INFLUENCE OF HEAT TREATMENTS ON THE NEAR SURFACE TRITIUM CONCENTRATION PROFILES [1*]

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Abstract

Austenitic stainless steel, type 316, absorbs significant quantities of tritium into the near surface (<1 μm) on exposure to tritium containing gases at room temperature. The tritium concentrations that develop in the near-surface region (<1 μm) are shown to persist for several years without changing. The current work shows the effect of heat treatments on the near-surface tritium-concentration profiles in stainless steel. Identical stainless-steel samples were exposed to tritium at room temperature and then were heated to different temperatures between 100 and 300°C for two hours under a stagnant argon atmosphere. After this initial preheating, the concentration profiles in the first 10 μm were measured by using a combination of a $ZnCl_2$ wash and an etching procedure. Tritium was thermally released by heating the samples to 550°C to measure the residual tritium present in the bulk of the sample. The data show two dominant features. First, preheating causes tritium to migrate both out of the sample and deeper than >1 μm into the bulk. This effect increases with increasing temperature. Second, depletion of tritium from the near surface does not occur until a temperature of 200°C.

I. INTRODUCTION

At ambient temperature, tritium interacts with all structural metals (aluminum, copper, stainless steel, etc.) to some extent.[1] Such interactions can lead to non-negligible tritium concentrations on the surface and in the near-surface of the metal.[2-4] The presence of high tritium concentrations in these locations is a large concern for all tritium-handling facilities. A large portion of these facilities is comprised of unheated structural metals that routinely come in contact with tritium-containing gases. Over time, tritium build-up in these materials can lead to radiological hazards and high disposal costs.

To mitigate tritium contamination in metals, thermal desorption is commonly employed.[5,6] The details of the heating profile (maximum temperature, dwell time, etc.) depend on the gas composition, activity, and location of the component to be degassed. To date, however, no systematic study has been performed showing how tritium migrates within the metal because 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 and 300°C. The surface and near-surface concentrations were measured using a combination of a $ZnCl_2$ 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.

II. EXPERIMENTAL SETUP AND METHODS

A series of SS316 samples with dimensions of $5.1 \times 0.3 \times 1.8$ cm^3 and surface roughness Ra ~300 nm was manufactured by Torrovap Industries Inc. and prepared according to procedures outlined previously.[3] These samples were cut from a common plate and subsequently 0.86 mm was eliminated. Any surface inclusions that arose from the manufacturing process exposed the base metal lattice. No further modification to the surface was done.

X-ray photoelectron spectroscopy (XPS) was performed using a non-tritiated sample. Spectra were collected on the surface and with a series of 60 s focused ion beam etches. The results show that iron (III) oxide dominates the surface while chromium is negligible (Fig. 1). After etching, both metallic iron and chromium are evident. Notably, a metal hydroxide peak in the oxygen 1s spectra is present. These spectra and trends agree with prior XPS data reported in the literature by Tardio *et al.*[7]

Prior to loading with tritium, the samples were sequentially washed in acetone, water, and isopropyl alcohol. The samples were then exposed to 77.5 kPa of DT gas (68.4% T) for eight hours at 25°C. After exposure, the samples were sealed in individual storage pods under dry helium (dew point less than or equal to -80°C) until retrieved for evaluation.

The tritium distribution in the near surface was measured using three experimental techniques: $ZnCl_2$ wash, acid etching, and thermal desorption. These techniques were discussed in detail in a previous publication.[2] Briefly, a

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$ZnCl_2$ wash is performed first to measure the quantity of tritium adsorbed to the stainless-steel surface as tritiated water. Following this wash, a series of sequential acid etches is performed to reveal the concentration profile within the stainless-steel substrate. Finally, a high temperature (550°C for 4 hours) thermal desorption was used to remove residual tritium from deeper within the sample. Several updates to the experimental method have been implemented since the previous publication. First, the mass lost from each sample during an acid etch was measured using a new Mettler-Toledo XPR56 balance, which has a minimum readability of 0.001 mg. Second, .25-mL aliquots were used to sample the tritium activity in each etchant solution, instead of the 1-mL aliquots previously used.

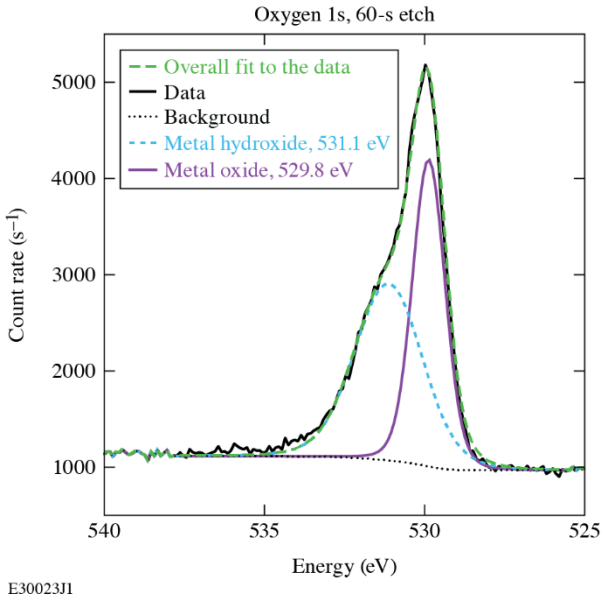

Figure 1; Oxygen 1s XPS spectra taken using a non-tritiated SS316 sample after etching for 60 s**.**

To measure the influence of moderate heat treatments on the tritium concentration profile, each sample was heated to a temperature between 100–200°C for 120 min using the thermal desorption setup. Prior to heating, the oven was purged with dry argon for 15 min before stopping the gas flow. The sample was then heated to temperature under the stagnant argon atmosphere. After cooling, the oven was again purged for 15 min to collect any desorbed tritium. All effluent from the furnace was passed through two spargers, each filled with 100-mL of water. After heating, the sample was subjected to a $ZnCl_2$ wash, followed by acid etching, and then high temperature thermal desorption. The distribution of tritium was also measured in several control samples. For these control samples, no pre-heating was performed; the samples were taken straight from the storage pod and placed into the $ZnCl_2$ wash.

III. RESULTS

The experimental methods outlined in the previous section was used to investigate the effect of pre-heating on the tritium distribution in the SS316 samples. Figure 2 shows the concentration profiles measured using the combination of the $ZnCl_2$ wash and the subsequent acid etching methods. The results of the $ZnCl_2$ wash are shown as the first data point in each series, while the remaining data points were obtained from the etching method. The derivation of the depth assigned to the first data point was described in detail in a previous publication.[4]

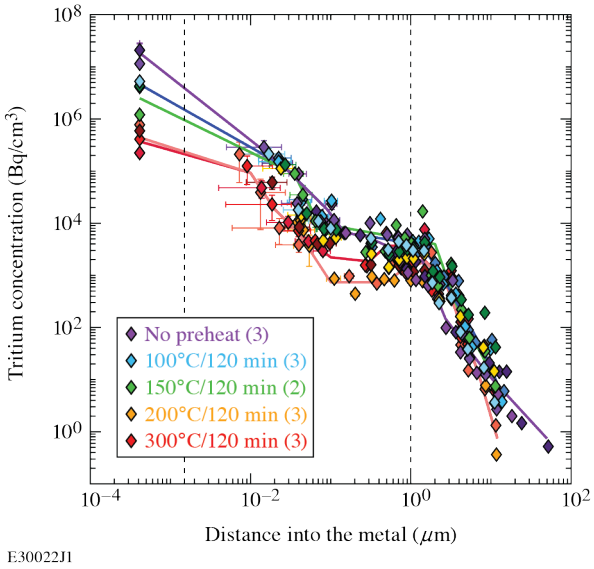

Figure 2. Tritium concentration profiles in the near surface of SS316 samples. Three pre-heating conditions are shown: no heating (purple), 100°C (blue), 150°C (green), 200°C (orange), and 300°C (red). Vertical dashed lines indicate different regions of the sample: surface (<1 nm), near-surface (<1 μm), and bulk (>1 μm).

The derivation assumes that tritium is contained within 2.5 adsorbed water layers present on the SS316 surface with each layer thickness being the distance between oxygen atoms in ice: 2.76 Å. Since the samples were kept under dry helium until retrieved for the measurements, little adsorbed water should be present. The vertical dashed lines roughly separate the different physical regions of the sample: surface, near-surface, and bulk. For these experiments, four pre-heating temperatures were used: 100, 150, 200, and 300°C. For each pre-heating condition, several separate samples were used to establish the reproducibility of the methods. A set of control samples were run with no pre-heating. These samples were subjected only to the $ZnCl_2$ wash, etching, and high temperature thermal desorption. The general shape of the concentration profiles is consistent with those reported previously.[4] However, the current results are lower in magnitude because of the shorter tritium exposure time. The data shown in Figure 2 were obtained from samples

that had been stored under dry helium between 8 to 623 days between tritium exposure and measurement. Storage time appears to have little, if any, effect on the concentration profiles.

Pre-heating the SS316 samples causes two notable changes in the concentration profiles. First, the surface activity decreases with increasing pre-heat temperature as expected. Second, the near-surface (1 nm–1 μm) tritium concentrations differ only for the 200 and 300°C case; the 100°C and 150°C pre-heating 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.

Integrating the concentration profiles shown in Fig. 2 yields the total tritium quantities contained within each region. These integrated activities are shown in Figs. 3 and 4 as a function of the pre-heating temperature, along with the tritium quantities collected during the argon purge after pre-heating and the activity collected during the high temperature thermal desorption. Results from the control samples are shown at 20°C. Figure 3 shows both the tritium activities remaining on the surface and the activities released from the sample during the pre-heating phase. Surface activities were measured using the $ZnCl_2$ method. Tritium released from the samples was measured by sampling the spargers prior to the high temperature desorption. In general, the surface activity decreases with increasing pre-heating temperature, while the activity released from the sample increases.

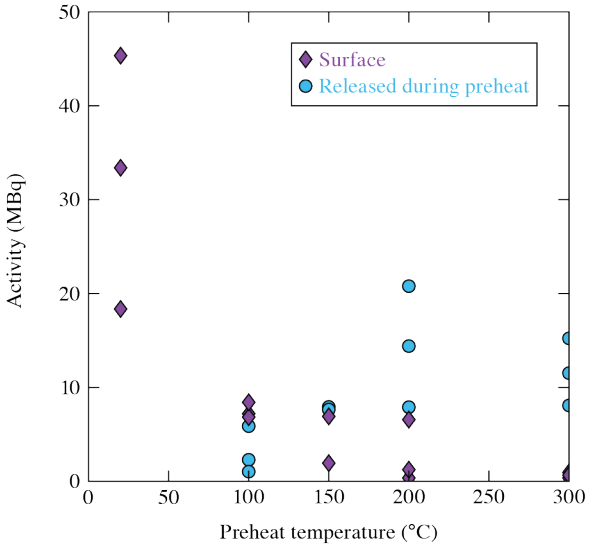

Figure 3. Activity remaining on the surface (purple) and activity released from the sample during pre-heating (blue) as a function of pre-heating temperature. Results from control samples are shown at 20°C.

Figure 4 shows the near-surface and bulk activities as a function of the pre-heating temperature. The near-surface activities represent the integral of the concentration profiles between 1 nm and 1 μm while the bulk activities are the sum of the integral for depths greater than 1 μm and the results of the high temperature desorption. These results show an increase in bulk activity with increasing pre-heating temperature. The near-surface activity appears to be constant until 200°C where there is a shift downwards in activity. This downward shift remains constant for 300°C pre-heating temperatures.

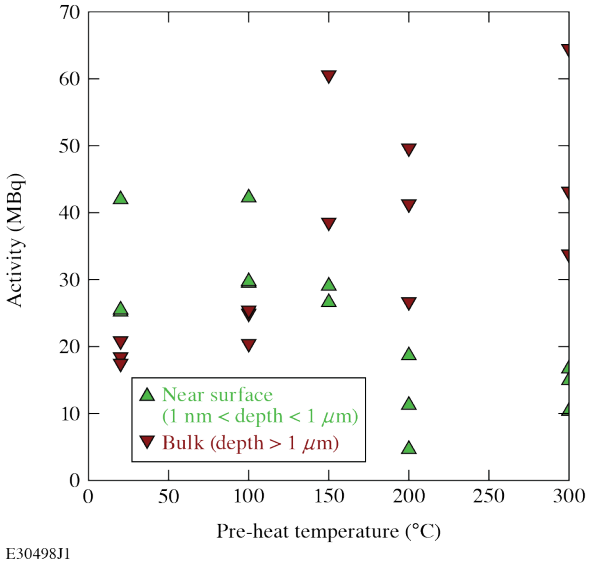

Figure 4; Activity remaining in the near-surface (green) and bulk (red) as a function of pre-heating temperature. Results from control samples are shown at 20°C.

Finally, the cumulative quantity of tritium remaining within each sample is plotted against storage time in Fig. 5. The control samples show no appreciable decrease in tritium inventory over the course of 540 days of storage. Tritium inventories in the pre-heated samples show a decrease in total inventory possibly from tritium loss to the oven walls. Such a loss may also add to some of the observed variation in the data. Further sources leading to the variation in the data may include: tritium loss from handling, differences in the microstructure of the samples, and compounding errors from multiple experimental techniques. Variation in samples like the ones in the current study has been observed in the past for a much larger set of data.[4] The exact cause of the variation is unknown.

IV. DISCUSSION

The experimental results show the influence of different pre-heating temperatures on the distribution of tritium in SS316. The results indicate how tritium migrates in SS316 while under an inert atmosphere at ambient temperature. The data show tritium concentration profiles that appear to be in an equilibrium state with a stable increasing concentration gradient towards the surface. This gradient persists even after 540 days of storage under dry helium gas for the control samples. This behavior and general concentration gradient are consistent with previous work

done with SS316 samples exposed to tritium for 24 h.4 As noted in previous work, tritium diffusion through normal octahedral sites in SS316 should occur at a much faster rate. Using the tritium diffusivity in SS316[8], tritons should migrate on average over 11 μm in one day. These results indicate that tritium in the near-surface is not bound in octahedral lattice sites.

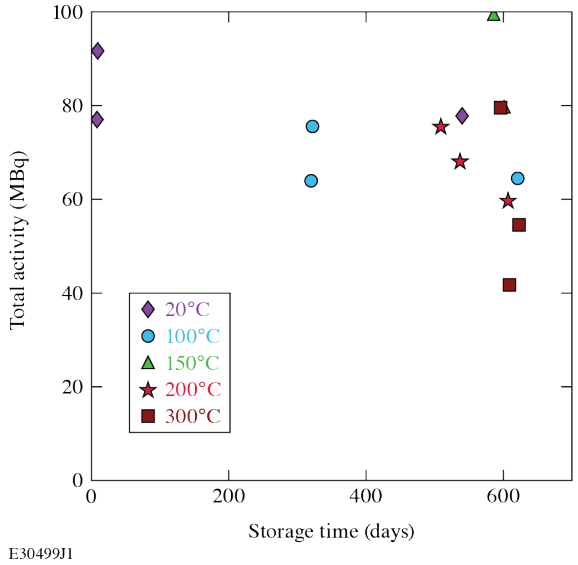

Figure 5; Total tritium activity collected from each sample plotted as a function of storage time. Activities shown include tritium released from the sample during the pre-heating phase. The various pre-heating temperatures are labeled in the figure. Control samples are labeled as 20°C.

Heating the SS316 sample causes tritium to desorb from the surface and migrate deeper into the metal substrate. This work shows decreasing surface activity with pre-heating temperature (Fig. 3) while the bulk activity increases over the same temperature range (Fig. 4). Taking the median values of the data shown in Fig. 3, 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 pre-heating phase. Past studies have shown that tritiated water desorption is the primary release mechanism of tritium from SS316.[9,10,11] 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 pre-heat temperature reaches 200°C (Fig. 4). Below this temperature, the near-surface activity remains relatively constant. Above 200°C, the total near surface activities remain constant at a lower value. 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.[12,13] The increase in migration above 200°C indicates that near surface tritium is not bound at octahedral sites in SS316. The strength of the bonds and the location of these sites suggest that the surface metal oxide enhances tritium retention through the formation of deep "trap" states. Hirabayashi *et al*. also observed tritium retention in the near-surface.[14] In that study, the authors measured the thermal desorption spectra of two SS316 samples, a reference unaltered sample and second sample which had the first 0.2 μm etched away. This etching removed a peak from the subsequent thermal desorption spectrum. Other studies have made similar observations indicating that oxygen in the metal oxide governs tritium retention in the near-surface region. [15,16]

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). This oxide may be the source of the observed metal hydroxide peaks in the XPS spectra (Fig. 1). 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.[17] Their results show a four-fold 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.[18] 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. Penzhorn *et al*.[13] observed an increase in hydroxide concentration in the near surface with sample aging. These authors also suggested the formation of tritiated metal hydroxides in the near-surface to explain their observed lack of tritium migration.

V. CONCLUSIONS

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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