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Helium and hydrogen release measurements on various alloys irradiated in SINQ

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Abstract

Three irradiations have been performed in the Swiss Spallation Neutron Source (SINQ) to establish a materials database for mixed proton and neutron fluxes for future spallation neutron and other accelerator sources. Samples of 316LN, F82H, AlMg3, and Zircaloy-2 from STIP-II have been analyzed for their total helium and hydrogen contents and their release characteristics with temperature. Helium and hydrogen release measurements showed considerable levels of deuterium and tritium species which generally mirrored those of hydrogen. Hydrogen release occurred from about 300 °C for the AlMg3 to about 800 °C for the Zircaloy-2. For the Zircaloy-2 and the steels, helium release began to occur at between 1100 and 1200 °C, which is consistent with previous measurements on irradiated steels. Modeling of the hydrogen release data for the 316 and F82H suggests two traps of differing energy dependent on the irradiation dose and temperature. The higher energy traps are probably voids created from vacancy coalescence.

1. Introduction

Three irradiations have been performed in the Swiss Spallation Neutron Source (SINQ) to establish a materials database for mixed proton and neutron fluxes for future spallation neutron and other accelerator sources. The first experiment (STIP-I) was done in SINQ Target 3 (Zircaloy-2) from 1998 to 1999, the second experiment (STIP-II) was done in SINQ Target 4 (Pb-filled 316 SS tubes) from 2000 to 2001, and the third experiment (STIP-III) was done from 2002 to 2003. The results of helium and hydrogen gas measurements on materials from STIP-I have been reported earlier [1].

Materials included in STIP-II were mainly austenitic and martensitic steels, including 316LN, F82H, and T91. Samples of 316, F82H, T91, AlMg3, and Zircaloy-2 from STIP-II have been analyzed for their total helium and hydrogen contents and their release characteristics. These data will provide important comparisons between measurements and calculations for evaluation of current spallation cross sections, and also indications as to the generation and retention of helium and hydrogen under spallation irradiations conditions. The later will be very useful for understanding the helium and hydrogen effects on hardening and embrittlement of the irradiated materials.

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2. SINQ Target-4 and STIP-II

The lower part of the SINQ target is illustrated in Fig. 1. The normal target rods were lead (Pb) clad with SS 316L tubes. Test specimens were included in a number of tubes located in the most intense irradiation zone, i.e. the lower central region. About 10 thermocouples were installed at different positions for monitoring the irradiation temperature in both the normal rods and the specimen rods, and indicated a temperature range of 80–450 °C throughout the two-year irradiation. Temperatures for individual samples were based on calculations. In STIP-II, more than 2000 samples from more than 40 different materials were irradiated up to 20 dpa. Different types of samples such as TEM disks, tensile, bend-fatigue, bend-bar, Charpy, mini-CT, and SANS were used for various measurements. Detailed information has been reported elsewhere [2].

3. Analysis samples

For the present study, a number of samples from the STIP-II irradiation were analyzed for their hydrogen and helium release characteristics. A

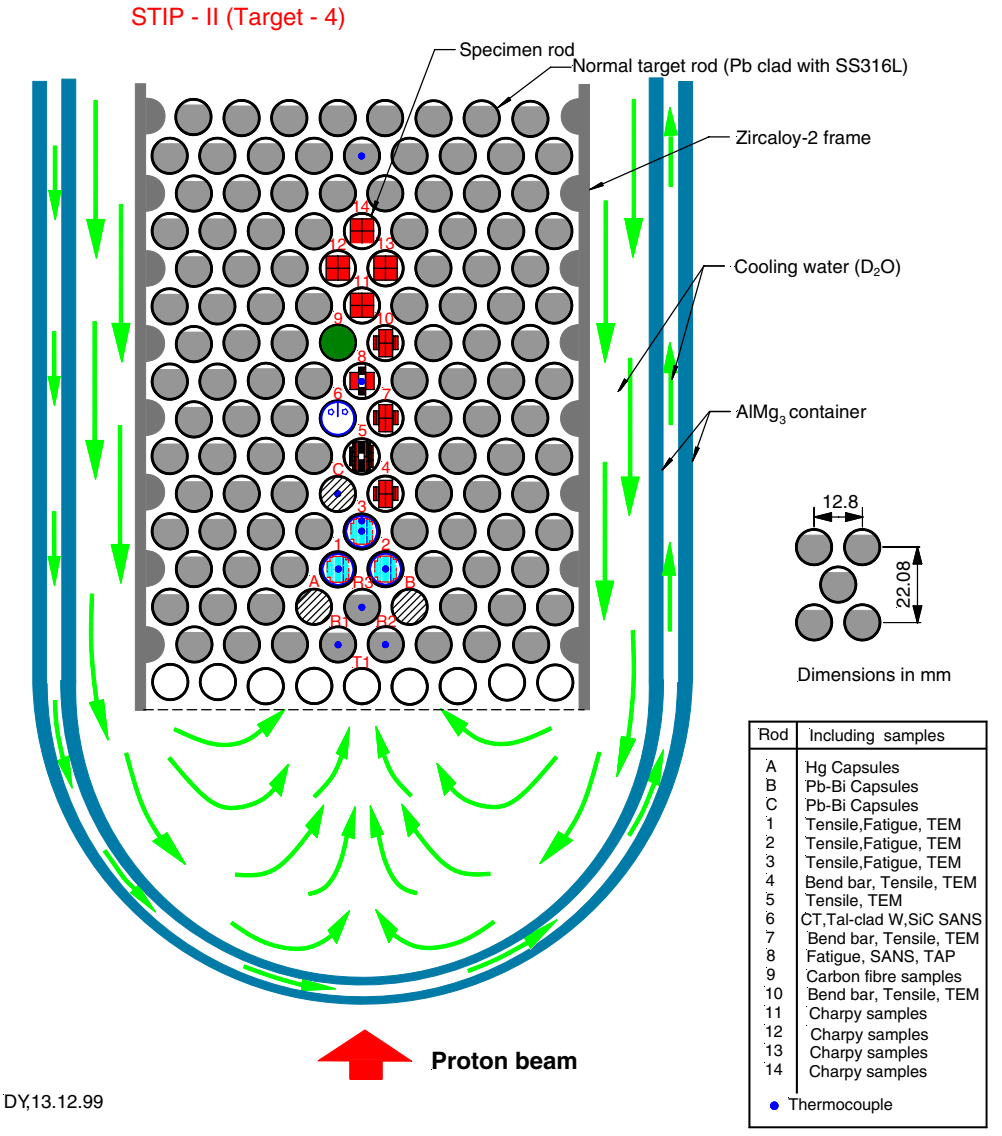

Fig. 1. Positions of the specimen rods in the lower part of the SINQ Target-4.

Table 1
STIP-II sample summary

Sample	Material	Position rod/X (mm)	Sample temperature (°C)	Irradiation dose (dpa)
A(1)	316 SS	10/30	<250	8.6
A(4)	316 SS	5/−2.5	428 ± 50	19.6
K(2)	F82H	10/−30	<250	10
K(4)	F82H	3/−2.5	400 ± 55	20.3
S(1)	Zircaloy−2	10/−10	<250	25.8
S(2)	Zircaloy−2	10/−30	<250	16
2A-R1	AlMg3	–	50	0.7

summary of these samples is given in Table 1. Total helium and hydrogen measurements have also been made, and these are reported separately [3]. The AlMg3 sample was in the form of a thin plate section; the remaining samples were in the form of 3 mm diameter disks. Each of the samples had been used previously for punching 1 mm diameter TEM disks, and thus had two or three small holes punched out of the sample.

Specimens for analysis were obtained by cutting pieces from the samples using small diagonal cutters. Before each use, the cutters were cleaned by wiping several times with a dry paper wipe. Prior to analysis, each specimen was rinsed in alcohol and air-dried. The mass of each specimen was then determined using a calibrated microbalance traceable to the National Institute of Standards and Technology (NIST).

4. Gas release measurements

Hydrogen and helium gas release was measured as a function of temperature using a specialized gas mass spectrometer system [4]. The analysis procedure involved dropping individual specimens, under vacuum, into a small cylindrical ceramic crucible whose temperature was increased in a very nearly linear profile from ~40 to ~1250 °C (~600 °C for the AlMg3) at a rate of ~25 °C/min. Prior to analysis, the analysis crucible was preheated to ~1300 K under high vacuum for several days to reduce hydrogen and helium background. During the pre-heating and subsequent analysis, the sample chamber was maintained at approximately room temperature.

Gas species observed for the release measurements included atomic masses 2 through 6, which included the hydrogen species H_2, HD, HT, DT, D_2, and T_2 (D = deuterium, T = tritium), and the helium isotopes ^{3}He and ^{4}He. Although the particular mass detector used could not separate the various helium and hydrogen species at the same atomic mass, the various species could be nominally separated by temperature and abundance. Specifically, it was assumed that gas release at mass 3 and 4 above about 1000 °C was attributable to ^{3}He and ^{4}He. This is a reasonable assumption given earlier measurements that have shown essentially complete hydrogen release from steels at temperatures <800 °C. Further, because of the general predominance of hydrogen in the gas release, mass 4 was assumed to be predominately from HT as opposed to D_2.

Primary calibration of the system for the various mass species was accomplishing using separate ^{4}He and H_2 calibrated leak sources attached to the analysis system. Secondary calibration for ^{3}He was based on measurements of a known ^{3}He/^{4}He gas source. Secondary calibration for HD and HT was based on the function $(1/M)^{1.25}$ which is appropriate for the quadrupole detector. Calibration measurements were conducted immediately following each sample analysis.

5. Results and discussion

5.1. Gas release measurements

Helium and hydrogen release measurements from the temperature ramp experiments are given in Figs. 2–5. The results showed several interesting trends. First, at lower temperatures, considerable levels of mass 3 and mass 4 species were observed that tended to mirror those of mass 2 (H_2). This suggests that there was considerable deuterium and tritium formation in the materials from spallation reactions, in addition to normal hydrogen. Relative to the H_2, HD levels were about 17% for the AlMg3 and about 25% for the steels and the Zircaloy-2. HT levels were a bit more variable, ranging from ~2% to 9% for the steels and ~8% for the AlMg3 and Zircaloy-2. Second, for the steels and Zircaloy-2, there appeared to be shifts in the temperature of the hydrogen release peaks which were dependent on the irradiation dose. Specifically, for the steels, the peak releases for the hydrogen species occurred from ~290 to ~380 °C for the lower dose sample and from ~425 to 465 °C for the higher dose samples. The width of the release peaks at the lower dose was also narrower. For the Zircaloy-2, a possible opposite effect was noted; ~730 °C for the lower

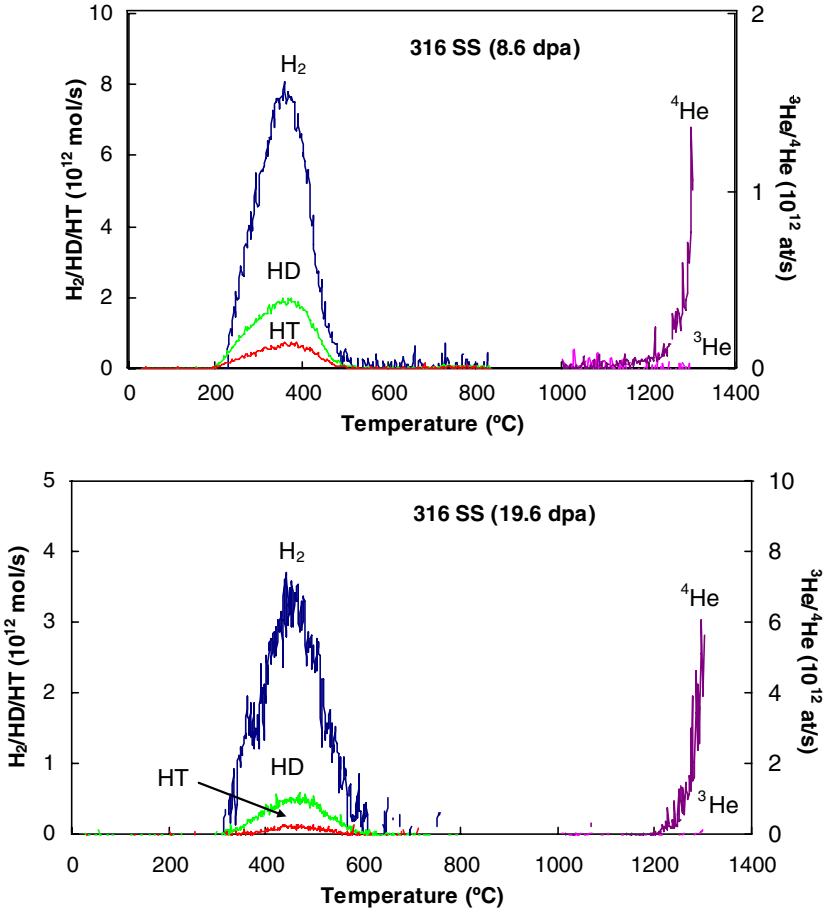

Fig. 2. Gas release from 316 SS versus temperature.

dose versus ~660 °C for the higher dose. Finally, hydrogen release in the Zircaloy-2 occurs at a significantly higher temperature than in the steel (~700 °C), and shows some evidence in the lower dose sample for a smaller secondary peak at ~400 °C. All of these results suggest different energy trapping sites for the hydrogen species that are dependent both on the material and on the irradiation dose and temperature.

Above about 1000 °C, the hydrogen species are assumed to be all released and the mass 3 and mass 4 species are then indicative of ^{3}He and ^{4}He. For the AlMg3, continued hydrogen release up to the maximum temperature of ~600 °C precluded separation of the helium and hydrogen releases. For the Zircaloy-2 and the steels, helium release begins at between ~1100 and 1200 °C, which is consistent with previous measurements on irradiated steels [5]. For the higher dose Zircaloy-2 sample, there was also evidence for a small ^{4}He release peak at ~1100 °C. Relative to the total helium in the sample, helium release at 1250 °C varied between the materials, being the lowest for the 316 SS at ~0.2% and the highest for the Zircaloy-2 at from ~0.8 to ~2.5%. For the F82H and the Zircaloy-2, there was a possible trend of increasing helium release with increasing irradiation dose. Although additional measurements would be needed to confirm such an effect, this could suggest differences in the helium gas trapping mechanisms for the various materials and irradiation conditions similar to that noted for the hydrogen releases.

5.2. Gas release modeling

Because hydrogen trapping (at vacancies, dislocations, voids, etc.) can be an indication of the degree of radiation damage to a material, an attempt was made to model the hydrogen release from the two different steels. The finite difference

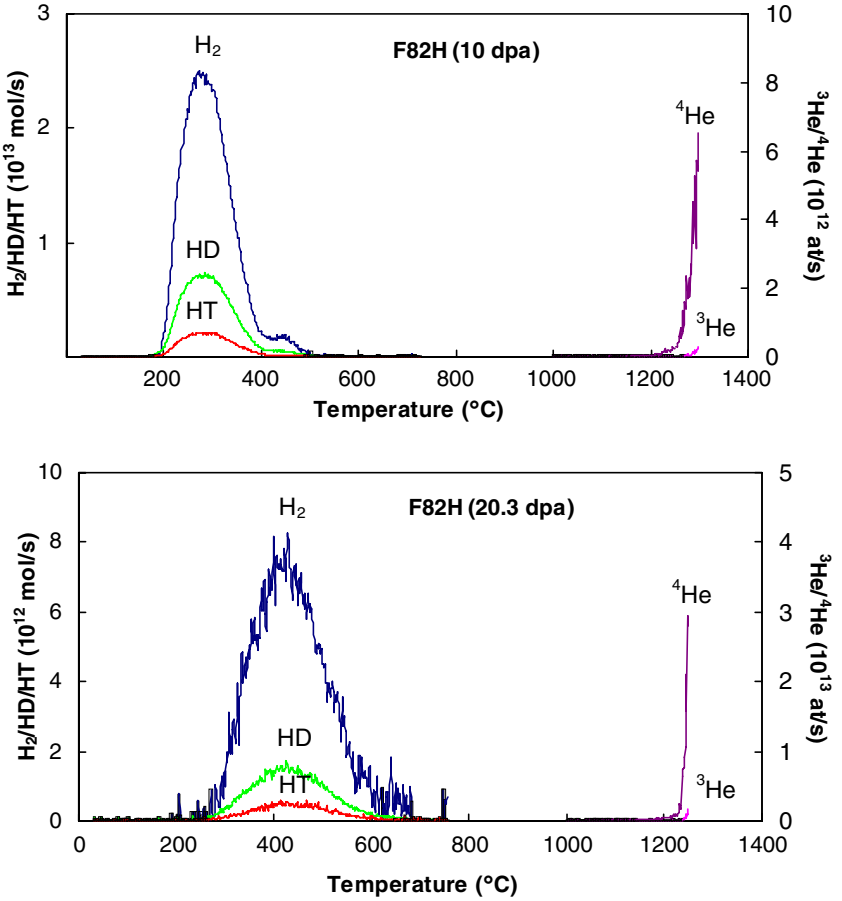

Fig. 3. Gas release from F82H versus temperature.

code DIFFUSE [6] was used to model the results. For this modeling, both the hydrogen diffusivity and the trapping parameters must be known. For the 316 stainless steel, the diffusivity measured by Sugisaki et al. [7] [$D = 4.2 \times 10^{-6}$ exp(-0.66 eV/kT) m^2 s] and a single trap energy of 0.96 eV (0.3 eV plus the diffusion activation energy of 0.66 eV) as determined by Hashimoto and Hino [8] were initially used in the calculations. Varying the single trap concentration over reasonable values, it was possible to match the lower dose sample release quite well with a trap concentration of 100 appm (see Fig. 6). Even when the higher irradiation temperature was assumed in the model for the higher dose sample, it was not possible to match the subsequent release that had shifted to a higher temperature without an unrealistic increase in trap density. Thus, it was apparent that a second trap had been generated by the higher irradiation dose and temperature. An indication of this can be seen for F82H in Fig. 3 as a small secondary release peak at ~450 °C which closely matches the temperature of the release in the higher dose sample. When a second trap of 1.1 eV was assumed with a concentration of 100 appm, a reasonably good fit to the data was achieved. It is postulated that the higher dose at the higher irradiation temperature generated a substantial number of voids. At the higher irradiation temperature of about 425 °C, vacancies are quite mobile and appear to agglomerate into voids, which trap hydrogen more deeply than other defects.

A similar behavior was noted for the F82H steel. For this analysis, the hydrogen migration parameters recommended by Serra et al. [9] [diffusivity given by $D = 1.1 \times 10^{-7}$ exp(-0.14 eV/kT) m^2 s and a trap energy of 0.72 eV (0.58 eV plus the diffusion activation energy of 0.14 eV)] were initially used. Fig. 7 shows the comparison of the normalized computed release to the measured data for

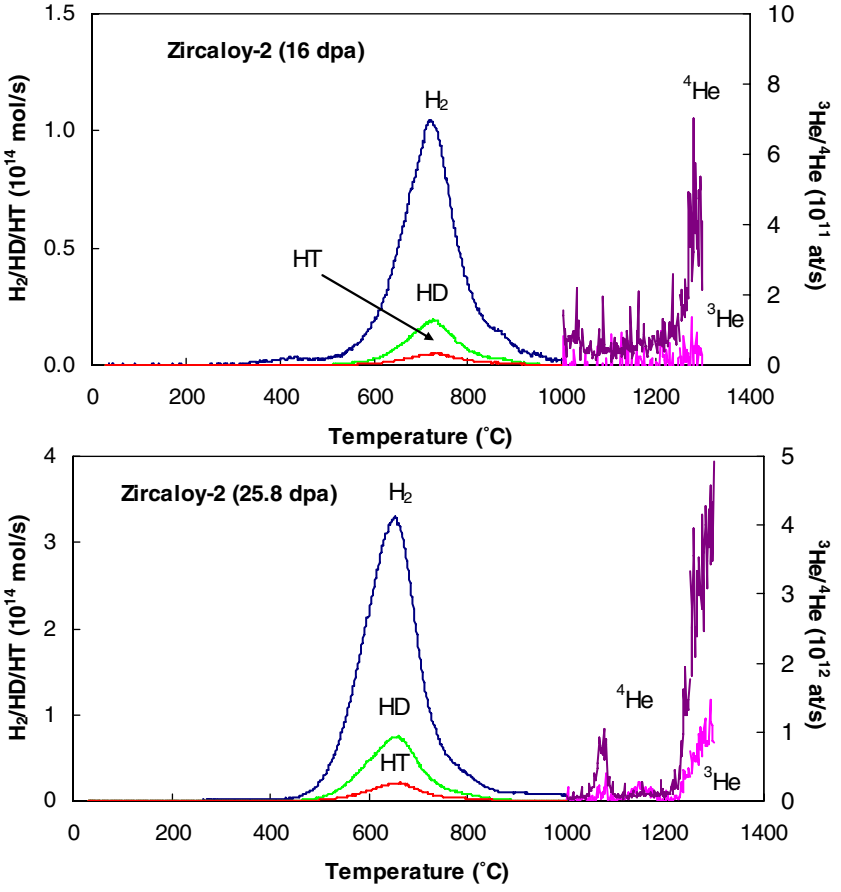

Fig. 4. Gas release from Zircaloy-2 versus temperature.

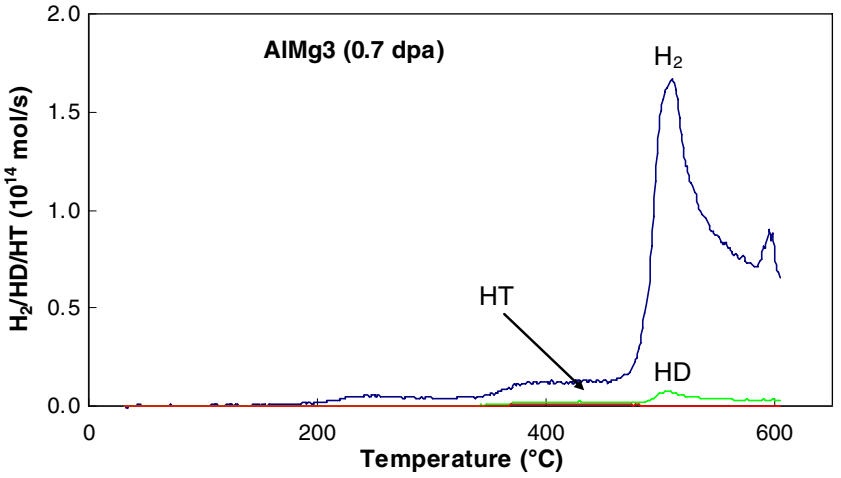

Fig. 5. Gas release from AlMg3 versus temperature.

the lower dose sample when a trap density of 100 appm was assumed. Attempts to also model the smaller secondary peak at ~450 °C were not successful because of overlap of the wider lower

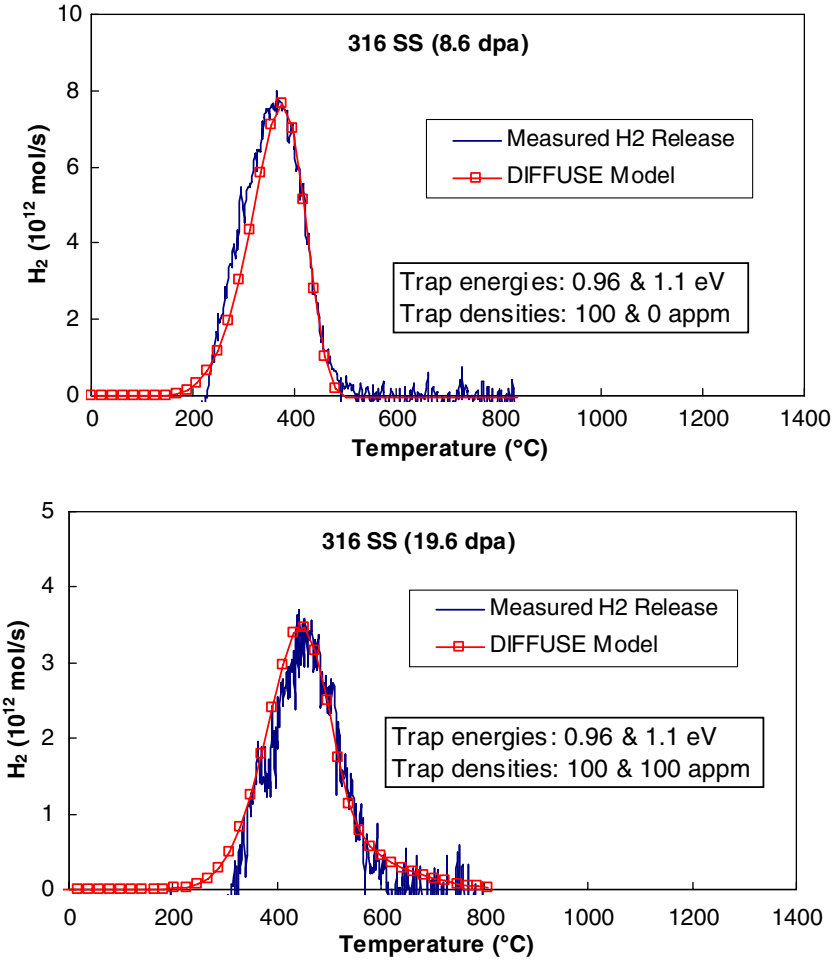

Fig. 6. Measured and DIFFUSE hydrogen release data for 316 SS.

temperature peak. Again, the higher dose sample release could not be modeled with a single trap energy. Adding a second trap with an energy of 1.1 eV and a density of 100 appm to account for void formation at the higher dose and temperature significantly improve the fit.

For the present study, modeling of the helium release was not attempted. TEM studies [10] indicate that the helium was largely trapped in bubbles and/or voids. At temperatures close to the melting point, it would be expected that these bubbles and voids would be highly mobile. The present data shows fairly rapid release of the helium beginning at about 1200 °C. At 1300 °C, which was the maximum temperature reached, helium release relative to the total helium in the material generally ranged from ~2% to 8%, with one sample (high dose F82H) showing a significantly higher fractional release at ~60%. Modeling of the helium release using DIFFUSE would be possible provided sufficient information was available on bubble and void migration parameters.

6. Summary and conclusions

Gas release measurements conducted on selected samples showed some interesting trends. For the steels, the main hydrogen release peak occurred a lower temperature and was narrower for the lower dose material as compared to the higher dose material. Significant deuterium and tritium releases were seen for all the samples, ranging from ~17% to ~30%, and from ~2% to ~9% of the total hydrogen, respectively. For the Zircaloy-2, hydrogen release occurs at a higher temperature, and exhibits a possible opposite temperature effect with irradia-

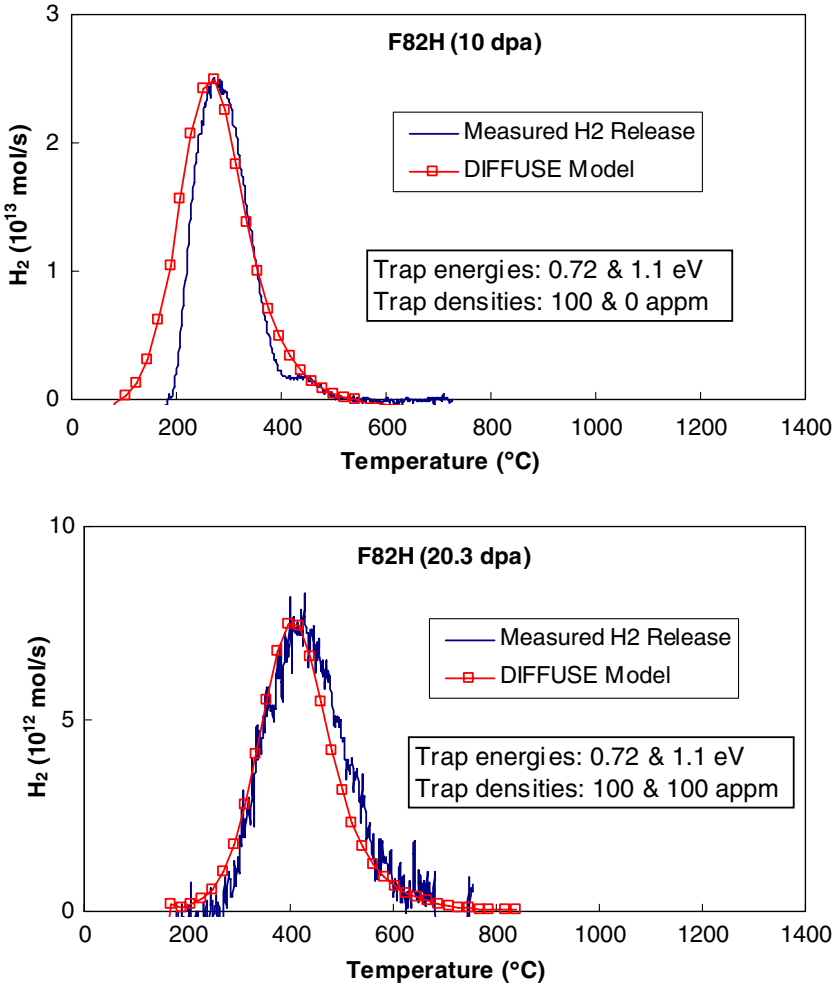

Fig. 7. Measured and DIFFUSE hydrogen release data for F82H.

tion dose as compared to the steels. Hydrogen release in the AlMg3 occurs at a lower temperature, and exhibits two peaks at ~440 and ~500 °C.

As expected, helium release from the materials does not occur in any significant amount until temperatures approaching ~80% of the melting point are reached. At 1250 °C, only ~0.2–2% of the total helium had been released from the steels or Zircaloy-2. There was a possible trend of increasing release fraction with increasing irradiation dose. Helium release from the AlMg3 was not measurable due to interference from continued hydrogen release at higher temperature.

Modeling the hydrogen release in the 316 SS and F82H material using the DIFFUSE code and a single trap showed reasonable agreement with measurements for the lower dose samples. For the higher dose samples, however, agreement was only possible by unreasonably increasing the trap destiny. Assuming a second trap at a somewhat higher energy allowed for a reasonable fit to the higher dose data using realistic trap densities. This suggests that the combination of higher irradiation temperature and higher dose is producing higher energy traps, probably voids created from vacancy coalescence. In future work we will compare TEM results of sample voids versus release temperature.

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