DE-FC07-05ID14665

The Effect of H and He on Irradiation Performance of Fe and
Ferritic Alloys

Final Report

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22 January 2010

Executive Summary

This Final Report covers the period of technical work performed under contract DE-FC07-05ID14665, entitled “The Effects of H and He on the Irradiation Performance of Fe and Ferritic Alloys.

The results are divided into three sections: (I) Irradiation Damage and Effects in Fe and the Influence of He and H, (II) Irradiation Damage and Effects in Ferritic Alloys and the Influence of He and H, (III) Mechanical Properties Analysis of Ferritic Alloys, and (IV) Neutron Irradiation Program for Fe and Ferritic Alloys. The program involved a substantial amount of experimental and modeling work on this alloy system. This report includes a short summaries of the larger bodies of work performed in this research program. Parts of the work are covered in two PhD dissertations which are available electronically.¹ Interested readers are encouraged to look at those sources for full details of those sections of the work scope.

¹ The PhD dissertations, in full, can be accessed at <http://proquest.umi.com/login> Searches should be performed on Okuniewski, Maria (author) and Pan, Xiao (author) to access those documents

Table of Contents

	Executive Summary	2
I.	Program Overview	4
II.	Irradiation Damage and Effects in Fe and the Influence of He and H.....	8
III.	Irradiation Damage and Effects in Ferritic Alloys and the Influence of He and H.....	13
IV.	Report Mechanical Properties Analysis of Ferritic Alloys	13
V.	Neutron Irradiation Program for Fe and Ferritic Alloys	20
VI.	Summary	20

I. Program Overview

This research program was designed to look at basic radiation damage and effects and mechanical properties in Fe and ferritic alloys. The program scope included a number of materials ranging from pure single crystal Fe to more complex Fe-Cr-C alloys. The range of materials was designed to examine materials response and performance on ideal/model systems and gradually move to more complex systems. The experimental program was coordinated with a modeling effort. The use of pure and model alloys also facilitated the ability to develop and employ atomistic-scale modeling techniques to understand the inherent physics underlying materials performance.

The technical approach in this program was designed to reveal a fundamental understanding of the irradiation-induced defect structures in Fe and selected Ferritic Alloys (all are bcc materials) and the influence of H and He on their stability and evolution. The approach is to use a combined experimental and modeling effort to build a robust, physically-meaningful understanding of the irradiation damage mechanisms. The program will start with the simplest possible system (single crystal bcc Fe) and build a complete understanding of the influence of added complexities leading up to advanced ferritic/martensitic steels. This approach will develop a fundamental understanding of the roles of various microstructural features (e.g. grain boundaries, dislocation population, lath and subgrain structures, alloying additions, etc.) in the irradiation performance. The individual and combined roles of H and He these processes will also be examined.

Program Goals

1. Develop fundamental understanding of irradiation-induced defect structures and the individual and combined roles of H and He in the damage evolution in Fe and associated alloys.
2. Extend and further develop this knowledge to simple Fe alloy systems (binary, ternary, etc.) and then to more complex ferritic/martensitic steels.
3. Use this knowledge to assess materials mechanical properties evolution under irradiation, materials design lives and help develop more irradiation resistant alloys, including situations with high H and He production rates.

Research Test Plan

The research test plan was formulated to accomplish the three major research goals presented and discussed above. An outline of the activities follows:

1. Fundamental studies of irradiation-induced defect structures in Fe with and without H and He

Initial experimental and modeling work was aimed at experimentally developing and analyzing damage defect structures in pure, single crystal Fe with and without H and He using PAS and TEM techniques to quantify microstructural-level defect structures. The experimental effort is complimented by MD and KLMC calculations to simulate the initiation and evolution of displacement-induced defects and defect structures. Cascade formation and early evolution is addressed using MD techniques, and the evolution of surviving defects and defect clusters is followed using KLMC techniques. These results are correlated with the experimental results to provide insight into the relative effects of atomic displacements, H and He on resulting damage microstructure.

2. Extend to simple Fe alloy systems (binary, ternary, etc.) and more complex ferritic/martensitic steels

Experimental and modeling work was aimed at analyzing damage defect structures in more complex Fe alloy systems, including binary and ternary alloys and advanced steels (e.g. mod 9 Cr – 1 Mo, HT-9, ODS steels) with and without H and He. More complex potentials for MD will be developed (Fe-Cr is the first priority) and other defect transport issues were addressed for these systems.

3. Assess materials mechanical properties evolution and design lives under irradiation, and develop more irradiation resistant alloys, including applications with high H and He production rates.

The understanding of defect structure stability and evolution, including extended defects structures (from kMC) was used to assess irradiation-induced materials mechanical properties changes and to provide insight into alloying and processing possibilities to improve materials irradiation performance. The Warp MD code was used for mechanical behavior studies, and future effort will start to link these microstructural level approaches, including dislocation evolution, pinning and dynamics, to constitutive equations for finite element (FEM) applications. This task concentrated on developing a strong link between damage evolution and mechanical/structural performance. In addition, guidance for future ferritic alloy improvement will be developed. The program was designed specifically to understand process which might lead to flow localization, a major problem in reactor structural materials.

An addition, not available or anticipated at the beginning of this work, was the opportunity to irradiate specimens in the Advanced Test Reactor (ATR). This development allowed us the possibility to obtain neutron irradiation data on the same materials studied using ion irradiation techniques in the main work in this program. Due to the ATR irradiation planning and schedule, that effort will culminate after the conclusion of the current program. Also, the costs of specimen fabrication, loading, and some post irradiation examination will be borne by the ATR User Facility Program. While this work falls outside of the scope of the original contract, we report the progress here since the work is directly linked to this program and will be of interest to the readers of this report.

The program Task Structure is shown in Table 1.

Table 1. Program Tasks

Task	Description
1	Damage in Pure Fe
1.1	Irradiations (dpa, H, He)
1.2	PAS Analysis
1.3	TEM and Other Analyses
1.4	MD Simulations
1.5	KMC Simulations
2	Damage in Complex Ferritics
2.1	Irradiations (dpa, H, He)
2.2	PAS Analysis
2.3	TEM and Other Analyses
2.4	MD Simulations
2.5	KMC Simulations
3	Mechanical Properties Model
3.1	Microstructure-Properties Correlation
3.2	Constitutive Model Development
3.3	FEM-Model Applications
4	Reporting/Coordination
4.1	Quarterly
4.2	Annual
4.3	Final

The Effects of H and He on Irradiation Performance of Fe and Ferritic Alloys

The work included the following materials systems and the radiation and analysis conditions in various aspects of the program.

Table 2 – Experiments and Association with other Studies

Alloy	Alloying	Temp (C)	Dose (dpa)	Comment
Fe	Single XL, C=0, H & He	300, 450	0 to 3.5 lons, IVEM/Tandem	Irradiation Effects <i>Completed</i>
Fe-14Cr, Fe-19Cr	Single XL, C=0, H	300, 450, 550	0 to 3.5 lons, IVEM/Tandem	Irradiation Effects <i>On-going</i>
Fe-9Cr	C= 0, 0.1, 0.5%	RT to 400	0	Tensile <i>Completed</i>
Fe-12Cr	C= 0.2, 0.5%	RT to 400	0	Tensile <i>Completed</i>
Mod 9Cr-1Mo	Commercial	400 &500	8, 16, 30, 60 Phenix Irr	TEM, Tensile, CT <i>On-going</i>
HT-9	Commercial	400 &500	8, 16, 30, 60 Phenix Irr	TEM, Tensile, CT <i>On-going</i>
MA-957	Developmental	400 &500	8, 16, 30, 60 Phenix Irr	TEM, Tensile, CT <i>On-going</i>

Table 2 also contains information about the places where the experiments in this program coordinate with other ongoing research efforts. A major consideration of the selection of the experimental conditions was the value of the current work to other materials studies. In particular, the intention was to develop some useful understanding of materials behavior based on model alloys that could be translated to more complex alloy systems that are considered for actual component fabrication. The information would also be useful for determining which alloying or processing parameters could be adjusted to improve alloy performance.

II. Irradiation Damage and Effects in Fe and the Influence of He and H

This section provides an overview of the work on the irradiation effects of H and He in Fe. A complete description of this section of work is contained in the PhD Dissertation of Dr. Maria Okuniewski, available on line at <http://proquest.umi.com/login> [searches should be performed on Okuniewski, Maria (author)].

Irradiations were carried out on pure Fe single crystals. The irradiations were conducted with ion beams at the Michigan Ion Beam Laboratory. Irradiation damage was controlled by implanting protons (p) and in a variety of cases the Fe was preimplanted with He in order to study the He effect with controlled levels of appm He/dpa. The typical implantation ranges are shown in Figure 1.

Figure 1. Ion implantation ranges for He and H in Fe

The full range of irradiation conditions for the ion implantation studies are shown in Table 3. The table shows the irradiation doses, irradiation temperatures and the relative levels of appm He/dpa. The experiments indicate that the studies covered useful range of conditions. The two irradiation temperatures were selected to represent a lower temperature range where the nucleation and growth of dislocation loops would dominate the microstructure, and an upper temperature range where the nucleation and growth of voids or bubble would dominate the microstructural evolution.

Table 3. All ion irradiated conditions investigated in this study. The specific conditions that were examined by TEM during this program quarter are highlighted with purple.

	dpa (H)	He to Damage Ratio (appm/dpa)	He (appm)	T (°C)
1	0	0	0	300
2	0	0	0	450
3	0.03	0	0	300
4	0.3	0	0	300
5	3	0	0	300
6	0.03	0	0	450
7	0.3	0	0	450
8	3	0	0	450
9	0.03	10	0.3	300
10	0.3	10	3	300
11	3	10	30	300
12	0.03	10	0.3	450
13	0.3	10	3	450
14	3	10	30	450
15	0.03	150	4.5	300
16	0.3	150	45	300
17	3	150	450	300
18	0.03	150	4.5	450
19	0.3	150	45	450
20	3	150	450	450
21	0	∞	0.3	450
22	0	∞	4.5	450
23	0	∞	45	450
24	0	∞	450	450

In addition to the radiation conditions shown above, a number of matching irradiation conditions were performed at the Intermediate Voltage Electron Microscope/Tandem Accelerator (IVEM/Tandem) facility at Argonne National Laboratory. In those cases, the irradiations were performed *in situ* so that the microstructural evolution could be followed as a function of dose.

Following irradiation, specimens were analyzed with a variety of analysis techniques including Positron Annihilation Spectroscopy (PAS), transmission electron microscopy (TEM), and nanohardness. Representative results are shown below.

PAS analysis was performed to examine both the relative changes in the S and W parameters as well as direct positron lifetime measurements. Results from the S and W parameters are shown in Figure 2.

Figure 2. S parameter versus W parameter at a positron energy of 46 keV giving an average positron depth of 2.3 μm . Data is normalized to unirradiated single crystal bcc Fe. The blue ellipse indicates the grouping of the 300°C irradiations and the red ellipse indicates the grouping of the 450°C irradiations

A wide variety of TEM conditions were examined, too numerous to include here. The work included sets of comparative micrographs showing the microstructural detail, in particular the dislocation loop structure and the void/bubble structure. A good example of the value of these types of sets of images is shown in Figure 3. This particular condition is the highest He level and highest dose level at 300°C. It is clear that numerous small bubbles are formed at this dose condition.

Figure 4 shows a series of doses in the IVEM/Tandem facility where the development of the radiation induced microstructure is seen. In these cases, high purity polycrystalline Fe specimens were used due to difficulties in preparing adequate specimens from the single crystal material.

Figure 5 shows an analysis and comparison of damage evolution results for this study compared to others.

Figure 3. The 3 dpa, 450 appm He, 300°C specimen observed in (a) bright field, (b) dark field, (c) underfocused, 3600 nm, bright field, and (d) overfocused, 3600 nm, bright under and over focused conditions.

Figure 4. Dark field images of unirradiated (a), a dose of 1×10^{17} ions/m² (0.035 dpa) (b), a dose of 3×10^{17} ions/m² (0.11 dpa) (c), and a dose of 1×10^{18} ions/m² (0.36 dpa) (d) for 150 keV Fe in polycrystalline Fe at 450°C taken in the Fe irradiated and electron beam region. The scale applies for all images. Defects were identified and selected in (c) and (d)

Figure 5. Areal defect density versus dose of *in-situ* TEM experiments. The results for this work are shown in red and blue markers. The dose in terms of dpa (on the secondary x – axis) only applies to the Fe experiments, not Xe.

Kinetic Monte Carlo (kMC) was used to model the systems in question here. The intent was to compare the evolution of void and bubble microstructure as a function of dose and He content. Figure 6 shows an example of these types of comparisons.

Figure 6. Void size spectrum for KMC simulations with 10 appm He/dpa (0.02, 0.2, and 1 dpa at 327°C) and *ex-situ* TEM results (3 dpa, 300°C).

It can be noted that in this example and in general, the kMC model underpredicts the void/bubble size distribution. The kMC results tend to indicate more and smaller void/bubbles nucleate and do not grow with dose. The reasons for these differences between predictions and experiment are still under investigation.

III. Irradiation Damage and Effects in Ferritic Alloys and the Influence of He and H

As a basis of comparison with the pure Fe material, a series of single crystal Fe-Cr alloys were examined. Due to the unavailability of the ion beam facility at Michigan, these irradiations were performed exclusively at the IVEM/Tandem Facility at ANL.

Figure 7. A comparison pure Fe, Fe-14Cr and Fe-19Cr single crystal material irradiated at doses of 0, 1×10^{14} , 4×10^{14} , 7×10^{14} and 1×10^{15} ion/cm² (from left to right).

These dark-field micrographs illustrate defect evolution in the FeCr system as compared with pure Fe when irradiated with 150keV Fe ions at 450°C. In the pure Fe, complex extended and nested loop structures form. In the FeCr alloys, by contrast, we do not see extended structures and instead see an increasing density of relatively small loops with increasing ion fluence.

IV. Mechanical Properties Analysis of Ferritic Alloys

This section provides an overview of the work on the mechanical properties issues in more complex Fe-Cr alloys with controlled levels of C. A description of this section of work is contained in the PhD Dissertation of Dr. Xiao Pan, available on line at <http://proquest.umi.com/login> [searches should be performed on Pan, Xiao (author)].

Four types of model alloys were selected for examination in this part of the program. They were Fe-9%Cr-0.1%C(M62), Fe-9%Cr-0.5%C(M67), Fe-12%Cr-0.2%C(M65), Fe-12%Cr-0.5%C(M66). The ingots were hot forged to obtain small slabs (600x200x40mm). After hot forging, the alloys were reaustenitized at 980°C for 30 minutes and cooled down in air to room temperature. This produced a very fine martensitic structure throughout the materials. Then each

type of model alloys was cut into three pieces for three different heat treatments. The exact isothermal transformation curves cannot be found for each type of model alloy. Bee and Honeycombe provided ferrite and precipitate morphologies for Fe-10%Cr alloy. An example of the resulting microstructures showing the effect of heat treatment is shown for one condition in Figure 8. The carbide size distribution is shown in Figure 9 for this particular condition.

Figure 8 SEM micrographs of model alloys Fe-9%Cr-0.5%C aged for 4 days

Figure 9 Particle size distribution for Fe-9%Cr-0.5%C at three heat treatments at 4 days aging

Figure 10 Tensile cradle for elevated temperature testing.

Following aging, miniature tensile specimens were fabricated to perform in situ tensile test at the Advanced Photon Source (APS) at ANL.

Tensile loading tests were performed on these more complex Fe-Cr-C alloys (see Table 2). During testing, the APS beam was selectively directed at various points of the gauge length as indicated in Figure 11.

Figure 11. Schematic of experimental diffraction setup.

The stress and strain could be tracked as a function of loading and the evolution of the plasticity-induced void formation – by separation of the carbides from the matrix – could also be tracked. This is accomplished by use of the diffraction rings, see Figure 12. Note that both the matrix and precipitate rings are visible so that the strains can be separated between the two.

Figure 12. 2D diffraction pattern of Fe-9%Cr-0.5%C alloy

The tensile test results show the normal engineering stress strain response as shown in Figure 13 for the materials conditions shown above in Figures 8 and 9. Note that the experiments were performed as a function of temperature up to 400°C .

Figure 13 Engineering strain and engineering stress curves of 4 types of model alloys (a) Fe-9%Cr-0.1%C, (b) Fe-9%Cr-0.5%C, (c) Fe-12%Cr-0.2%C, and (d) Fe-12%Cr-0.5%C, tested at room temperature, 100°C, 200°C, 300°C, and 400°C

The fracture surface for this particular condition is shown in Figure 14.

Figure 14 Fracture surfaces of 4 types of model alloys tested at room temperature Fe-9%Cr-0.5%C-4d

SAXS analysis was also performed on the specimens to identify the point(s) at which plasticity-induced voids form during the tensile process. Typical SAXS curves are shown in Figure 15. These images indicate the location of void formation and are processed for various locations along the tensile axis of each specimen. From this information, we are able to look at the temperature dependence of the point of flow localization during tensile loading. These results are shown in Figure 16 where the major point of void evolution occurs at the maximum (engineering) load which is the ultimate tensile strength. These results indicate that there is only minor void development before this point in loading, but it becomes predominant at the UTS. This response is due to the separation of the precipitates from the matrix, and controls the UTS.

Figure 15 Fitting results of SAXS profiles for Fe-9%Cr-0.5%C-16d tested at room temperature.

Figure 16 Porod A vs. applied strain for Fe-9%Cr-0.5%C-16d tested at room temperature.

These measurements were also made as a function of test temperature as shown in Figure 17. The results clearly show the temperature dependence of the matrix-particle separation which is, in turn, controlled by the interfacial strength between the matrix and particles as well as the particle distribution and interfacial stress state.

Figure 17 Porod A vs. applied strain for Fe-9%Cr-0.5%C-16d tested at room temperature, 100°C and 400°C.

These techniques are also capable of separating the relative loading parameters in the loading direction and perpendicular to the loading direction and in the matrix and carbide particles separately. These data are shown in Figure 18.

(a)

Figure 19 Elastic lattice strain of Fe-9%Cr-0.5%C-16d tested at RT (a) matrix, (b) particle

Note that while the matrix is elastic-plastic, the carbides are essentially totally elastic and consequently carry most of the load. This is also indicated in Figure 20 where the particle and matrix loading are also shown, as is the difference in elastic-plastic behavior. Figure 21 shows the “tensile-like” curve for the carbide and matrix loading as a function of axial strain. Note the much higher levels of loading in the carbides, again due to the ability of the matrix to deform plastically and redistribute the load.

Figure 20 Applied stress vs. lattice strain for Fe-9%Cr-0.5%C-16d

Figure 21 Axial lattice strain vs. applied strain for matrix and particle of Fe-9%Cr-0.5%C-16d tested at (a) room temperature, (b) 100°C ,and (c) 400°C.

Further modeling work was carried out to utilize the particle versus matrix response as a basis for characterizing the tensile response. The model uses basic materials loading parameters to predict tensile response by properly distributing the response between the particle and matrix. Further, since the plastic deformation is included, the material tensile response can be modeled over the entire loading curve. An example of the model fit versus independent experimental data is shown in Figure 22. Further details of the model development are provided in the PhD Dissertation of Dr. Xiao Pan.

Figure 22 UMGM model evaluation with FEM calculation

V. Neutron Irradiation Program for Fe and Ferritic Alloys

As a major addition to the end of this program, we were able to develop a neutron irradiation campaign to examine the same materials described above in the ATR. Irradiations have been planned and started during the final year of this program. The experimental conditions which are being examined are shown in Table 4. These experiments will not be ready for examination for a few years, except perhaps the lowest dose experiments.

Table 4 – ATR Irradiation Experiments, Project Number - 29609

Alloy	Temp (C)	Dose (dpa)	Specimen Types
Model Alloys Fe, Fe-9Cr, Fe-12Cr, Fe-14Cr, Fe-19Cr	300, 450, 550	0.01, 0.1, 0.5, 1, 5, 10,	TEM, Miniature Tensile
Commercial Alloys Mod 9Cr-1Mo, HT-9	300, 450, 550	0.01, 0.1, 0.5, 1, 5, 10,	TEM, Miniature Tensile
Developmental Alloys MA-957	300, 450, 550	0.01, 0.1, 0.5, 1, 5, 10,	TEM, Miniature Tensile

VI. Summary

This program which examined the basic irradiation and mechanical properties performance of several model Fe and Fe-Cr alloys has developed a strong set of experimental results and new evaluation techniques which will be of value to the development and use of commercial and developmental alloys in advanced reactor systems.

The coordination with a materials modeling program also provided some new insights. For both the experimental and modeling efforts, there are new possibilities for further work. One major example is the value of performing ATR irradiation on the same set of materials.