through the ratio of the tritium solubilities in the two regions.⁸

The final assumption is that negligible quantities of tritium desorb from the surface during the storage period between charging the sample with tritium and each experiment. Little tritium is expected to desorb during this period because the samples were stored under dry helium at 1 atm. Measurements of the residual tritium in the storage vessels show that less than 5% of the activity is lost to the vessel during the storage period. Tritium concentrations redistribute throughout the sample by diffusing from the water layer into the metal lattice to attain an equilibrium state.

Experimental Setup and Procedures

1. Surface Modifications

The surfaces of each sample underwent various pretreatments intended to modify the metal surface. All samples measured $5.1 \times 1.8 \times 0.3 \text{ cm}^3$, and their surfaces were machined away to remove manufacturing defects and to expose the metal lattice. The samples were cleaned first with acetone followed by de-ionized water, and finally dried with isopropyl alcohol. Samples receiving no additional treatment are referred to as “as received” or AR. The next modification involved mechanically polishing the AR samples to yield finer surface finishes. Several mechanically polished samples were then electroplated with gold to a thickness of $1.7 \text{ }\mu\text{m}$. To bind the gold to the surface, a nickel strike interface was necessary. This interfacial layer had a thickness of $6 \text{ }\mu\text{m}$. Another subset of the mechanically polished samples was treated with methods III and IV described by Boulange-Petermann *et al.* for generating hydrophobic and hydrophilic surfaces.¹¹ In this technique, the samples were washed with 0.5 M of NaOH and then placed in either a 0.2-M or a 4-M nitric-acid bath. Lower acid concentrations are expected to yield more hydrophobic surfaces, while higher acid concentrations should yield hydrophilic surfaces.

The remaining mechanically polished samples were divided into three sets and each set was electropolished for a different duration. The first set (EP2) was electropolished for 10 min while the second set (EP3) was electropolished for 5 min. The third set (EP) was electropolished for an unknown time, as determined by the polisher. The intent of increasing the duration of electropolishing was to extend the surface chromium concentrations deeper into the metal lattice. Increased chromium concentrations are expected to reduce tritium adsorption.¹²

Several samples from the third set of electropolished samples were subjected to one of two treatments intended to enhance either the Fe or the Cr concentrations in the near-surface region.⁷ These treatments were intended to test the impact of surface composition on the tritium absorption into stainless steel.

2. Surface Analysis

The surface roughness of each finish was measured using a Zygo NewView 100 interferometer or a Zygo NEXView interferometer (Table 147.V). No surface roughness data were available for Batch C oxidation treatments.

The near-surface compositions obtained with x-ray photoelectron spectroscopy (XPS) for select samples are shown in Figs. 147.44 and 147.45. The surfaces of samples treated to enhance either the Fe concentrations (oxidation treatment #1) or the Cr concentrations (oxidation treatment #2) exhibited two distinct regions, each with different Fe and Cr concentrations. In the present study, the average surface concentrations of Fe and Cr were used because the experimental methods represent average tritium interactions with the entire sample’s surface. The near-surface composition for the EP sample shows an increase in the Cr content compared to AR, polished, and the nitric-acid-treated samples. However, the EP process suppressed the Fe content compared to AR and the acid and oxidation treatments. It is also clear that the 0.2- and 4-M acid treatments increased both the Cr and Fe content of the near surface compared to AR, but the increase in Cr between the two acid treatments is nearly identical.

Comparatively, oxidation treatment #2, and the polished samples have a Cr and Fe composition that falls in between the two acid treatments. Therefore, if the surface composition controls tritium absorption, the total quantity of absorbed tritium in polished samples and samples undergoing oxidation treatment #2 should be between the tritium quantities contained within the samples treated with either concentration of nitric acid.

Figures 147.45–147.47 compare the Fe and Cr $2p_{3/2}$ photoelectron spectra as a function of depth into the metal sample. To collect these data, the surfaces were etched at a rate of 6.7 nm/min and a spectrum collected every 15 s. The resulting collection of spectra for a single sample shows the evolution of the oxidation states of Fe and Cr as a function of depth. In

Table 147.V: Measured surface roughness (R_a) for various surface finishes.

Batch A		Batch B		Batch C	
Finish	R_a (nm)	Finish	R_a (nm)	Finish	R_a (nm)
AR1	434	AR2	351	AR3	535
EP2	110	Polish #12	338	Polished	81
EP3	85	Polish #8	316	EP	92
0.2-M HNO ₃	74	Polish #3	46		
4 M	73	Gold	57		

general, the results show a decrease in the oxide concentration and an increase in the elemental composition of each metal with increasing depth. Additionally, each set of spectra indicate that all surfaces (except EP samples and samples that underwent oxidation treatment #1) are dominated by a mix of iron (III) and iron (II) oxides, with a smaller concentration of chromium (III) oxide.

3. Sample Loading

All stainless-steel samples were charged with tritium by exposing the samples to a deuterium–tritium (DT) gas mixture at 25°C for 24 h. After exposure, the samples were stored in separate metal containers under a dry helium atmosphere. Three separate batches of samples were charged with tritium using the pressures and tritium purities given in Table 147.VI.

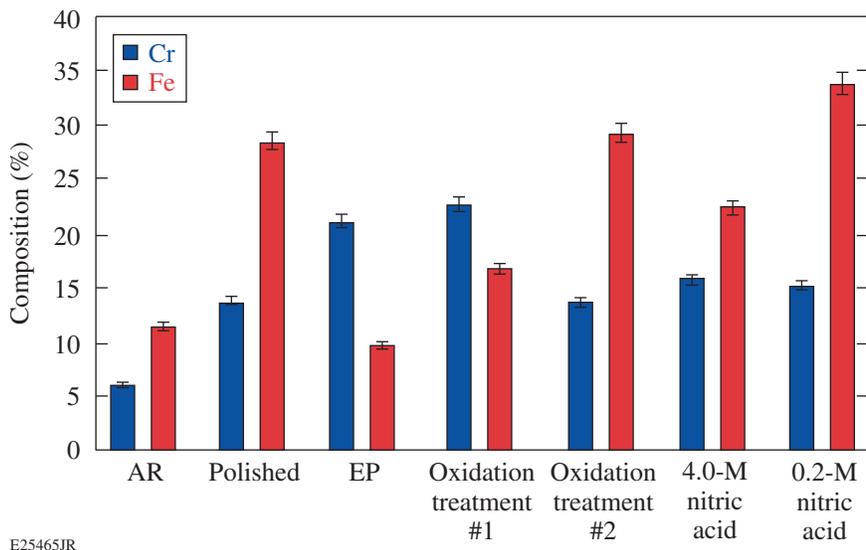


Figure 147.44 Measured Cr and Fe content in select samples using x-ray photoelectron spectroscopy (XPS).

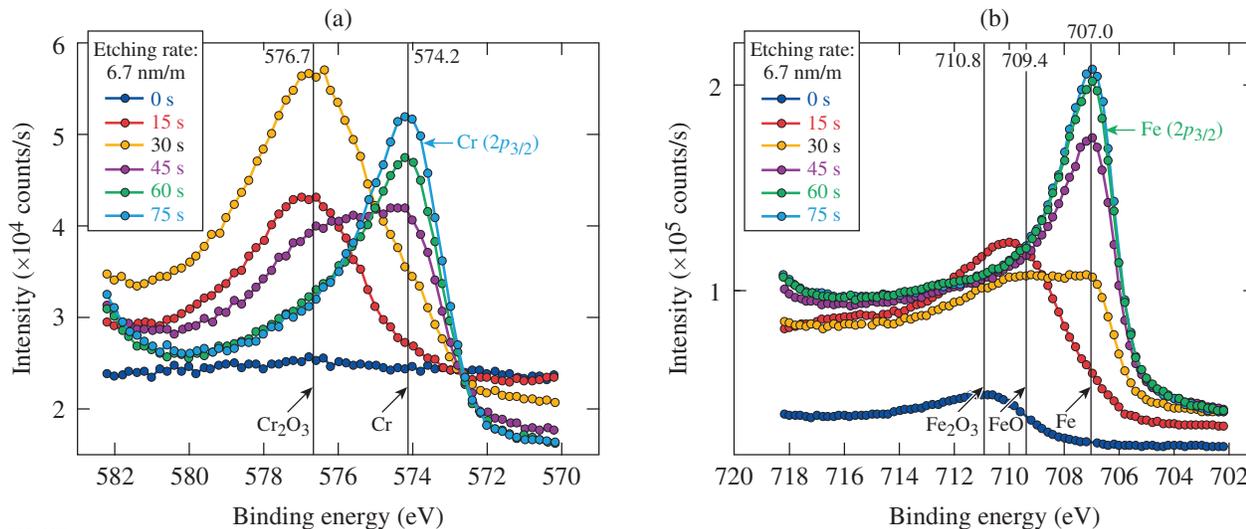


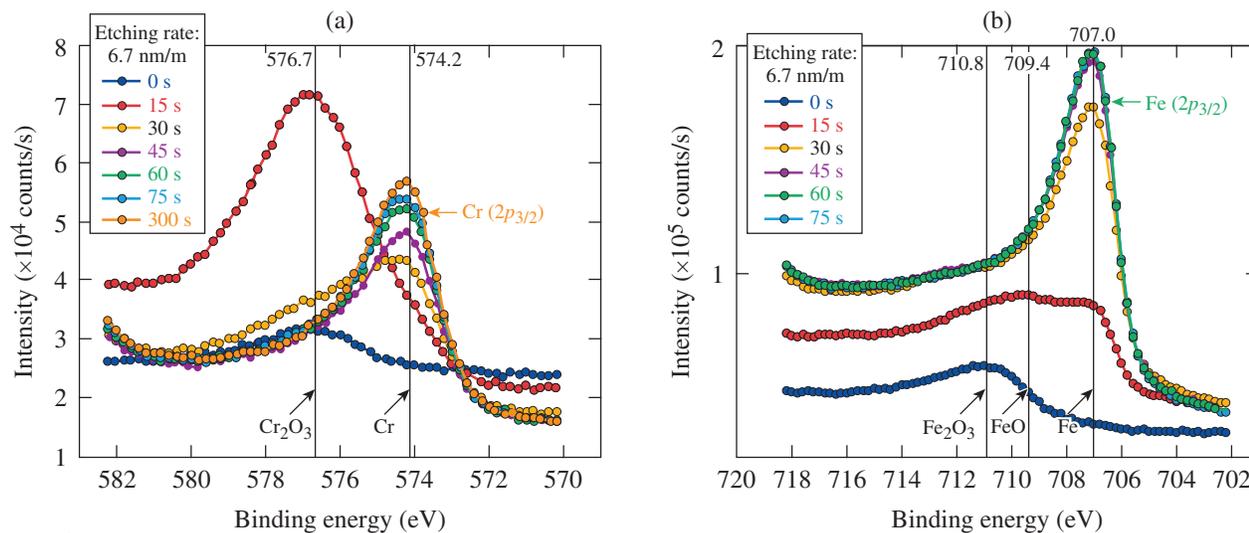
Figure 147.45 XPS photoelectron spectra for (a) Cr and (b) Fe atoms bound to the surface of as-received (AR) samples.

Table 147.VI: Sample loading and storage conditions.

Batch	Pressure (Torr)	Tritium (%)	Storage time (days)
A	550	57	13 to 29
B	530	58	8 to 29
C	550	59	6 to 18

4. Experimental Procedure

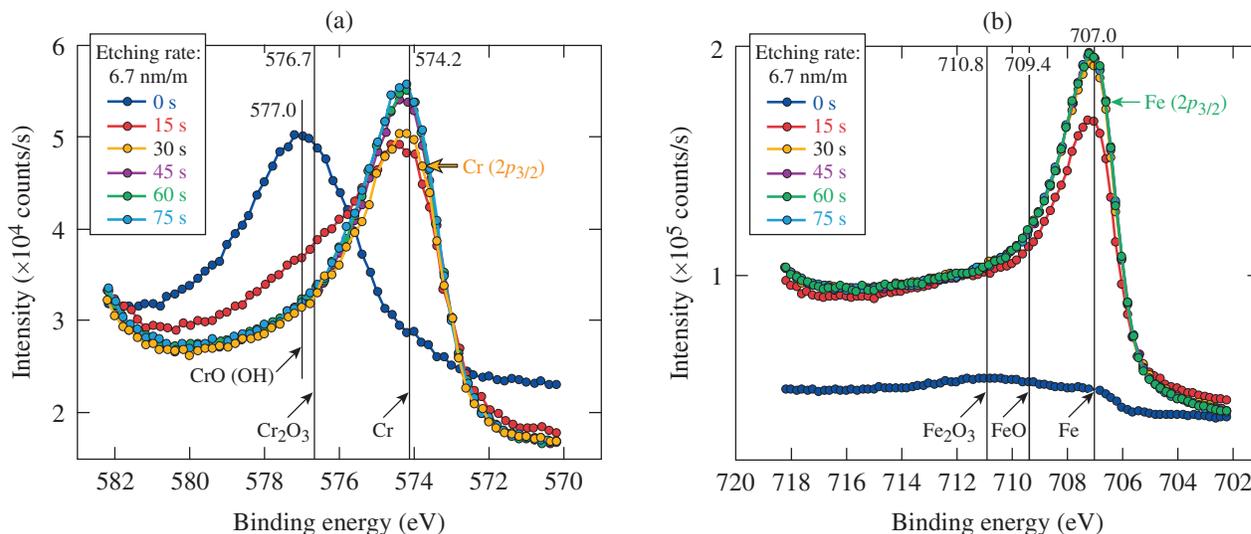
Total tritium inventories were measured with temperature-programmed desorption (TPD) as described in previous work.⁹ Tritium migration in the near-surface region was measured with plasma-induced ion sputtering, also described elsewhere.⁸



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Figure 147.46

XPS photoelectron spectra for (a) Cr and (b) Fe atoms bound to the surface of samples treated with 4 M of HNO₃.



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Figure 147.47

XPS photoelectron spectra for (a) Cr and (b) Fe atoms bound to the surface of samples treated with 0.2 M of HNO₃.

Results and Discussion

The total quantity of tritium removed during thermal desorption experiments shows a strong dependence on the surface composition as illustrated in Figs. 147.48 and 147.49. Each thermal desorption experiment was run at least twice, using separate and fresh samples to verify reproducibility. The AR samples were included to gauge how the various surface modifications influence the total tritium inventory and to provide a reference between the different loading batches. The observed variation in the tritium inventories between the different batches has not been resolved yet, but it is likely a result of subtle changes in the loading, storage, and handling procedures.

The data in Fig. 147.48 demonstrate that, relative to AR1 samples, electropolishing reduces the total quantity of tritium absorbed by the metal. However, increasing the electropolish-

ing duration from 5 to 10 min caused no further reduction in the total tritium inventory.

The data in Fig. 147.48 also demonstrate that the nitric-acid treatments result in significantly higher quantities of tritium absorbed into the samples, as compared with AR1 samples. The higher inventories are evident even though the acid treatment increased the Cr content in the near surface (Fig. 147.44). Contrary to expectations, these results suggest that the increased Cr concentration did not reduce tritium adsorption or absorption.

In general, mechanically polishing a SS surface leads to a reduction in the quantity of absorbed tritium (Fig. 147.50). However, this reduction in total tritium inventory is not exclusively caused by smoother surfaces. For example, polish #12 and polish #8 samples from Batch B in Fig. 147.50 had a surface roughness similar to the AR2 samples but retained half the tritium present on AR2 samples. Additional polishing of both samples in Batch C to reduce the surface roughness about eightfold from ~351 nm to 46 nm did not reduce the absorbed tritium content.

The measured total tritium inventories in gold-plated, SS (Au-SS) samples suggest that the electroplated gold layer does not act as a barrier to tritium absorption. The Au-SS samples contain less tritium than the AR2 samples, but comparable inventories to the polish #3 samples (Fig. 147.50). This suggests that the reduction in absorbed tritium, when comparing Au-SS to AR2 samples, is likely a result of polishing the samples, not electroplating them with gold.

The data provided in Fig. 147.49 again suggest that increasing the near-surface Cr concentration does not alter the absorption of tritium into the substrate. First, the EP samples have

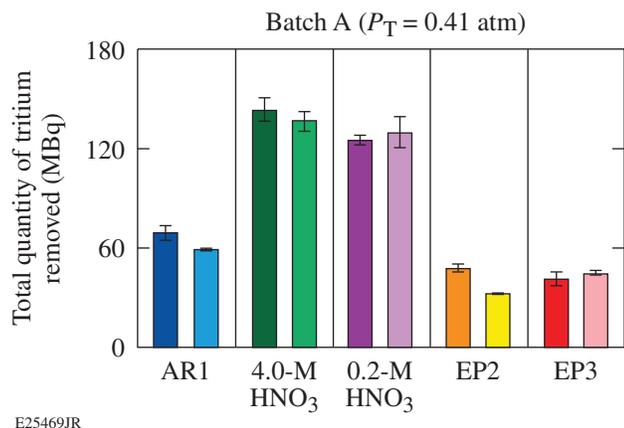


Figure 147.48
Quantities of tritium removed during thermal desorption experiments using samples loaded with tritium in Batch A.

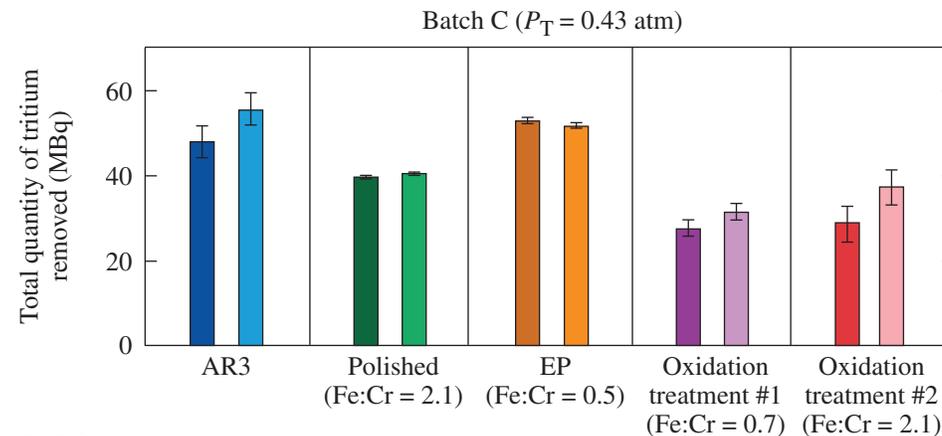


Figure 147.49
Quantities of tritium removed during thermal desorption using samples from Batch C.

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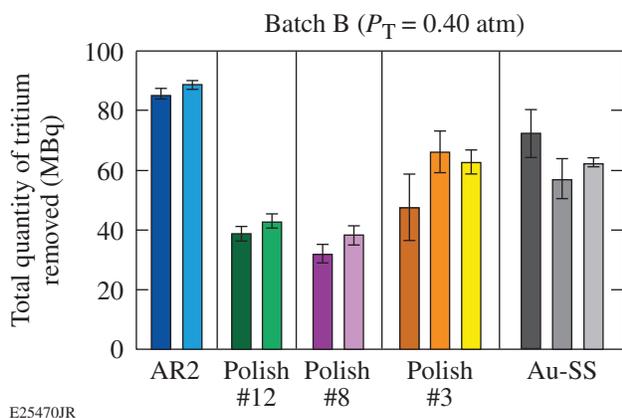


Figure 147.50
Quantities of tritium removed during thermal desorption experiments using samples loaded with tritium in Batch B.

significantly higher Cr concentrations in the near surface, as compared with the AR samples (Fig. 147.44). However, the EP samples show comparable tritium inventories to the AR3 samples. This is, again, contrary to the expectation that increased Cr concentrations in the near surface lead to lower tritium inventories. Furthermore, samples treated with oxidation treatment #1 showed comparable Cr concentrations to the EP samples (Fig. 147.44), but significantly lower total tritium inventories (Fig. 147.49). Finally, samples treated with oxidation treatment #2 show comparable tritium inventories to oxidation treatment #1, even though the Cr and Fe concentrations are significantly different (Fig. 147.44). These results suggest that the chemical composition of the near surface of stainless steel does not influence the absorption of tritium. It should also be noted that an increase in near-surface Fe concentrations does not account for the observed differences in total inventories. Significantly different tritium inventories were recorded for

samples that underwent the nitric-acid treatments and the oxidation treatment #2. However, the Fe and Cr concentrations were comparable.

The results shown in Fig. 147.48 also confirm that simply polishing SS surfaces reduces the tritium inventory in SS samples. Furthermore, mechanical polishing a surface does not reduce the tritium inventory to the same degree as oxidizing a surface.

The results in Fig. 147.49 show no correlation with surface roughness (0 to 0.54 μm) to the total activity determined by thermal programmed desorption. Different surface alterations show similar roughness values but drastic variability in the total activity as seen for polish #4 and the nitric-acid treatments. This trend suggests that an increased surface area is not indicative of increased tritium absorption. The data may suggest that the role of the surface area in the absorption of tritium may contribute little compared to the chemical absorption processes.

Using the data shown in Figs. 147.48–147.50, the surface concentration of adsorbed water (Q) can be determined using QTRIMM. These concentrations were determined by varying Q values until the calculated and measured total tritium inventories agreed. Averages of the data shown in Figs. 147.48–147.50 were used in this fitting procedure. The minimization was accomplished using *MATLAB*'s nonlinear least-squares fitting routine. The results of the fits are shown in Table 147.VII for the various surface finishes and loading batches.

The calculated Q values correspond to submonolayer water coverage of the surface, which is on the lower end of the expected values.¹³ These low values are likely a result of the limiting assumption of equal isotopic exchange prob-

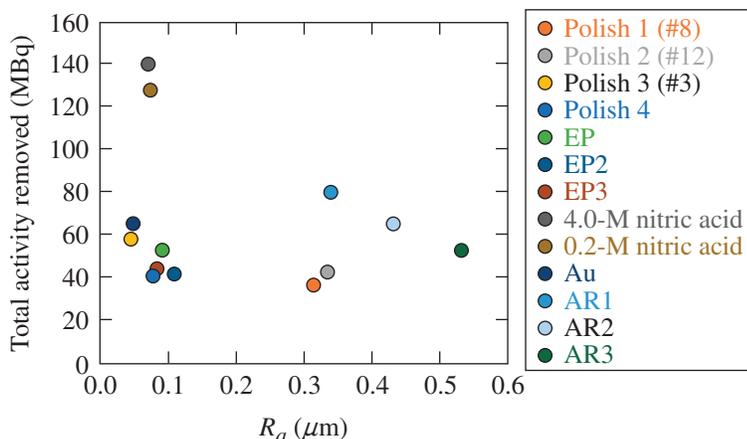


Figure 147.51
Total activity collected from various samples as a function of surface roughness.

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Table 147.VII: Results of fitting thermal and pulsed-plasma data using QTRIMM. Q values were determined from thermal-desorption data, while the removal efficiencies were determined from pulsed-plasma experiments.

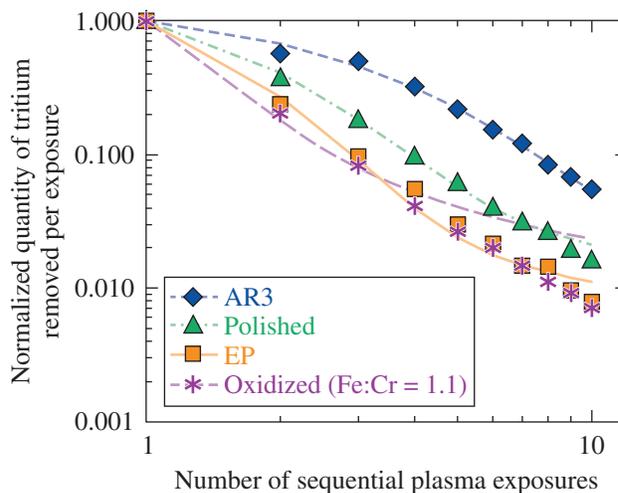
Batch	Metal finish	Q ($\mu\text{mol}/\text{m}^2$)	Removal efficiency	$A_{\text{surf}}/A_{\text{total}}$ (%)
A	AR1 (Fe:Cr = 1.8)	22.04	n/a	49
A	4-M HNO ₃ (Fe:Cr = 1.3)	55.74	n/a	57
A	0.2-M HNO ₃ (Fe:Cr = 2.1)	50.21	n/a	57
A	EP2	11.39	n/a	40
A	EP3	12.66	n/a	42
B	AR2	31.7	0.41	88
B	Polish #12	11.6	0.59	68
B	Polish #8	9.1	0.61	62
B	Polish #3	19.4	0.52	79
C	AR3	15.7	0.34	73
C	Polished	10.7	0.63	65
C	EP (Fe:Cr = 0.5)	16.0	0.75	74
C	Oxidized (Fe:Cr = 0.7)	6.2	0.91	51
C	Oxidized (Fe:Cr = 2.1)	7.7	0.84	56

abilities. Lowering the exchange probability for the formation of double isotope species T₂O on the metal surface will result in an increase in the calculated quantity of adsorbed water. The derived Q values indicate that $\geq 44\%$ of the total tritium inventory is initially located within the adsorbed water layers (Table 147.VII).

The Q values found from fitting thermal-desorption data agree with data obtained from pulsed-plasma experiments. No plasma data were collected for Batch A. Representative results obtained from samples supporting AR, polished, EP, and Fe-oxidized surfaces from Batch B that were subjected to a pulsed plasma are shown in Fig. 147.52. The data shown have been normalized to the quantity of tritium removed during the first exposure in each respective series to allow for direct comparison of the trends in each data series. These trends indicate that the mechanism for tritium migration to the surface is diffusion from the metal lattice between each plasma exposure.⁸

Figure 147.52 also shows fits to the data using QTRIMM. These fits were calculated by using Q values obtained from thermal-desorption fits and by varying only the removal efficiency (ϵ) until the data and calculations agreed. To be consistent, only Q values obtained from QTRIMM fitted to thermal desorption data for samples with the same surface finish and

charged with tritium in the same batch were used to fit pulsed-plasma data. The resulting fits to data show excellent agreement for all data series, except for samples that underwent selective oxidation pretreatments. Removal efficiencies found for each fit are given in Table 147.VII for each surface modification.



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Figure 147.52 Comparison of the results obtained from pulsed-plasma experiments to best fits (calculated using QTRIMM) of various samples charged with tritium in Batch B. The error in each data point is $\pm 5\%$.

Conclusions

The experimental data show that modifying the near surface (≤ 40 nm) of a SS surface by polishing, EP, selective oxidation, or nitric-acid treatments can significantly alter the total quantity of absorbed tritium. These results suggest that a significant fraction of the total tritium inventory initially resides on the surface since as these modifications affect only the near surface of the metal substrate (< 10 nm).

The nitric-acid treatments of the electropolished SS 316 surfaces increased the total tritium inventory by 200% when compared against untreated (AR) samples and 300% compared to EP samples. These results suggest that nitric-acid treatments created more hydrophilic surfaces when compared to untreated (AR) samples.

The differences in the total tritium inventories for the various surface treatments appear to be related to the quantity of water adsorbed on the surface. Increasing or decreasing the water content appears to increase or decrease the total tritium inventory. Figures 147.48 and 147.49 suggest that a 50% reduction in water concentration results in a 35% reduction in total tritium inventory in the electropolished case. On the other hand, increasing the water content by a factor of ~ 2.4 increased the total tritium inventory by 200% in the nitric-acid-treatment case. Measuring the water isotherms is necessary to confirm the calculation results.

The absorption and migration of tritium in each SS sample can be described using QTRIMM. Comparing the output of this model to thermal-desorption data allowed us to determine the surface concentration of adsorbed water. Using this surface concentration, the initial contribution of adsorbed tritium to the total inventory was determined to be $\geq 44\%$. Additionally, by using the Q values derived from fitting thermal-desorption data, we could accurately describe the migration of tritium to the surface for each sample during pulsed-plasma experiments.

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