

Influence of Heat Treatments on Near-Surface Tritium Concentration Profiles

M. Sharpe, W. T. Shmayda, and J. J. Ruby

Laboratory for Laser Energetics, University of Rochester

At room temperature, tritium interacts with all metals (aluminum, copper, stainless steel, etc.) to some extent.¹ Such interactions can lead to a buildup of tritium on the metal's surface and just under the surface of the metal.²⁻⁴ The presence of high tritium concentrations in these locations is a large concern for all tritium-handling facilities. These facilities contain a large quantity of metals that routinely come in contact with tritium gas. Over time, tritium buildup in these metals can lead to radiological hazards and high waste disposal costs. To mitigate tritium contamination in metals, it is common to heat the metal to high temperatures.^{5,6} The details of this thermal desorption method (maximum temperature, dwell time, etc.) depend on the contaminated metal as well as the expected tritium dosing. To date, however, no systematic study has been performed showing how tritium migrates within the metal as a result of a chosen thermal desorption temperature and time. The current work addresses this gap in knowledge by showing how the tritium distribution within stainless steel, type 316 (SS316) responds to temperatures between 100°C and 300°C. The surface and near-surface concentrations were measured using a combination of a ZnCl₂ wash and sequential acid etching to reveal a high-resolution tritium concentration profile. Tritium deeper within the metal was measured using high-temperature thermal desorption to remove residual tritium from the bulk metal.

To measure the effect of heating on the tritium distribution within SS316, a series of samples were first exposed to tritium gas for 8 h at 25°C. Each sample was then heated to temperatures between 100°C and 300°C for 120 min under a stagnant, dry argon atmosphere. The tritium distribution was then measured by performing a ZnCl₂ wash first to remove surface tritium. Following this wash, the samples were then acid etched to reveal the tritium concentrations immediately under the surface (<100 μm). Finally, the residual tritium deeper in the samples was measured using high-temperature thermal desorption (550°C for 4 h). For comparison, several control samples were not heated prior to the ZnCl₂ wash, acid etching, and high temperature thermal desorption procedures.

The resulting concentration profiles (Fig. 1) show two notable deviations from the control samples. First, the surface activity decreases significantly with increasing preheating temperature as expected. Second, the near-surface (1 nm to 1 μm) tritium concentrations differ for only the 200°C and 300°C cases; the 100°C and 150°C preheating appears to have had no influence on the near-surface concentrations. Heating to temperatures greater than or equal to 200°C resulted in decreased concentrations in the near surface (~0.1 μm).

Integrating the concentration profiles shown in Fig. 1 reveals the total tritium remaining within each region of the SS316 sample. These integrals (Fig. 2) show that surface-bound tritium decreases with increasing preheating temperature, while tritium deeper in the metal (>1 μm) increases. Tritium quantities in the intermediate region (<1 μm) remain constant until the sample is heated to 200°C or greater. Above 200°C, the quantity of tritium decreases to a new, lower value.

These data indicate how tritium migrates within SS316 in response to moderate heating. Heating SS316 causes tritium to desorb from the surface and migrate deeper into the metal. Taking the median values of the data shown in Fig. 2, the quantity of tritium "lost" from the surface is greater than the tritium activity released from the surface. This indicates that tritium preferentially migrates into the metal as opposed to desorbing from the surface. Desorption from the surface is possibly not as favorable due to the gas conditions. The samples were kept under dry argon during the preheating phase. Past studies have shown that tritiated

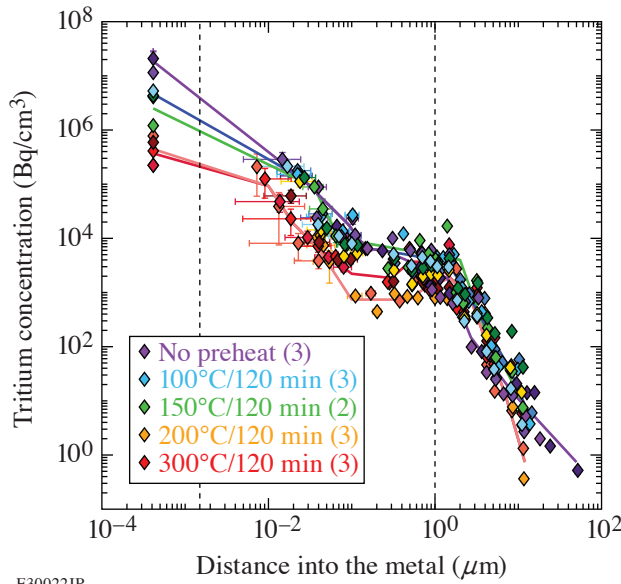


Figure 1
Tritium concentration profiles in the near surface of SS316 samples. Five preheating conditions are shown: no heating (purple), 100°C (blue), 150°C (green), 200°C (orange), and 300°C (red). Vertical dashed lines indicate different regions of the sample: surface (<1 nm), near-surface (<1 μm), and bulk (>1 μm). Each preheating condition was repeated with different SS316 samples that were exposed to tritium at the same time.

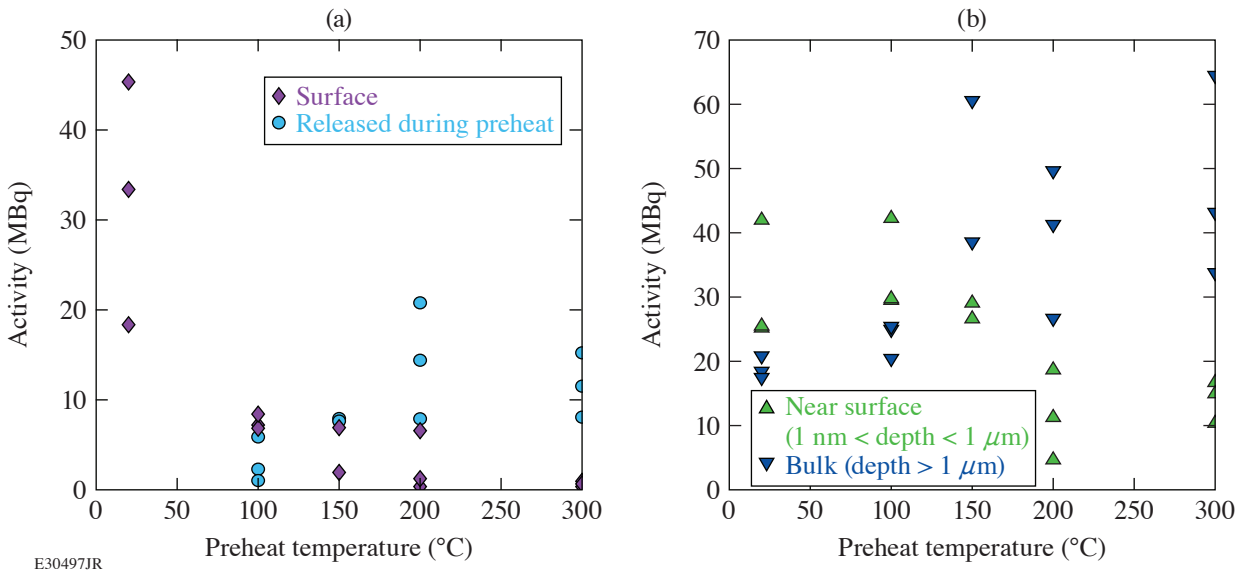


Figure 2
(a) Integrated tritium remaining on the surface and released during preheating and (b) tritium remaining in the near surface and bulk with respect to the preheating temperatures. Results from control samples are shown at 20°C.

water desorption is the primary release mechanism of tritium from SS316.⁷⁻⁹ By limiting this mechanism for tritium desorption from the surface, tritium will preferentially migrate in the direction of the concentration gradient deeper into the metal.

Tritium quantities in the near surface do not appreciably change until the preheat temperature reaches 200°C (Fig. 1). These results indicate that a minimum temperature of 200°C is required to trigger near-surface tritium mobility for migration deeper into the substrate or desorption from the surface. Previous work has also demonstrated that heating SS316 to at least 200°C is required for the onset of desorption.^{10,11} The increase in migration above 200°C indicates that tritium immediately below the surface is not bound at octahedral sites. The depletion of the near surface tritium and the increased desorbed tritium quantities by heating to 200°C suggests that tritium is bound in a hydrated iron (III) oxide: FeO(OH). Such binding explains three observations: First, hydrogen isotopes can be bound strongly to oxygen impurities in metals. Korzhavyi and Sandström used a density functional

theory calculation to simulate hydrogen interacting with an oxygen defect in copper.¹² Their results show a fourfold increase in the binding energy, as compared to a site without oxygen. Assuming oxygen in stainless steel has a similar effect, such deep trap states may explain the observed lack of tritium migration during the lengthy storage periods. Second, dehydration of hydrated iron (III) oxide occurs at 200°C (Ref. 13). Because tritium would be bound in the hydrate, dehydration would remove tritium from the near-surface region. Finally, dehydration may supply the oxygen and hydrogen/tritium necessary for tritiated water desorption from the surface. In this scenario, the primary pathway for tritium desorption is present even for dry inert gas atmospheres: the metal effectively supplies the water molecules for desorption.

The effect of heat treatments on the tritium distribution in SS316 samples was measured. It was found that the heating causes tritium to migrate both out of the sample and deeper into the bulk of the material. Tritium preferentially migrates deeper into the metal for temperatures less than 200°C, with very little desorbing from the surface. On reaching 200°C or above, dehydration of the hydrated iron (III) oxide occurs. The dehydration process reduces the tritium inventory in the near surface by allowing tritium to either desorb from the surface as tritiated water or diffuse deeper into the metal.

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1. M. Nishikawa *et al.*, *J. Nucl. Mater.* **277**, 99 (2000).
2. A. Perevezentsev *et al.*, *Fusion Sci. Technol.* **41**, 746 (2002).
3. M. D. Sharpe *et al.*, *Fusion Eng. Des.* **130**, 76 (2018).
4. M. Sharpe, C. Fagan, and W. T. Shmayda, *Fusion Sci. Technol.* **75**, 1053 (2019).
5. A. N. Perevezentsev *et al.*, *Fusion Sci. Technol.* **52**, 84 (2007).
6. S. Rosanvallon *et al.*, *Fusion Sci. Technol.* **60**, 855 (2011).
7. K. Akaishi *et al.*, *J. Vac. Sci. Technol. A* **26**, 321 (2008).
8. M. J. Quinlan *et al.*, *Fusion Sci. Technol.* **54**, 519 (2008).
9. Y. Torikai *et al.*, *Fusion Sci. Technol.* **41**, 736 (2002).
10. W. T. Shmayda *et al.*, *Fusion Sci. Technol.* **68**, 766 (2015).
11. R.-D. Penzhorn *et al.*, *Fusion Sci. Technol.* **64**, 45 (2013).
12. P. A. Korzhavyy and R. Sandström, *Comput. Mater. Sci.* **84**, 122 (2014).
13. N. N. Greenwood and A. Earnshaw, eds. *Chemistry of the Elements*, 2nd ed. (Elsevier, New York, 1997).