Tritium uptake by SS316 and its decontamination

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Abstract

As-received and highly polished SS316 specimens were loaded with HT at 473–573 K. The uptake by polished samples was found to be up to five times that of as-received ones, when loading was performed immediately after polishing. This disparity vanished when polished specimens were subjected to a prolonged exposure to air prior to loading. The tritium loss from tritium-loaded SS316 specimens was examined by chemical etching and by thermal release in a flow system using various carrier gases at several temperatures. While at moderate temperatures the type of carrier has an impact on the tritium release rate, at higher ones this effect disappears. Moisture in the carrier gas has little influence on the loss rate of bulk tritium. Etching depth profiles of specimens previously heat-treated in the presence of air or $Ar + H_2$ and of untreated specimens are given. Evidence for chronic tritium liberation from SS316 at 298 K is provided.
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1. Introduction

The uptake of tritium by stainless steel and the subsequent decontamination of this material are of considerable practical and economical relevance to the operation and de-commissioning of fusion machines. In view of this, there is continuing need for a thorough understanding of the mechanisms of tritium outgassing from stainless steel surfaces under a variety of conditions and the development of efficient as well as reliable de-tritiation techniques.

Previous investigations have primarily dealt with the decontamination of SS316 previously contaminated at ambient temperature [1–3]. This work concentrates on the uptake characteristics of SS316 at elevated temperatures and its decontamination.

2. Experimental

Most experimental equipment and procedures used for sample loading and thermal release studies have been described in detail previously [4]. A few of the $1.5 \times 1.5 \times 0.05$ cm^3 specimens were polished with a suspension of 0.06 μm grain size alumina and with very fine emery paper.

To investigate the time-dependent thermal release of tritium from SS316 at various temperatures using different carrier gases, having dew points in the range 181–273 K, a conventional flow apparatus provided with two pairs of bubblers placed downstream, which can be valved-in alternatively, was used. Synthetic air, Ar and Ar containing 3% H$_2$ were used as carrier gases. In some experiments the moisture content of the gaseous carrier was controlled at various levels using either a special bubbler cooled by ice or a silicone rubber humidifier. Moisture was monitored with a NS Dewpoint Meter, Model 100D from Alpha Moisture System, Bradford, England.

Tritium-loaded specimens were etched by introducing them successively into one of 24 small flasks containing an acid mixture (conc. HCl:HNO$_3$ = 3:1) diluted with de-ionised water. After an appropriate reaction

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time, the specimen was removed from the acid and rinsed repeatedly with de-ionised water. To quantify the tritium liberated during each etching step, an aliquot was taken from this solution and its tritium content was determined by conventional LSC. The etching procedure was repeated until the specimen was completely dissolved. The surface layer thickness removed in each singular etching step was calculated from the known dimensions of the specimen and the determined weight loss.

3. Results and discussion

3.1. Tritium loading

Table 1 summarizes the loading conditions of a number of specimens with gaseous HT (24% T). Tritium loadings were determined either by full etching or by thermal release runs, in which the specimens were heated progressively up to a final temperature of 1073 K over a period totaling three hours. Both techniques delivered essentially the same results. The tritium uptake data at 473, 523 and 573 K given in Table 1 satisfy the Arrhenius relation. They yield the activation energy 49.0 kJ/mol, which is consistent with that for the diffusivity of hydrogen in SS316 [5].

The effect of polishing the surface of SS316 specimens on loading is illustrated in a semi-logarithmical plot in Fig. 1. Under identical loading conditions, i.e. 573 K and a HT pressure of 1.2 kPa over three hours, a recently highly polished specimen incorporated considerably more hydrogen (up to five times as much) than an as-received one (see Table 1). When, however, a highly polished specimen was stored under ambient air for one month (specimen 2-X-OX), the loading was again closely similar to that of an as-received specimen. While the increase in loading is attributed to the removal by mechanical treatment of the chromium oxide surface layer known to strongly inhibit the rate of uptake, the recovery of the original properties can be explained by a re-growth of this protective chromium oxide layer [2,6].

3.2. Depth profiles by etching

With the objective of removing only a fraction of the total tritium trapped in the bulk, a few specimens were heated for only a short time at an elevated temperature. The released gaseous HTO and HT, possibly together with some tritiated hydrocarbons, were collected separately in bubblers and quantified by LSC; tritium remaining in the bulk was determined by full chemical etching. In Fig. 2 (lower figure) the depth profile of an untreated specimen is compared with that of a specimen previously heated for 15 min at 573 K under an Ar carrier gas containing 3% H$_2$. The untreated specimen

Table 1
Summary of loading results

Specimen designation	Loading date	Loading conditions kPa, K, h	Average loading on date of experiment MBq/specimen	Approx. dates of experiments	Loading shortly after exposure to HT MBq/specimen	Storage period, month	Chronic release, %
L	25.02.02	1.00, 473, 3	1.01±0.4 (4)	(07–23).10.02	1.24±0.4 (3)	8	18.5
N	03.09.02	1.00, 573, 3	5.85	17.10.03	10.8	13	45.8
1-X-AR	12.08.03	1.19, 573, 3	7.69 (2)	(20.08–03.10).03	na	<1	–
1-X-POL	12.08.03	1.19, 573, 3	25.77 (3)	(18.08–08.10).03	na	<1	–
C-AR	09.01.01	1.19, 523, 3	2.8 (9)	(19.01–16.03).01	na	<1	–
E-POL	13.02.01	1.19, 523, 3	14.6 (5)	(28.02–26.04).01	na	<1	–
2-X-AR	28.08.03	1.20, 573, 3	8.59 (1)	12.09.03	na	<1	–
2-X-OX	28.08.03	1.20, 573, 3	7.34 (3)	(03.09–09.10).03	na	<1	–
Π	25.10.02	0.13, 473, 8	0.10±0.02 (10)	(01–10).11.02	na	<1	–
L	12.02.02	1.19, 523, 3	4.63±0.97 (6)	(10–25).11.02	nd	9	–
P	17.10.02	1.23, 473, 8	1.62±0.45 (9)	(20–31).10.02	na	<1	–

AR = as-received, POL = highly polished, OX = re-oxidized in air during 1 month, () = number of performed measurements, na = non-applicable, nd = not determined.
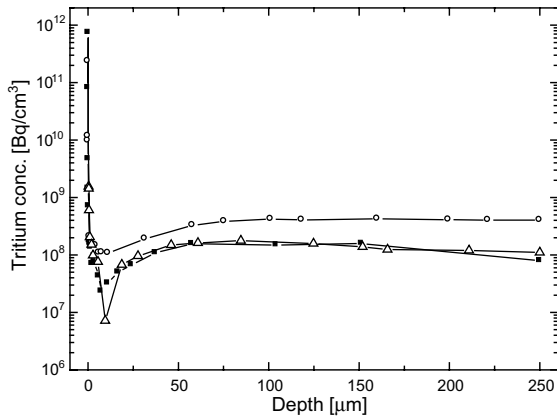
Fig. 1. Etching and loading results of tritium in as-received (■, 1-X-AR), in polished and loaded immediately (○, 1-X-POL), and in polished and loaded after one month of storage under air (△, 2-X-OX) SS316 specimens.
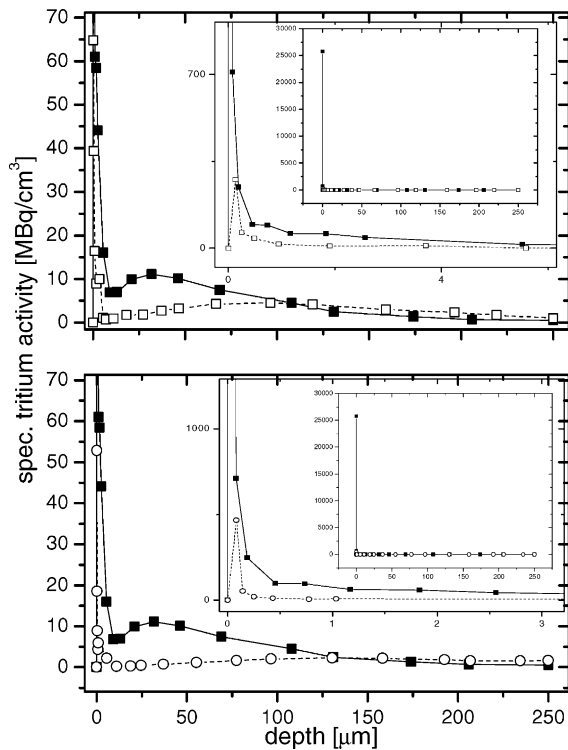

Fig. 2. Effect of carrier gas composition on the tritium release from the perspective of a depth profile obtained by etching: specimen heated to 573 K for 15 min under air (○) or under argon containing 3% hydrogen (□) in comparison with an as-received specimen (■), all from series Π.

shows a characteristic minimum at the center of the specimen (250 μm), which is explained by the fact that the achieved loading is below the equilibrium solubility.

The maximum at about 30 μm is due to losses towards the final stage of the loading procedure as well as to the chronic release at ambient temperature described above. At the outermost surface of the untreated specimen, i.e. at a depth of <0.2 μm, the concentration of tritium is particularly high, i.e. 26 000 MBq/cm^3 (see also smallest figure in lower Fig. 2). In comparison to this, the depth profile of the thermally treated sample shows that (i) the outermost surface concentration (peak value at a depth of about 0.2 μm (middle size figure)) has diminished to a level of only 250 MBq/cm^3, and (ii) the overall tritium inventory in the bulk has decreased significantly, i.e. 61% of the original inventory has been thermally released (collected in bubblers), and (iii) the bulk depth profile peak was shifted more towards the center of the specimen. Most likely some molecular hydrogen from the carrier gas has diffused into the metal bulk thereby slowing down the tritium loss from the specimen.

As opposed to this, a short 15 min exposure to a synthetic air stream at 573 K causes (i) a somewhat less pronounced decrease in tritium concentration at the outmost surface down to 500 MBq/cm^3, but (ii) a more depleted bulk depth profile with practically no maximum (see upper Fig. 2). By the short thermal treatment this specimen has lost 76% of its original tritium inventory to the carrier gas. The larger tritium fraction released thermally when air is used as carrier gas is consistent with the lower tritium content in the bulk obtained from etching. In comparison, in the experiment in which Ar + 3%H$_2$ was used as carrier gas only 61% of the tritium was lost thermally (see Fig. 2).

From the above it can be concluded that while the addition of hydrogen to the carrier gas promotes a more efficient liberation of the tritium from the topmost surface, it at the same time – at least initially – retards the release of tritium trapped in the bulk.

3.3. Thermal release

Polishing clearly reduces the thermal release rate of tritium from SS316 at 473 K under an argon carrier gas. As depicted in Fig. 3 the rate of tritium loss from a specimen loaded immediately after polishing and from one polished but loaded after being stored under air for approx. one month, are considerably slower than the loss rate from one loaded as-received specimen. This unexpected result is possibly due to the substantial loss of surface roughness associated with polishing.

Table 1 provides evidence for a chronic tritium release from SS3a16, i.e. specimens loaded many months before being used in the present work, contained considerably more tritium than that measured at the time when the release experiment was performed. Under the assumption that the tritium is liberated at a constant daily rate, a chronic release rate of 0.08% and 0.15%/day
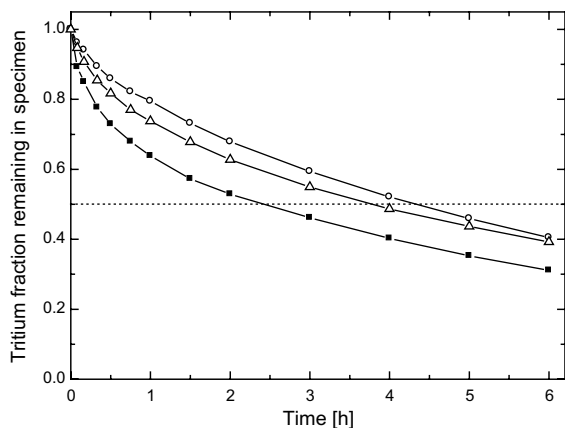
Fig. 3. Thermal release results of tritium from as-received (■, 1-X-AR), of loaded immediately after polishing (○, 1-X-POL), and of loaded after polishing and storing under ambient air for one month (△, 2-X-OX) SS316 specimens.

is estimated for the as-received specimens L′ and N, respectively, in good agreement with earlier results re-

ported by Surette and McElroy [1]. While there are indications that the beta radiation emitted by tritium catalyses the chronic release process, there is further work required to elucidate the mechanism.

3.4. Effect of the type of carrier gas on the thermal release of tritium

In a series of runs the thermal liberation rate of tritium from SS316 was compared at progressively increasing temperatures in a flow system using argon, air or argon containing 3% hydrogen as carrier gas (see Fig. 4). The results indicate that of all three examined carrier gases, air leads to the best results, i.e. promotes the fastest liberation of tritium. While at 523 K there is still a clear difference between Ar and Ar + 3%H_2, this difference dwindles as the release temperature is raised. At 673 K the type of carrier gas is practically immaterial. This allows the conclusion that at high temperatures after the initial removal of the topmost tritium (see Fig. 2) the transport processes in the bulk play a predominant role in stainless steel decontamination.
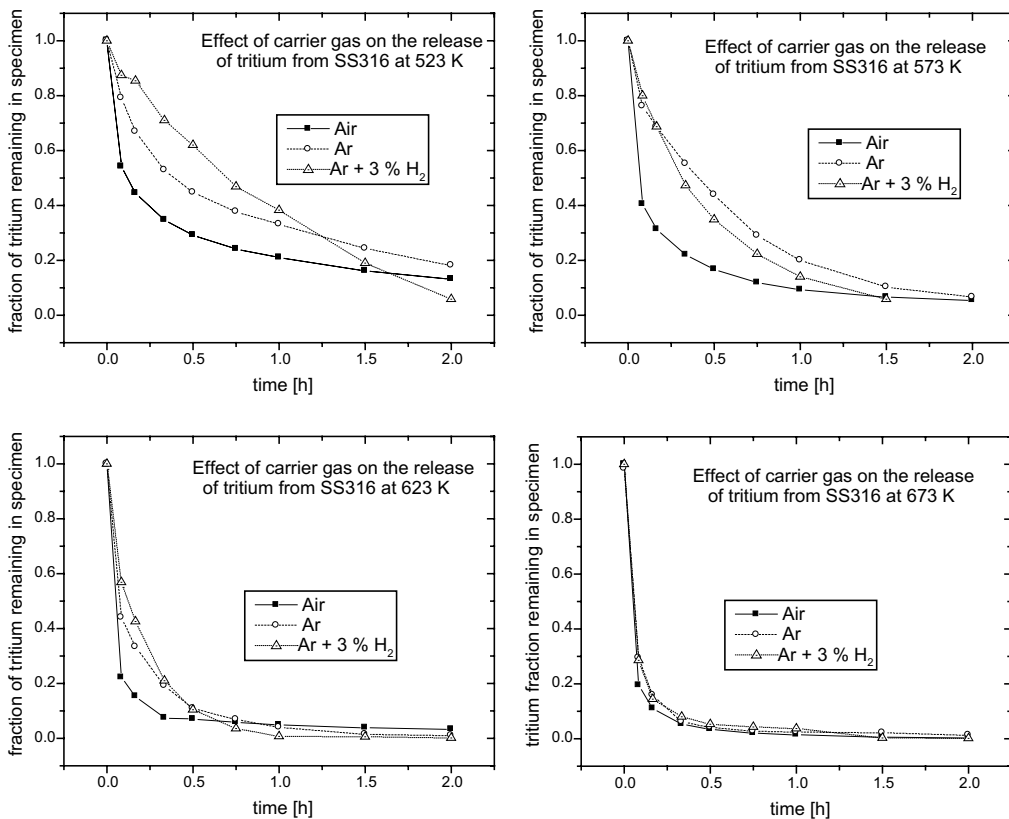

Fig. 4. Thermal release properties of tritium-loaded specimens (series P) at various temperatures under air, argon or argon containing 3% hydrogen.
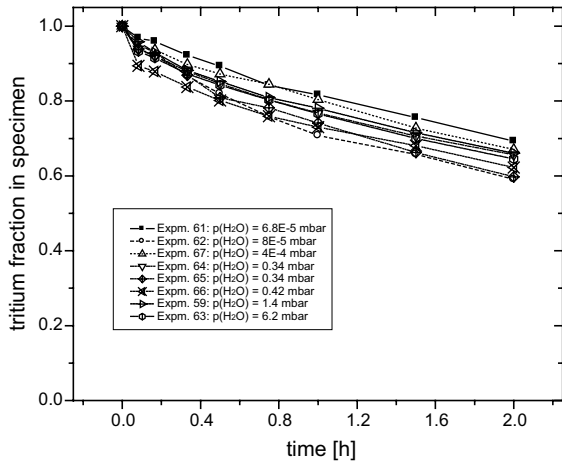
Fig. 5. Thermal release of tritium from SS316 specimens (1-X-AR and 2-X-AR) under argon with different partial pressures of moisture.

3.5. Effect of moisture in the carrier gas on the thermal release rate of tritium

The possible effect of moisture in an argon carrier gas on the rate of tritium release from SS316 was investigated systematically at 473 K (see Fig. 5). As apparent from the results, the effect of the partial pressure of H_2O, varied from 10^{-6} up to 0.61 kPa, is small and gives rise to no clear trend. The HTO/HT ratios were generally of the order of 1000, i.e. the large majority of the tritium is released as water. This agrees well with observations reported by other investigators [2,4]. In line with the results given in Section 3.4, at high temperatures the release of tritium from specimens loaded at elevated temperature is no longer governed by gas/solid interactions but is principally determined by tritium transport processes through the bulk.

4. Conclusions

Polishing of SS316 enhances the tritium uptake by SS316 drastically, but if the polished specimens are allowed to re-oxidize in air this effect disappears. Polishing, on the other hand, inhibits the tritium release rate. Tritium incorporated into stainless steel at elevated temperatures requires elevated temperatures for efficient conditioning. Because of the comparatively high specific concentrations of tritium on the surface and subsurface, it is possible to achieve with mild methods (sweeping with moist air, cleaning with water, light abrasion, etc.) a significant initial liberation of tritium. But this initial release overestimates the achievable decontamination because the majority of the tritium still remains in the bulk. Some of this tritium escapes from the bulk in a slow chronic release process of the order of $0.12 \pm 0.04\%$/day. All tritium can be released thermally at temperatures of 573 K or above, but then neither the type of carrier gas, i.e. air, argon or argon containing $3\%H_2$, nor the partial pressure of moisture in the carrier gas have a significant impact on the rate.

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