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Helium and hydrogen measurements on pure materials irradiated in SINQ Target 4

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ABSTRACT

Several 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. Pure metal dosimetry materials from the second irradiation (STIP-II) have been analyzed for their total helium and hydrogen contents and their release characteristics with temperature (TDS). Total helium results are similar to those observed earlier from the first irradiation experiment (STIP-I), with concentrations ranging from ~500 to ~1000 appm. Hydrogen contents varied over a larger range from ~100 to ~60 000. $^3He/^4He$ ratios were generally consistent with expectations, except for Ti, Nb, and Ta which showed lower values due to ^3He from decay of irradiation-generated tritium. Some differences were observed in the hydrogen TDS data for the control and irradiated materials, including some evidence for additional lower-temperature release and for multiple release peaks. Additionally, differences were noted in the releases for irradiated material that been cleaned versus material that had no cleaning.

1. Introduction

Four 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, the third experiment (STIP-III) was done from 2002 to 2003, and the fourth experiment (STIP-IV) was done from 2004 to 2005. The results of helium and hydrogen gas measurements on materials from STIP-I have been reported earlier [1].

Materials included in the second irradiation (STIP-II) included austenitic and martensitic steels, Ni-, Zr- and Al-alloys and pure metal dosimetry materials. Some 316LN, F82H, Zircaloy-2 and $AlMg_3$, and the dosimetry materials 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 provide 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 irradiated materials. The results of the different alloys have been published elsewhere [2]. The results of the dosimetry materials are reported in this paper.

2. SINQ Target-4 and STIP-II

The test specimens were included in SINQ Target-4 in a number of rods located in the most intense irradiation zone, i.e. the lower central region. The normal target rods were lead (Pb) clad with SS 316L tubes. Approximately 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. 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-compact tension, and small angel neutron scattering were used for various measurements. Detailed information has been reported elsewhere [3].

3. Analysis samples

Most of the samples for He/H analysis were in the form of TEM-sized disks. Analysis specimens were obtained by cutting pieces from the samples using small diagonal cutters. Prior to analysis, each specimen was rinsed in alcohol and air-dried. The mass of each specimen ranged from ~0.25 to 20 mg, and was determined using a calibrated microbalance. Samples for hydrogen analysis included both irradiated and unirradiated control material, and except for several initial measurements, all were rinsed in room-temperature acid prior to analysis to remove surface impurity layers. The initial measurements provided an opportunity to observe any possible effects on the He or H release from the cleaning step.

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4. Gas release measurements

Total helium measurements were performed by isotope-dilution gas mass spectrometry following vaporization in a resistance-heated graphite crucible in a high-temperature vacuum furnace [4]. The absolute amount of ^{4}He released was measured relative to a known quantity of added ^{3}He 'spike'. Total hydrogen measurements were also conducted by gas mass spectrometry using a separate analysis system [5]. The analysis procedure involved dropping individual specimens into a small evacuated ceramic crucible heated up to ~1300 °C. Prior to analysis, the sample crucible was pre-heated to ~900 °C for an extended period of time to reduce hydrogen background. Before initial vacuum pumping, the sample chamber and crucible volume were subjected to a low-pressure (~200 mTorr) argon discharge for ~30 min to aid in the desorption of water that could be dissociated by the hot crucible during analysis and thus contribute to the measured hydrogen release.

Hydrogen and helium gas release was also measured as a function of temperature using the same analysis system. In this case, the temperature of the crucible was increased in a very nearly linear profile from ~40 °C to a maximum of ~1250 °C (depending on material) at a rate of ~25 °C/min. 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 close to the melting point was attributable to ^{3}He and ^{4}He. Additionally, 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 $(1/\text{mass})^{1.25}$ which is reasonable for the quadrupole detector.

5. Results and discussion

5.1. Total He/H gas concentration measurements

The results of the total He and H measurements are given in Table 1. The results are given as concentrations in atomic parts per million or atomic parts per billion, and for helium, as isotopic ratios. Hydrogen concentrations measured in the unirradiated control materials are also shown. The results in the table are averages of duplicate or replicate analyses. Absolute uncertainty (1σ) in the individual helium analysis results, determined from the cumulative uncertainties in the sample mass, the isotope ratio measurement, and the spike size, is estimated to be ~1–2%. Absolute uncertainty in the hydrogen analyses, for high hydrogen concentrations (>~500 appm), is estimated at 5–10%. As mentioned above, however, additional uncertainty may also be present from possible low-level hydrogen release from water layers or hydrated metal oxides remaining on the surface of the samples after the discharge cleaning, that are subsequently dissociated by the hot crucible.

Measured ^{4}He concentrations in the samples (Table 1) ranged from 488 appm for Nb-2 to 1489 appm for Au-11. The observed helium contents were generally consistent with expectations based on the combined proton and neutron exposures. Reproducibility between the duplicate helium analyses averaged ~4%. The normal analysis system reproducibility for samples with known homogeneous helium content is ~0.5%, indicating some dose gradients across the samples.

Helium isotopic ratios (^{4}He/^{3}He) ranged from 0.5 for Nb-2 to 20.6 for Fe-20. Except for the Ti, Nb, and Ta, the ratios are consistent with values observed previously for other proton-irradiated materials [6]. The low ratio values for these three materials are likely due to ^{3}He formation from the decay of tritium in the materials. As is evident in the gas release measurements (Figs. 1–8), these materials had very high levels of hydrogen species, including tritium. A similar trend was noted earlier in analyses of Fe and Ni from the Los Alamos Neutron Science Center [7].

Measured hydrogen concentrations in the samples (Table 1) ranged from 132 appm for Au-11 to 59800 appm for Nb-2. Note, that the hydrogen values in Table 1 are for hydrogen released as H_2 only, as only mass 2 was observed for these particular measurements. Additional hydrogen in the form of HD and HT are not included. Reproducibility between the duplicate analyses averaged ~25%, which is consistent with the range of variability observed in measurements of a standard hydrogen-containing steel maintained at PNNL. As noted above, the hydrogen levels were very high in three of the samples, Ti-7, Nb-2, and IB-1 (Ta), and also had higher variability. From the gas release measurements (Figs. 1–8), the additional contribution from HD and HT is of the order of ~10%. Except for gold, residual hydrogen levels in the unirradiated control materials were significantly lower than that observed in the irradiated materials. Within experimental uncertainty, the level of hydrogen in the control and irradiated gold material were comparable.

Table 1
Measured helium and hydrogen in STIP-II samples.

Sample	Material	Fluence (10^{25}/m^2)		Measured He		Measured ^{1}H (appb)[c]	
		Proton	Neutron	^{4}He/^{3}He Ratio[a]	(appm[b])	Sample	Control
Al-19	Al	4.45	9.06	18.9 ± 0.5	1114 ± 34	499 ± 160	71 ± 18
Ti-7	Ti	3.5	7.83	3.4 ± 0.4	1165 ± 83	37100 ± 16100	470 ± 72
Fe-20	Fe	2.45	7.02	20.6 ± 0.4	922 ± 26	804 ± 200	120 ± 76
Ni-1	Ni	2.45	7.02	17.9	955 ± 17	1030 ± 708	99 ± 13
Cu-23	Cu	2.45	7.02	13.1 ± 0.1	922 ± 21	1410 ± 42	56 ± 4
Nb-2	Nb	0.96	5.37	0.5 ± 0.0	488 ± 32	59800 ± 7850	149 ± 18
IB-1	Ta	3.24	8.71	2.2 ± 0.0	1059 ± 83	35300 ± 140	7020 ± 400
Au-11	Au	3.5	7.83	20.2 ± 0.4	1489 ± 8	132 ± 22	185 ± 47
Pb-1	Pb	2.95	7.0	6.1 ± 0.3	1001 ± 83	3340 ± 905	17 ± 0

[a] Measured ^{4}He/^{3}He atom ratio.
[b] Mean and 1σ concentration in sample in atomic parts per million (10^{-6} atom fraction).
[c] Mean and 1σ concentration in sample and control in atomic parts per billion (10^{-9} atom fraction).

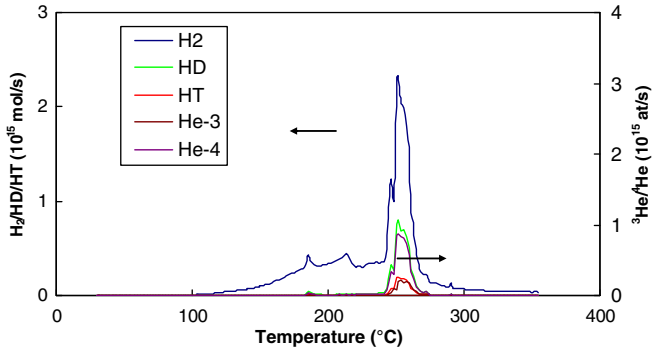

Fig. 1. He/H release from Pb-1 sample.

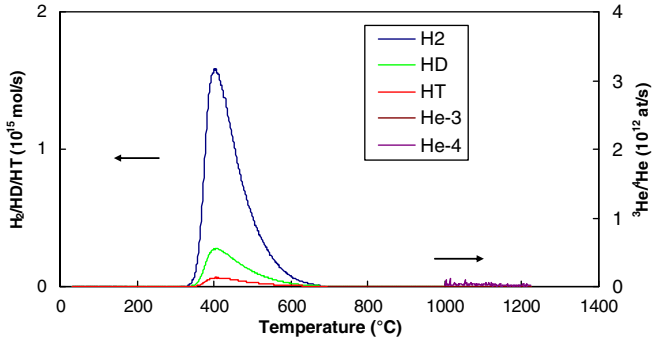

Fig. 2. He/H release from IB-1 sample.

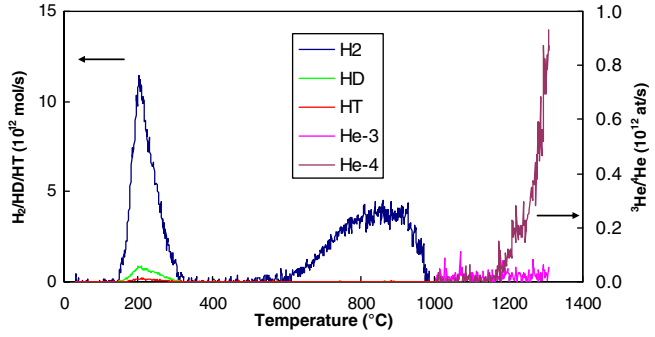

Fig. 3. He/H release from Fe-20 sample.

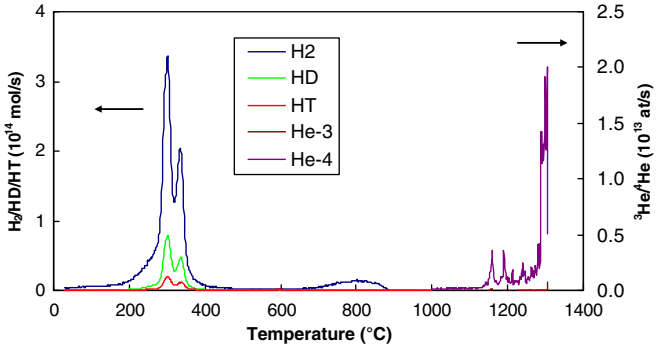

Fig. 4. He/H release from Ni-1 sample.

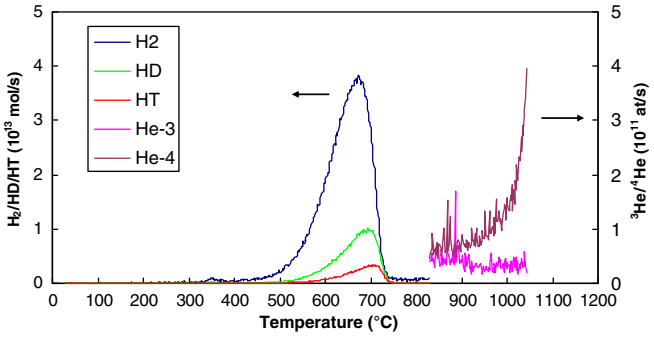

Fig. 5. He/H release from Cu-23 sample.

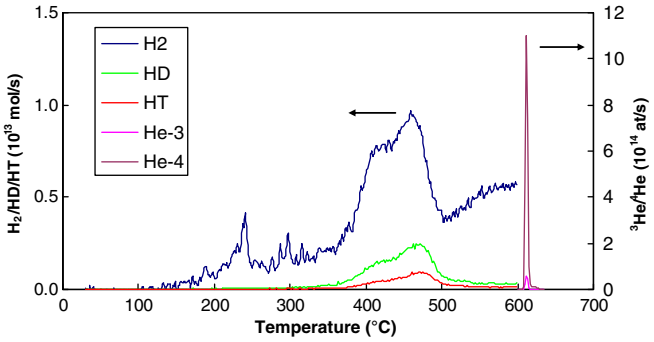

Fig. 6. He/H release from Al-19 sample.

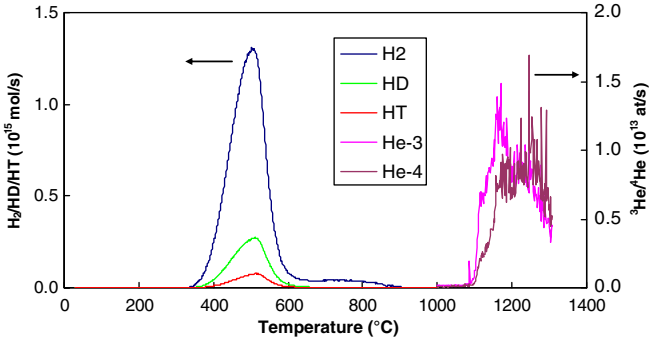

Fig. 7. He/H release from Ti-7 sample.

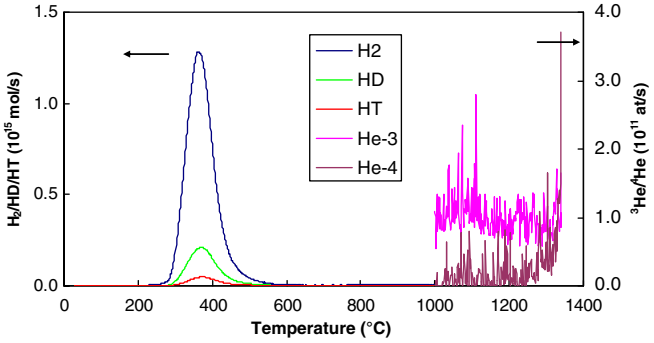

Fig. 8. He/H release from Nb-2 sample.

5.2. Gas release measurements

Helium and hydrogen release measurements with temperature are shown in Figs. 1–8. The results show several interesting trends. First, at lower temperatures, considerable levels of mass 3 and mass 4 were observed that tended to mirror those of mass 2 (H_2). This indicates that there was considerable deuterium (as HD) and tritium (as HT) formation in the materials from spallation reactions, in addition to protium. Relative to H_2, the HD levels ranged from ~6 for Fe to 10% for Ni and Cu. For HT, the relative levels generally ranged from ~2% to 3%, except for Fe at ~0.2% and Pb at ~6%. Hydrogen species release occurred either as single peaks (Ta, Cu, Ti, Nb) or as multiple peaks (Pb, Fe, Ni, Al). Single peaks suggest a single trapping site whereas multiple peaks suggest multiple trapping sites of differing energies.

In the temperature range reasonably below the melting point, helium release was generally much smaller than the hydrogen release, suggesting that helium atoms were in small clusters (bubbles, or combined with vacancy or interstitial atoms). In the case of lead, however, the helium release was co-mingled with the hydrogen release below the melting point, with some burst releases above the melting point. This was confirmed by vaporization analysis of several of the lead specimens following TDS, which showed no remaining helium. In the Ta sample no helium release was seen up to 1220 °C, which can likely be attributed to the high melting point of Ta. As a fraction of the total helium measured in the sample (Table 1), helium release ranged from only ~0.2% for Cu to ~65% for Al. The reason for the low helium release in copper, even close to the melting point, is not completely understood, but may indicate high helium retention until the copper melts.

Because of space constraints, plots of the hydrogen release in an initial group of un-cleaned samples are not included here. However, these initial analyses did provide an opportunity to see if surface effects were affecting the hydrogen release profiles. As a general trend, the un-cleaned samples showed more hydrogen release peaks. This suggests that surface layers could be affecting the recombination of hydrogen at the surface, resulting in multiple release peaks.

6. Summary and conclusions

Helium and hydrogen concentrations were measured in proton-irradiated pure metal samples irradiated in SINQ Target 4. He-4 concentrations ranged from 488 appm to 1489 appm, and were generally consistent with expectations based on the combined proton and neutron exposures. Helium isotopic ratios ($^4He/^3He$) ranged from ~0.5 to ~20.5. Except for Ti, Nb, and Ta, the ratios are consistent with values observed for previously analyzed proton-irradiated materials. The low ratio values for Ti, Nb, and Ta are most likely due to ^3He formation from decay of irradiation-produced tritium in the materials.

Measured hydrogen (H_2) concentrations ranged from 132 appm to 59 800 appm. Hydrogen in the form of HD and HT was of the order of ~10% of the total hydrogen. Except for gold, residual hydrogen levels in the unirradiated control materials were significantly lower than that observed in the irradiated materials.

Helium and hydrogen release measurements with temperature showed considerable deuterium and tritium in the materials, in addition to protium. Relative to H_2, HD levels ranged from ~6% to 10% and HT levels ranged from ~0.2% to 6%. As expected, helium release with temperature was much smaller than the hydrogen release (except for Pb), and occurred at higher temperatures. As a fraction of the total helium measured in the sample, helium release ranged from ~0.2% for Cu to ~65% for Al.

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