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Journal of Nuclear Materials 283–287 (2000) 1438–1442

journal of nuclear materials

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Accelerated helium and hydrogen production in ^{54}Fe doped alloys – measurements and calculations for the FIST experiment

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Abstract

F-82H alloys isotopically enriched in ^{54}Fe up to 86% were irradiated in the high flux isotope reactor (HFIR) to determine the accelerated production of helium and hydrogen due to isotopic effects. Results are compared to calculations using isotopic helium production cross-sections from ENDF/B-VI or GNASH and measured neutron spectra. Helium measurements demonstrated an accelerated helium (appm)/dpa ratio of 2.3 after a 1.25-year irradiation, an increase of a factor of 4.3 over natural iron. The accelerated helium production is due to higher helium production cross-sections for ^{54}Fe and ^{55}Fe. Alloys doped with ^{55}Fe could achieve helium/dpa ratios up to about 20, well above the fusion reactor ratio of 10. Hydrogen measurements were performed using a newly developed quadrupole mass spectrometer system at PNNL. Calculations predict that hydrogen production will be accelerated by about a factor of 13 over natural iron. However, measurements show that most of this hydrogen is not retained in the samples.

1. Introduction

Helium analyses of natural iron irradiated in HFIR indicated non-linear, accelerated helium production [1]. This effect was ascribed to isotopic transmutation since gas production cross-sections vary significantly. In order to study these isotopic differences in helium and hydrogen production, iron alloys enriched in ^{54}Fe were fabricated in Japan [2]. The nominal F-82H alloy composition is 7.1Cr–1.8W–0.55Si–0.40Mn–0.17V–0.1C–0.04Ta. ^{54}Fe in the alloy comprised 96% of the iron or 86% of the total alloy by weight. For comparison, similar alloys were produced both with natural iron and with natural iron doped with varying amounts of boron.

Transmission electron microscopy (TEM) alloy specimens were irradiated in the JP17 and JP22 irradiations in HFIR [3,4]. Neutron dosimetry measurements and radiation damage calculations for the JP17 experiment were reported previously [5]. Dosimetry monitors have not yet been analyzed for the JP22 irradiation. The JP17 irradiation had an exposure of 43.5 EFPD leading to about 2.8 dpa and 1.0 appm helium in natural iron. The JP22 irradiation had a longer exposure of 458.2 EFPD leading to about 29 dpa and 10.5 appm helium in natural iron. Calculations in this paper used the JP17 dosimetry data normalized to the JP22 exposure conditions.

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0022-3115/00/$ - see front matter
PII: S0022-3115(00)00301-9

2. Helium measurements

Four alloy samples were analyzed for helium content at Pacific Northwest National Laboratory. The composition of each specimen is listed in Table 1. Samples C103 and C203, which were fabricated with natural iron, also contained small additions of boron (1 and 58 appm ^{10}B, respectively). The helium content of each specimen was determined by isotope-dilution gas mass spectrometry following vaporization in a high-temperature vacuum furnace [6]. The absolute amount of ^{4}He released was measured relative to a known quantity of added ^{3}He 'spike'. The results of the helium analyses are given in Table 1. Absolute uncertainty (1σ) in the individual helium analysis results is estimated to be approximately 1%.

3. Helium production calculations

The helium production cross-sections differ for each iron isotope, as shown in Fig. 1. The cross-sections were taken from the ENDF/B-VI libraries [7]. During the course of each irradiation, the iron isotope ratios change due to (n,γ) reactions, followed by the subsequent decay of the radioactive isotopes of ^{55}Fe (2.73 y) and ^{59}Fe (44.5 d). Greenwood et al. [1] demonstrated these effects using mass spectrometry to measure the altered iron isotopic ratios. As the iron isotope ratios transmute, the helium production will increase or decrease accordingly to the isotopic cross-sections shown in Fig. 1. These cross-sections were integrated over the HFIR neutron energy spectrum to determine the helium production rates. The calculated ratios of fast neutron helium production relative to that of natural iron are 1.85 (^{54}Fe), 0.93 (^{56}Fe), 1.89 (^{57}Fe), and 0.16 (^{58}Fe).

Helium production cross-sections have not been measured for the radioactive isotopes ^{55}Fe and ^{59}Fe. In Ref. [1], the semi-empirical computer code THRESH2 was used to calculate the helium production rate ratios. These calculations predicted a ratio of 5.95 for $^{55}Fe(n,\alpha)/^{N}Fe(n,\alpha)$, although the ratios for the other iron isotopes differed somewhat from the ENDF/B-VI values listed above. A new calculation was performed at Argonne National Laboratory using the GNASH computer code [8]. GNASH is based on the Hauser–Feshbach formulation of the statistical model with pre-equilibrium and direct reaction corrections. Optical model parameters were taken from the literature. The GNASH calculations are also shown in Fig. 1. As can be seen, the $^{55}Fe(n,\alpha)$ reaction has by far the largest cross-section of any of the iron isotopes with a ratio of $^{55}Fe(n,\alpha)/^{N}Fe(n,\alpha) = 30.3$. It should be noted that this reaction has a large positive Q-value of +3.584 MeV. It is thus possible that the reaction has a small thermal neutron cross-section, as suggested in Greenwood et al. [1].

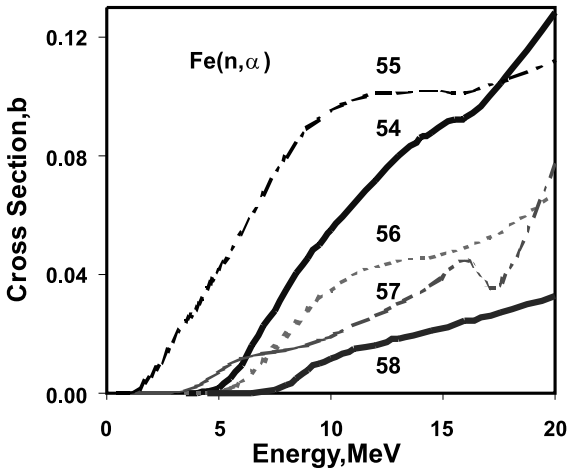

Fig. 1. ENDF/B-VI neutron cross-sections for the (n, helium) reactions for iron isotopes. The ^{55}Fe cross-section was calculated with the GNASH computer code.

Helium production was integrated over short time intervals for each irradiation. For the samples FN-51 and C603, which are enriched in ^{54}Fe, the calculations using the above cross-section ratios underpredict the measured helium values by about 50%. In order to fit the JP-17 helium measurement for sample FN-51, it is necessary to increase the fast neutron helium production in ^{54}Fe by about 86%. This cross-section is not very well known at lower neutron energies, which are the most important in the HFIR neutron energy spectrum. This new measurement, therefore, suggests that the ^{54}Fe (n,α) cross-section in ENDF/B-VI is too low, especially at low energies. The higher helium level seen in the JP-22 irradiation for sample C603 also requires some adjust-

Table 1
Helium concentrations in FIST samples

Sample	Run	Iron	He (appm) average[a]
FN51	JP-17	96%^{54}Fe	4.52 ± 0.05
C603	JP-22	96%^{54}Fe	64.8 ± 0.2
C103	JP-22	Natural	21.8 ± 0.1
C203	JP-22	Natural	320 ± 8

[a] Mean and S.D. (1σ) of duplicate analyses.

ment of the helium production cross-section in ^{55}Fe. Mathematically, it is possible to fit the data with either a greatly elevated rate of fast neutron production in ^{55}Fe or a weak thermal neutron effect in ^{55}Fe, as originally suggested [1]. If the effect is solely due to fast neutrons, then the ratio of helium production in ^{55}Fe to that of natural iron would have to be about 37:1. This ratio is only slightly higher than the GNASH value of 30.3:1. On the other hand, if the ^{55}Fe/natural iron helium production ratio is reduced to the lower THRESH2 predicted value of 5.95, then the helium data can be well fit using a small thermal neutron helium production cross-section in ^{55}Fe of about 0.011 barns. Irradiation of ^{55}Fe in a purely thermal neutron field or irradiations using cadmium covers would be needed to determine the thermal neutron ^{55}Fe(n,α) cross-section. Since we do not know either the fast or thermal helium cross-sections for ^{55}Fe, we can only give a range of values that would fit the data. The most likely answer is that there is a thermal neutron cross-section in ^{55}Fe of about 0.01 barns and that the fast helium cross-section ratio to natural iron is about 6.

The data and calculations are compared in Fig. 2. The dotted line is calculated without considering any helium production from ^{55}Fe. The curve starts to bend over at high dpa due to the burnup of ^{54}Fe. The solid line includes helium production from ^{55}Fe using a thermal neutron cross-section of 0.01 barns and a fast helium cross-section of 6 times the natural iron helium production. It is important to note that this calculation would give the same results using a fast helium ratio of 37 or a purely thermal cross-section of 0.014 barns.

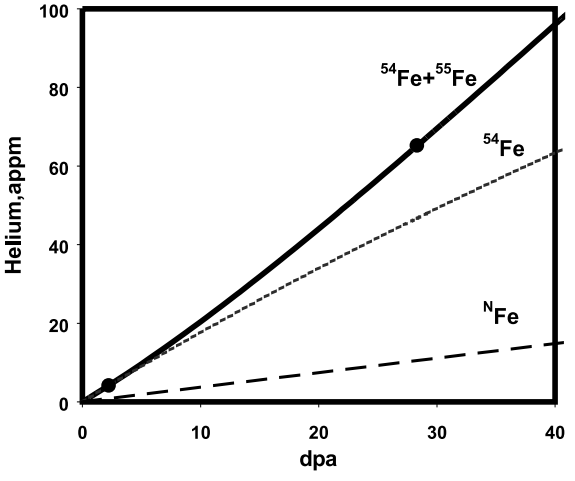

Fig. 2. Measured helium production (solid dots) compared to calculations with only the modified ^{54}Fe cross-sections (dotted line) and with both ^{54}Fe and ^{55}Fe modified cross-sections (solid line). Helium from natural iron is shown for comparison (dashed line).

Hence, we can confidently predict helium production in iron in a mixed-spectrum reactor such as HFIR. The calculations were extended to higher exposures to predict achievable helium/dpa ratios in HFIR for these alloys, as discussed below.

In the case of the natural iron alloys doped with boron (C103 and C203) the high thermal neutron fluences in these HFIR experiments totally transmuted the B-10 to helium. Converting from weight percent to atom percent, this would predict 4 appm helium from B-10 in sample C103 and 321 appm helium from B-10 in sample C203. Using the same iron isotopic cross-sections derived for the ^{54}Fe doped alloys, we would predict 20 appm helium from the natural iron alloys. Adding this to the B-10 values would predict 24 appm helium in sample C103 compared to the experimental value of 22 appm helium ($C/E = 1.10$). Similarly, the calculated value for sample C203 is 344 appm helium compared to the measured value of 321 appm helium ($C/E = 1.07$). This level of agreement is well within the uncertainties on the boron concentrations. Hence, the ^{54}Fe and ^{55}Fe cross-sections also give good agreement for natural iron, similar to that seen previously in Ref. [1].

4. Hydrogen measurements and calculations

The transmutation of the iron isotopes changes the hydrogen production in a similar manner to the helium production. We have recently developed a new hydrogen system at PNNL that allows the measurement of about 5 appm hydrogen in milligram-sized irradiated specimens. Details of this new system are described in another paper at this conference [9]. The same samples that were analyzed for helium were also analyzed for hydrogen and the results are summarized in Table 2. As can be seen, the unirradiated samples appear to contain about 44 appm hydrogen. The FN51 samples in JP-17 contained an average level of 340 appm hydrogen while the C603 samples in the longer JP-22 irradiation had a similar average amount of hydrogen at 396 appm. Calculations using the ENDF/B-VI and GNASH cross-sections for the various iron isotopes, as shown in Fig. 3, predict that the samples should have about 182 and 2119 appm hydrogen for the JP-17 and JP-22 irradiations,

Table 2
Hydrogen concentrations in FIST samples

Sample	Run	Hydrogen (appm)	
		Measured	Calculated
FN92	None (control)	44 ± 7	0
FN51-2	JP-17 (250°C)	186 ± 86	182
FN51-1	JP-17 (250°C)	494 ± 126	182
C603	JP-22 (300°C)	396 ± 21	2119

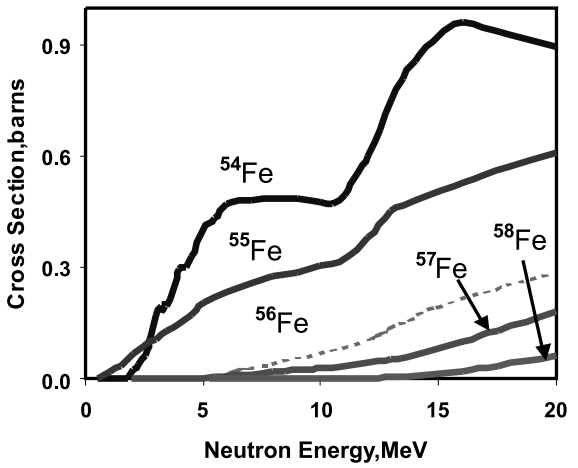

Fig. 3. ENDF/B-VI neutron cross-sections for the (n, hydrogen) reactions for iron isotopes. The ^{55}Fe cross-section was calculated with the GNASH computer code.

respectively. The results show that the JP-17 samples contain somewhat more hydrogen than would be predicted. This may indicate a possible thermal neutron hydrogen production in Fe-55 or simply that the GNASH calculation is too low. On the other hand, the JP-22 results are well below the calculations indicating that hydrogen is simply not being retained. We should note that the JP-22 samples were irradiated at 300°C whereas the JP-17 samples were at a lower temperature of 250°C. Obviously, more work is needed to understand both the production and retention of hydrogen in these materials. However, the present results give some indication of the level of hydrogen that is retained under these conditions and clearly show an increase in hydrogen compared to unirradiated material.

5. Recommendations for future irradiations

The present work demonstrates that elevated helium production can be achieved in iron by enriching with ^{54}Fe or ^{55}Fe. Irradiations with natural iron produce a nearly constant ratio of helium (appm) to dpa of about 0.54 using the ENDF/B-VI calculated rate. It should be noted that this rate is somewhat higher than the ENDF/B-V Gas Production File value of 0.37, as quoted in Greenwood and Baldwin [5], for example. The present experiment achieved a helium/dpa ratio of 2.3, an increase of a factor of 4.3 over natural iron. In order to simulate fusion reactor conditions, we would like to achieve a helium/dpa ratio of about 10. Using the present alloys, which are nearly fully-enriched in ^{54}Fe, it would only be possible to achieve a helium/dpa ratio of about 3:1 with a similar irradiation in HFIR lasting about 4 years, as shown in Fig. 2. HFIR produces about 22.7 dpa in iron per full power year of operation. If alloys were produced with an initial doping with ^{55}Fe, then fusion-like ratios of helium/dpa could be easily achieved. Regardless of whether the ^{55}Fe effect is due to thermal or fast neutrons, ^{55}Fe will produce about 37 times more helium than natural iron in HFIR. Pure ^{55}Fe would thus produce a helium/dpa ratio of about 20:1. The desired fusion helium/dpa ratio of 10:1 could be achieved by doping natural iron with 50% ^{55}Fe or with a mix of ^{54}Fe and ^{55}Fe. This production rate would, however, decrease with time as ^{55}Fe either decays (2.73 y) or is transmuted to ^{56}Fe. It would be possible to offset these losses by using a mix of ^{54}Fe and ^{55}Fe so that ^{54}Fe would be transmuted to ^{55}Fe to replace these losses. Total replacement is possible if we match the initial ^{54}Fe/^{55}Fe ratio to the ratio of the decay rate of ^{55}Fe to the transmutation rate of ^{54}Fe of about 3.5:1. In this case, we could achieve a nearly constant helium/dpa ratio of about 5.9:1. Of course, one would have to allow for losses of ^{55}Fe due to decay from the time of production and including possible reactor down times.

^{55}Fe is a low-energy X-ray emitter. Hence, it could be safely handled in relatively large quantities for production of doped alloys, although cost considerations might be a more serious problem. An alternative would be to first irradiate ^{54}Fe to breed ^{55}Fe, then use this transmuted material to make the alloy for the fusion simulation experiment. For example, a two-year irradiation of ^{54}Fe in HFIR would breed about 8%^{55}Fe. The ^{54}Fe will decrease about 15%, the difference mostly going to ^{56}Fe. The decay of ^{55}Fe produces ^{55}Mn, which rapidly transmutes to ^{56}Fe. This transmuted iron would then produce an initial helium/dpa ratio of about 3.3:1 increasing to about 4:1 after a year of irradiation. In order to achieve higher helium/dpa ratios, it would be necessary to isotopically separate the ^{55}Fe produced from the ^{54}Fe irradiation (or purchased commercially) and then use the separated ^{55}Fe for further alloy preparation. In this way, one could produce alloys with any desired helium/dpa ratio including 20:1 (pure ^{55}Fe), 10:1 (50:50 mix of Fe and ^{55}Fe), or a steady-state production at 6:1 (3.5:1 ratio of ^{54}Fe to ^{55}Fe).

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