Available online at www.sciencedirect.com
Journal of Nuclear Materials 363–365 (2007) 462–466
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Migration and release behavior of tritium in SS316 at ambient temperature

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Abstract

BIXS measurements indicate that immersion into water or chemical etching of SS316 contaminated with tritium at moderate temperatures causes an immediate reduction of the outermost surface concentration of tritium. The fraction of surface tritium removed by water, i.e. 30–50%, is small in comparison to the total tritium present in the specimen. Allowing a specimen to age whose surface and subsurface had been removed by etching up to a depth where the concentration of tritium is mostly constant revealed that within a few months a re-growth of tritium up to a saturation value higher than half of that originally present on the specimen takes place. Concurrently, a small but steady liberation of tritium at rates increasing from 0.1 to 0.3 kBq/h was noticed.

PACS: 62.30.−h; 68.35.Fx

Keywords: Stainless steel; Tritium retention; Tritium removal

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1. Introduction

Type 316 stainless steel (SS316) contaminated with tritium constitutes a regular waste from facilities handling sizable quantities of tritium. When used for tritium containment the incorporation and release of tritium into this material may have an impact on the chemical purity of the enclosed gas. Thus detailed understanding of the short and long-term mechanisms of interaction between tritium and SS316 at ambient temperatures are important. This information is also needed for an environmental and economical evaluation of many waste conditioning and storage issues.

While the system tritium–stainless steel has been the subject of numerous investigations under a broad variety of conditions [1–3] there is little knowledge on the surface trapping and retarded liberation of tritium from this material under ambient conditions. Austin and Elleman [4] obtained tritium depth profiles in SS304 and SS316 specimens and showed that a tritium-trapping layer of high specific activity establishes on the metal surface. Hirabayashi and Saeki [5] verified with a depth profile that gaseous tritium penetrates more than 30 μm into SS316 after 35 days of exposure at 13.3 kPa and

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doi:10.1016/j.jnucmat.2007.01.043

298 K. Surette and McElroy [6] reported the occurrence of a persistent tritium release from stainless steel exposed to tritium at ambient temperature. Torikai et al. [7] provided first evidence for a chronic release of tritium from stainless steel exposed to this gas at elevated temperatures and demonstrated that this release originates not only from the metal surface and subsurface but also from the bulk. The latter conclusion was drawn from the long-term time-evolution of the distribution of tritium in the bulk and on the surface of SS316 [8,9].

The aim of this paper is to improve knowledge on the mechanisms that govern the migration of tritium in stainless steel at ambient temperatures and the effect of etching as well as immersion into water on its release.

2. Experimental

SS316 specimens (15 × 15 × 0.5 mm^3) were loaded at 1.2 kPa with a gaseous hydrogen/tritium mixture containing 24% tritium. The loading achieved at 573 K after 3 h of exposure was 10 MBq/specimen. Details on the procedure are given in [7] and references therein.

Tritium depth profiles in SS316 were obtained by chemical etching and by β-ray-induced X-ray spectrometry (BIXS), a technique capable of determining tritium on the surface and in the bulk of solids [10]. To analyze tritium on the surface argon is constantly purged across the specimen holder with a rate of 40 ml/min and the characteristic Ar(Kα) X-rays at 2.9 keV, induced by the β-rays of tritium, are measured. X-rays were determined at ambient temperature with a high-resolution low energy Ge semi-conductor detector type GUL0055P from Canberra. The conversion efficiency for Ar(Kα) adopted in this work was 1 count/s = 3.56×10^5 Bq/cm^2.

Another procedure used to obtain tritium depth profiles in SS316 consisted in successive etching at ambient temperature with an acid mixture diluted in water and tritium counting of the supernatant solution by liquid scintillation counting (LSC) [9]. The surface layer removed from SS316 after each etching step was calculated from the weight loss of the specimen. The etching depth (resolution <0.02 μm) was controlled by the duration of the treatment.

Tritium released chronically as HTO from specimens being subjected to BIXS-counting was continuously removed from the BIXS chamber with a stream of dry argon and collected in a bubbler with water placed downstream (see Fig. 1). Water aliquots were periodically analyzed for tritium by LSC. In a few measurements, in which a CuO bed at 800 K and an additional bubbler were installed downstream, the HTO fraction was determined to lie within the range 0.95 < HTO/(HTO + HT) < 0.98. This is well in line with observations from other investigators [6,8,11,12].

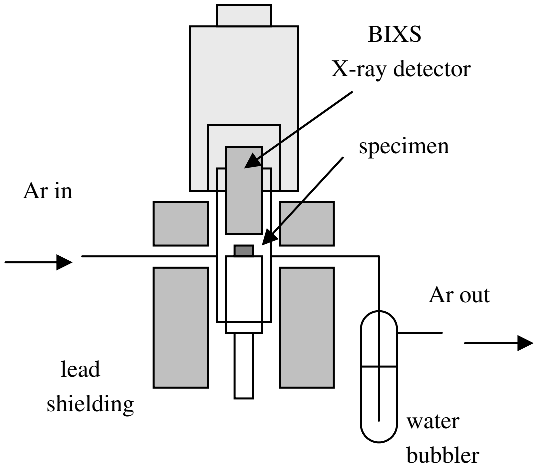

Fig. 1. BIXS chamber and adjacent bubbler.

3. Results and discussion

3.1. Tritium depth profiles

A typical tritium depth profile obtained by acid etching of a SS316 specimen loaded with tritium under the conditions given above is depicted in Fig. 2 (open circles). The hydrogen solubility under the conditions of loading, i.e. 4.5×10^8 Bq/cm^3 [2], is included as reference. As apparent, the tritium concentration drops steeply by several orders of magnitude from the topmost surface until a depth about of 7 μm and then increases again up to depths of 70–80 μm, remaining essentially constant further on into the bulk. The depth profile of another SS316 specimen loaded under the same conditions and etched to a depth of 77 μm (black circles) confirm the good reproducibility of the technique. Both specimens display a rather thin tritium-trapping layer of less than 0.05 μm width and very high specific tritium concentrations in the GBq/cm^3 range. The topmost surface layer width determined by chemical etching is consistent with observations by Hatano et al. [13] and Louthan and Derrick [14],

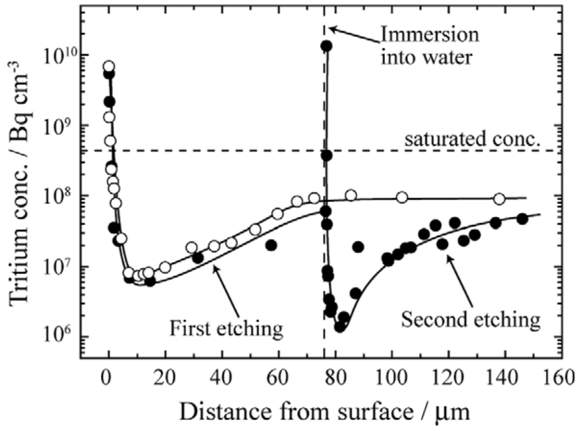

Fig. 2. Tritium depth profile of two SS316 specimens loaded under identical conditions: (a) reference specimen etched once (○) and (b) specimen further used for BIXS and chronic release tests etched twice (●). The horizontal broken line gives the calculated solubility under the conditions of loading. The depth profile to the right of the vertical broken line was obtained after the specimen was immersed into water and kept under an argon stream for 700 h.

who estimated its thickness to be in the nm range. It is noteworthy, that the main features of the profile shown in Fig. 2 are analogous to those reported by Austin and Elleman [4] using a different experimental approach, i.e. electropolishing in a H_3PO_4/H_2SO_4/H_2O solution.

3.2. Mechanism of tritium release

Of the two specimens described in Fig. 2, the one from which a 77 µm layer had been removed (black points) was further examined by BIXS. It was assumed that the concentration of tritium deeper into the bulk of this specimen was as uniform as of the other. The characteristic argon X-ray spectra obtained before and after etching are displayed in Fig. 3(a) and (b), respectively. Consistent with expectations, acid etching causes a drastic reduction in surface contamination not only because the exchangeable tritium is completely removed, but also some of that trapped in the subsurface zone (<80 µm). These BIXS measurements reveal that from a total initial surface activity of 158 kBq/cm^2 only 1.1 kBq/cm^2, i.e. 0.7%, remained on the surface immediately after etching.[1]

If after etching the tritium concentration on the surface is followed by BIXS over an extended period of time it is seen that the concentration of tritium, $C(t)$, slowly but steadily increases according to the expression

$$C(t) = 5 \times \exp\left(-\frac{t}{1800}\right) + 87\left\{1 - \exp\left(-\frac{t}{1800}\right)\right\}(\text{kBq/cm}^2),$$

which approaches a maximum of 87 kBq/cm^2 after a period of >7 months. The characteristic Ar X-ray spectrum is shown in Fig. 3(c) and the evolution of the Ar(Kα) X-ray peak in Fig. 4. The maximum is more than half that of the original surface concentration.

The release rate of gaseous tritium species from the specimen into the sweep gas (Fig. 4), on the other hand, first drops rapidly from initially 2.4 kBq/h down to approx. 0.2 kBq/h and then gradually increases again as the surface becomes progressively saturated in tritium. The time dependency of the rate, $R(t)$, is described by the equation

$$R(t) = 0.027 + 5 \times 10^{-5}t \ (\text{kBq/h}),$$

where t is in hours. The progressing release of tritium is also evident from a comparison between the tritium depth profile in a specimen obtained shortly after loading and another specimen of the same series kept for 3240 h under an argon stream after loading (Fig. 5). It is seen that a rather significant depletion of tritium from the sub surface has taken place. Consequently, even at ambient temperature, tritium shows a propensity to migrate to the surface and either remain trapped there, most probably as a hydroxyl group, or recombine with an already existing hydroxyl group to yield tritiated water releasable into the atmosphere.

To assess the amount of exchangeable tritium, the specimen under BIXS examination for 4700 h was immersed into de-ionized water for 48 h and then removed, dried with desiccant paper and reintroduced into the BIXS chamber, all within a few minutes. By this treatment the total tritium concentration on the surface, measured by BIXS across a depth of 0.2 µm, decreased from initially 83 kBq/cm^2 down to about 56 kBq/cm^2. The initial scattering is attributed to the evaporation of residual tritiated water. From then on the tritium surface activity replenished again presumably towards the bulk concentration value, i.e. 83 kBq/cm^2 (Fig. 4, right of broken line). It follows that the majority

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[1] The total counting rate is obtained by peak integration over the energy.

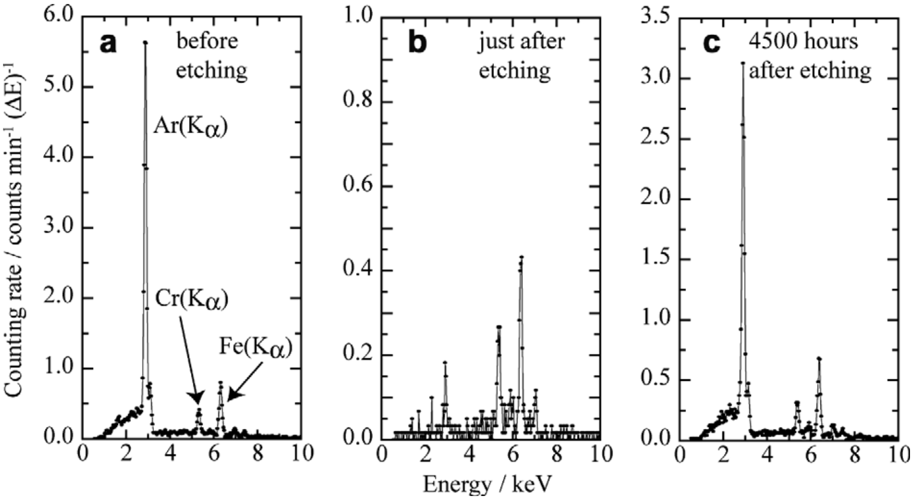

Fig. 3. Characteristic BIXS spectrum of a tritium-contaminated SS316 specimen: (a) after loading with tritium (158 kBq/cm^2), (b) shortly after etching (1 kBq/cm^2), and (c) 4500 h after etching (83 kBq/cm^2).

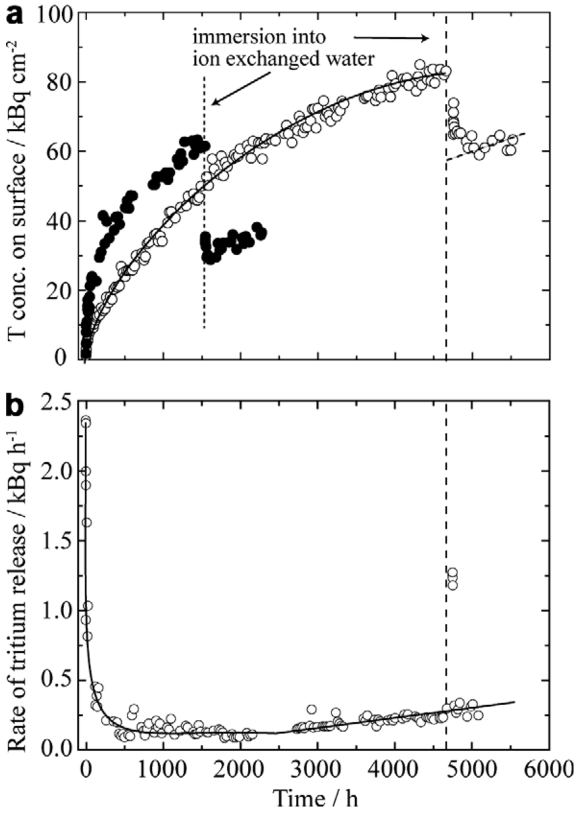

Fig. 4. Time-evolution of tritium on the surface of two pre-etched SS316 specimens (○, ● (a) upper figure) and on these specimens after immersion into water and drying of the surface (right of the broken lines). The rate of liberation of tritium into argon carrier gas from one specimen before and after immersion into water (b) is also shown (○ lower figure).

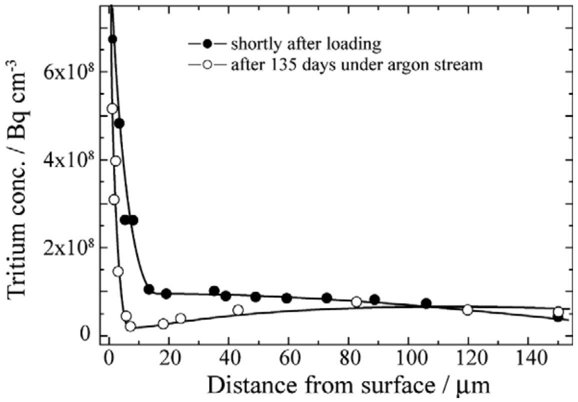

Fig. 5. Comparison between the tritium distribution in a tritium-loaded specimen and a specimen of the same series that was under an argon stream for 3240 h.

of the tritium on the outer surface of the examined specimen, i.e. >70%, is non-exchangeable. When the thickness of the trapping layer was taken to be 2 nm the specific concentration on the surface contributing to the exchangeable fraction was estimated to be 1.5×10^{11} Bq/cm^3. Another specimen (Fig. 4, black points) showed a similar tritium re-growth on the surface but a larger exchangeable fraction of nearly 50% (it should be noted that this fraction, i.e. 0.5%, is rather small compared to the total tritium inventory in the specimen).

Tritium liberated into argon purge gas after immersion of the specimen into water shows an initial high rate, i.e. approx. 1.3 kBq/h, which first drops to about 0.3 kBq/h and from then on slowly increases following the previous pattern (Fig. 4, right of broken line).

After keeping the specimen for 700 h under these conditions in the BIXS chamber the tritium depth profile in the specimen pre-etched up to 77 μm was again determined by etching (see Fig. 2, to the right of the vertical broken line). Clearly, it closely resembles in shape as well as with respect to topmost and bulk activity the ones obtained before immersion into water. In other words, the surface depth profile eliminated after etching 77 μm is fully restituted by tritium bulk migration and release. The depth profile that develops after prolonged time shows like the original ones an exponential decrease in tritium concentration from the topmost surface through an approx. 0.2 μm thick layer and thereafter an exponential increase from the end of this layer towards the bulk, the tritium concentration approaching 10^8 Bq/cm^3. The tritium concentration on the topmost surface layer is the highest (of the order of 10^{10} Bq/cm^3).

When the released tritium is taken together with that accumulating on the surface of SS316 at ambient temperature the depth profile can be modeled with a one-dimensional diffusion equation [7]. A comparison of freshly etched with aged specimens indicate that the concentration drop in the 10–50 μm subsurface region can be attributed to chronic release and the very high concentrations of tritium on the surface to trapping in a thin ceramic-type surface layer. Whether the tritium diffusing to the surface and trapped there is released only via isotopic exchange with atmospheric moisture (or residual moisture in the argon sweep gas) or whether it is liberated through a reaction with OT or OH groups on the surface still needs to be clarified. The gradual restitution of the original tritium distribution on the surface and in the bulk after the specimen has been taken out of the water constitutes further evidence for the movableness of tritium in SS316 at ambient temperature and is consistent with an oxide film effect.

3.3. Waste conditioning issues

A simple surface decontamination of stainless steel – even if contaminated at moderated temperatures – by rinsing or wiping with water or immersing into it will be of limited success. A re-growth of tritium on the surface and a slow release of tritium with progressively increasing rates are further adverse effects. This type of waste treatment is therefore not promising.

Heating tritium-contaminated material is still considered to be the best approach for a thorough decontamination. Out of technical reasons or a reuse perspective mild temperatures are generally preferred. However, because tritium will migrate both to the surface as well as to the bulk, exceedingly long times may be needed to achieve a high degree of decontamination. Therefore, heating at elevated temperatures is currently the only practical option.

4. Conclusions

Tritium-contaminated SS316 develops a layer rich in tritium on the metal surface and releases gaseous tritium chronically. The specific tritium concentration of this layer is very high, but its contribution to the total tritium inventory small. Chemical or abrasive mechanical surface treatments are hence not sufficient to achieve a high degree of decontamination of stainless steel previously exposed to tritium at moderate or elevated temperatures.

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