Design of Radiation-Tolerant Structural Alloys for Generation IV Nuclear Energy Systems

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Project Objective: The prime objective of this program is to improve the radiation tolerance of both austenitic and ferritic-martensitic (F-M) alloys projected for use in Generation IV systems. The expected materials limitations of Generation IV components include: creep strength, dimensional stability, and corrosion/stress corrosion compatibility. The material design strategies to be tested fall into three main categories: (1) engineering grain boundaries; (2) alloying, by adding oversized elements to the matrix; and (3) microstructural/nanostructural design, such as adding matrix precipitates. These three design strategies were tested across both austenitic and ferritic-martensitic alloy classes.

Table of Contents

Task Research Significance and Benefits	6
A. Evaluation of Ferritic-Martensitic Steels.....	7
A.1 Grain Boundary Engineering, Radiation Response, and Stress Corrosion Cracking Response of Ferritic-martensitic Steels.....	7
A.1.1 Background	7
A.1.1.1 Microstructure of T91	7
A.1.1.2 Grain Boundary Engineering.....	11
A.1.1.3 Creep of T91.....	12
A.1.1.4 Proton Irradiation of F-M alloys.....	13
A.1.1.5 Stress Corrosion Cracking of F-M alloys in Supercritical Water.....	15
A.1.2 Experiment, Results and Discussion	15
A.1.2.1 CSL Enhancement of F-M alloy T91.....	15
A.1.2.1.1 Creep of T91.....	19
A.1.2.1.2 Analysis of Creep Tests	25
A.1.2.2 Proton Irradiation of F-M alloys.....	27
A.1.2.2.1 Irradiation Induced Hardness	30
A.1.2.2.2 Microstructure of unirradiated and irradiated F-M alloys.....	32
A.1.2.2.3 Correlation of Hardening with Irradiated Microstructure of F-M alloy, T91 ...	37
A.1.2.2.4 Grain boundary microchemical analysis.....	39
A.1.2.3 Stress Corrosion Cracking of F-M alloys at 400°C in deaerated SCW	42
A.1.2.3.1 Fractography.....	43
A.1.2.3.2 Effect of Irradiation and GBE on CERT Behavior.....	46
A1.3 Conclusions.....	48
A.2 Response of the 12Cr steel HCM12A to Proton and Heavy Ion Irradiation	50
A.2.1 Background	50
A.2.2 Experiment.....	50
A.2.3 Results.....	52
A.2.4 Discussion	61
A.2.5 Conclusions.....	63
A.3 Radiation Response of a 9 Cr Oxide Dispersion Strengthened ODS to Heavy Ion Irradiation	64
A.3.1 Background	64
A.3.2 Experiment.....	64
A.3.3 Results.....	65
A.3.4 Discussion	66
A.3.4.1 Microstructural stability at 500 °C.....	66
A.3.4.2 Microstructural Stability at 600 °C	73
A.3.4.3 Microstructural Stability at 700 °C	78
A.3.4.4 Comparison of Oxide Stability at Varying Irradiation Temperatures	83
A.3.5 Conclusions	87
B. Evaluation of Austenitic Steels	88
B.1 Oversize Element Effects on Irradiated Microstructures & IASCC	88
B.1.1 Background	88
B.1.2 Research Approach for Task B.....	94

B.1.3 Detailed Description of Accomplishments at PNNL.....	96
B.1.4 New Alloy Production and Ni-Ion Irradiations	96
B.1.4.1 Heavy-Ion Irradiations at PNNL.....	99
B.1.4.2 Transmission Electron Microscopy Procedures for Ni-Ion Irradiated Samples....	100
B.1.4.3 Hf Effects on Radiation-Induced Microstructures in Ni-Ion Irradiated Samples..	101
B.1.5 Neutron Irradiations.....	109
B.1.5.1 Bor60 Fast-Reactor Irradiations.....	110
B.1.5.2 Cold-Worked 316SS (Boris 5 and Boris 6).....	118
B.1.5.3 Characterization of Neutron-Irradiated FeCrNi (+Zr) Alloys.....	121
B.1.5.4 Cold-Worked 316SS Thimble Tube (PWR Irradiations).....	129
B.1.5.5 Discussion of Microstructural Evolution During Neutron Irradiation.....	131
B.1.6 Modeling Radiation-Induced Segregation and Defect Structure Evolution in Austenitic Stainless Steels: Influence of Oversized Element Additions.....	138
B.1.6.1 Radiation-Induced Segregation of Major Alloy Elements.....	138
B.1.6.2 Hf Addition Effects.....	138
B.1.6.3 Zr Addition Effects	141
B.1.6.4 Ti Addition Effects.....	146
B.1.6.5 Dose Rate Effect on Radiation-Induced Segregation	149
B.1.6.6 Evaluation of Inverse-Kirkendall Reference Parameters.....	153
B.1.6.7 Modeling Minor Element Segregation.....	157
B.1.6.8 Modeling Oversized-Solute Binding Effect on RIS	162
B.1.6.9 Calculated Bias Effect on Microstructure Evolution.....	165
B.1.6.10 Modeled Dose Rate, Temperature and Microstructure Influence on Void Formation.....	167
B.1.6.11 Modeling Cluster Stability during Void Incubation	171
B.2 Oversized Solute Additions	176
B.2.1 Background	176
B.2.1.1 Oversized Solutes and Stress Corrosion Cracking.....	176
B.2.1.2 Modeling of Radiation-Induced Segregation	178
B.2.1.3 RIS Modeling with Impurities.....	182
B.2.1.4 RIS with Oversized Solute Additions	184
B.2.1.5 Microstructure of Oversized Solute Alloys.....	185
B.2.2 Experimental Procedures	186
B.2.2.1 Proton Irradiations	187
B.2.2.2 Hardening, Microstructure and Microchemistry Analysis.....	188
B.2.2.3 Stress Corrosion Cracking Testing	189
B.2.3 Results and Discussion.....	190
B.2.3.1 Radiation-Induced Segregation	190
B.2.3.2 Modeling of RIS	190
B.2.3.3 MIK-T Model Results	192
B.2.3.4 Experimental RIS.....	196
B.2.3.5 RIS: Model vs. Experiment	198
B.2.3.6 Radiation-Induced Microstructure.....	202
B.2.3.7 Effects on Irradiation-Assisted Stress Corrosion Cracking.....	209
B.2.4 Summary and Conclusions.....	213
B.3 Grain Boundary Engineering of INCOLOY Alloy 800H.....	215

B.3.1. Materials and Methods.....	215
B.3.2. Grain Boundary Engineering (GBE)	215
B.3.2.1 Coincidence Site Lattice Boundaries (CSLBs).....	216
B.3.2.2 Misorientation.....	217
B.3.2.3 Grain Size	218
B.3.2.4 Verification and Comparison.....	219
B.3.2.5. Hardness	220
B.3.2.6. Thermal Stability of GBE.....	220
B.3.3. Grain Boundary Composition.....	221
B.3.4. Specimen Preparation for Mechanical Tests.....	224
B.4 Alloy 800H Radiation Stability.....	226
B.4.1. Materials and Methods.....	226
B.4.2. Irradiated microstructure of 800H	227
C. References.....	231
D. Patents	242
E. Publications (Accepted, submitted, or in print).....	242

NERI Progress Report
“Design of Radiation-Tolerant Structural Alloys for Gen IV Nuclear Energy Systems
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Final Report

Task Research Significance and Benefits

The present research has the potential to advance economic and safety performance of current and future nuclear power systems, integrating fundamental and applied science resources to design advanced core component structural materials with the required resistance to radiation and environmental degradation. The research benefits a wide range of areas from fundamental science to applied alloy development. The research strategy and the combination of university and national laboratory resources enable important NERI objectives to be achieved:

(1) The objective of this research is to help solve critical materials degradation problems for next generation LWRs and Generation IV reactor systems. The development of new damage-resistant alloys will allow advanced power reactors to be designed and operated for improved performance, efficiency, reliability and economics.

(2) Advanced materials concepts are being developed and scientific breakthroughs facilitated to overcome a principal obstacle facing nuclear fission reactors. The focus on next generation LWR concepts will promote relatively near-term (within 10 years) benefits for the safe and economical operation of commercial nuclear power. This is essential considering the current status of the nuclear power industry worldwide.

(3) The effective integration of university (UW and UM) and national laboratory (INL, PNNL, and JAEA), team members focuses their scientific research and development infrastructures on nuclear energy issues and fosters a leveraged approach to address basic and mission-oriented research. Industry partners and collaborators ensure that radiation material science breakthroughs are effectively transferred to advance the state of nuclear technology. International cooperation and U.S. leadership in the research is ensured by the collaborative experimental activities as part of two separate multi-national projects led by EPRI. Principal investigators play an important role in the oversight of these projects and foster continuous interactions to transfer novel materials concepts into engineering application.

(4) The unique research team and shared activities among university, national laboratory and industry promotes and maintains nuclear science and engineering to meet future technical challenges. The relationship among participants is one of the strengths of this research and fosters the development of new radiation materials science expertise through research activities by university students and junior staff at national laboratories.

A. Evaluation of Ferritic-Martensitic Steels

Ferritic-Martensitic (F-M) steels are expected to be key structural materials in many generation IV concepts. F-M steels are expected to be used as high dose components in sodium and lead-reactors, low-dose components in gas-cooled reactors, and possibly as high-dose components in supercritical water reactors. These steels offer better swelling resistance and radiation stability as compared to austenitic steels but suffer from grain boundary and/or matrix creep and loss of strength at high temperatures, and unacceptably low toughness at lower temperatures. The evaluations of ferritic-martensitic in this report are described in three major sections:

1. Grain Boundary Engineering, Radiation Response, and Stress Corrosion Cracking Response of Ferritic-martensitic Steels
2. Response of the 12Cr steel HCM12A to Proton and Heavy Ion Irradiation
3. Radiation Response of a 9 Cr Oxide Dispersion Strengthened ODS to Heavy Ion Irradiation

A.1 Grain Boundary Engineering, Radiation Response, and Stress Corrosion Cracking Response of Ferritic-martensitic Steels

One of the material design strategies to be adopted for improving creep strength is grain boundary engineering (GBE). The main challenge is to develop novel methods to stabilize the microstructure against irradiation effects to make the alloy effectively “radiation-tolerant”. GBE will increase the fraction of special boundaries, reducing RIS to those boundaries and strengthening grain boundaries against sliding and deformation. Another major area of concern is the SCC behavior of these steels in supercritical water (SCW). They have generally exhibited high corrosion rates in SCW, and except for HT-9, almost negligible susceptibility to stress corrosion cracking. There is no data base on the effect of irradiation on the SCC behavior in SCW. It is thus important to understand the changes in microstructure and microchemistry upon irradiation of these alloys and how that might affect the SCC susceptibility. GBE is also being explored as a technique to improve their SCC behavior.

A.1.1 Background

A.1.1.1 Microstructure of T91

T91 is a low carbon, 9Cr-1MoVNb steel that is used in the two phase, ferritic-martensitic structure. The standard heat treatment consists of a solution anneal at 1066°C for 46 min to completely austenitize the microstructure and dissolve the carbides, and a tempering treatment of 790°C for 42 min to relieve the stresses and enhance toughness. The resulting microstructure

consists of tempered martensite laths forming subgrains in a ferrite matrix, with (V, Nb) carbonitrides precipitated mainly on dislocations within the subgrains and $M_{23}C_6$ precipitated on the prior austenite grain boundaries (PAGBs) and on sub-grain boundaries [A.1]. The sub-grain structure produced by martensitic transformation and the precipitation of carbides and carbonitrides are the primary microstructure features responsible for high temperature creep strength. Since the microstructure influences the mechanical properties it is critical to understand and to have a clear picture of its evolution during heat treatment.

Fig A.1 illustrates schematically the structural levels in the martensitic microstructure of T91 after austenitization. The prior austenite grain (PAG) is divided into packets which contain well aligned martensite laths. A packet is a region in which the laths have the same habit plane and orientation. The packet is, essentially, a single crystal of martensite. The laths within a given packet are in close crystallographic alignment. Most of the PAGBs are randomly oriented, and the martensite-lath boundaries are predominantly small-angle grain boundaries. Fig A.2 is the SEM micrograph of T91 after austenitization treatment. The average PAG size is $10\mu\text{m}$ and the average packet size is $3\text{--}4\mu\text{m}$. The individual martensite laths are typically about $0.4\text{--}0.5\mu\text{m}$ in the thin dimension. The size of the PAG depends on austenitization time and temperature while the size of the martensite laths is independent of the size of PAG.

Figure A.1 Schematic of the microstructure of T91 after austenitization.

Figure A.2 Microstructure of T91 after austenitization

Figure A.3 shows a schematic of the microstructure of T91 after tempering. During tempering carbides and carbonitrides precipitate on the PAGBs and lath boundaries. The diffusion rate along high-angle boundaries such as random boundaries is higher than that along low-angle boundaries. Carbides are expected to be formed more easily around the PAGBs because the PAGBs act as the faster diffusion paths. Dislocations rearrange to form subgrains within the laths (a subgrain is basically a sub-structure within the deforming grain, bounded by dislocation networks and formed due to misorientations). Recrystallization occurs, and equiaxed ferrite grains form at the expense of the original laths. Carbide particles retard grain growth by pinning grain boundaries. Eventually a microstructure of equiaxed grains and spheroidal carbides is produced. Figs A.4a, A.4b and A.4c show the SEM image of tempered F-M alloy T91. Due to the complex nature of the microstructure different etching solutions were used to highlight different aspects of the microstructure. Fig A.4a shows the PAGB and the packet boundary, Fig A.4b shows the subgrains and Fig A.4c shows the carbides on the PAGBs and lath boundaries. Figs A.5a and A.5b are the TEM micrographs of T91 after tempering showing the typical tempered lath structure with an average width of $0.5\mu\text{m}$ and precipitates along with dislocation cells respectively.

Figure A.3 Schematic of the microstructure of T91 after tempering.

a)

b)

c)

Figure A.4 SEM Micrographs of T91 after tempering showing a) PAGBs and packet boundaries, b) subgrains and c) carbides on PAGBs and packet boundaries.

Figure A.5 TEM microstructure scans of T91 in the tempered condition showing a) lath, b) carbides along with dislocation cell.

A.1.1.2 Grain Boundary Engineering

Grain boundary engineering is expected to increase the fraction of special boundaries, reduce RIS to those boundaries and strengthen grain boundaries against sliding and deformation. GBE involves a series of thermo-mechanical treatments designed to increase the coincident site lattice boundary (CSLB) fraction. The CSL model refers to the 2-D superlattice that forms at certain angle-axis combinations in which a fraction of the lattice points from one crystal coincide with those from the adjacent crystal [A.2-A.3]. GBE begins by introducing a small amount of deformation into the sample either by compression or tension. A finite fraction of the energy expended in cold work is stored in the metal as strain energy associated with various lattice defects created by the deformation. The subsequent annealing step causes recovery and realignment of the grain boundary region into a lower energy state that reduces the mismatch between the boundaries of the grains and converts a fraction of the high-energy boundaries to low-energy boundaries [A.4].

Lehockey et al. [A.5], and Thaveeprungsriporn and Was [A.6] have shown a strong dependence of steady-state creep rate on grain boundary misorientation. Creep rate reduction by a factor of 30 in UHP Ni-16Cr-9Fe [A.7], a factor of 15 in alloy 625 [A.8] and a factor of 12 for iron base alloy V-57 [A.9] by GBE have been reported. Watanabe [A.9] was the first to show a strong relationship between grain boundary sliding and misorientation angle and speculated that if grain boundary sliding is a factor in intergranular fracture, then misorientation angle is an important parameter governing intergranular stress corrosion cracking.

Alexandreaanu [A.10] recently showed a strong dependence of grain boundary sliding on misorientation angle in Ni-16Cr-9Fe by demonstrating that CSLBs are considerably more resistant to grain boundary sliding than are random high angle boundaries. He also performed a set of experiments that showed that grain boundary deformation induces intergranular cracking of UHP alloy 600 in primary water at 360°C. This is the direct evidence of a cause-and-effect relationship between grain boundary sliding and intergranular stress corrosion cracking and underscores the importance of GBE in achieving long term mechanical integrity of reactor components.

A.1.1.3 Creep of T91

F-M alloys are expected to be used as high dose components in sodium and lead-reactors and in accelerator driven systems, low-dose components in gas-cooled reactors, and possibly in high-dose components in supercritical water reactors. F-M alloys have a high thermal conductivity, a low thermal expansion coefficient, and are less susceptible to the thermal fatigue than austenitic steels. Because of these attractive properties these steels have been used extensively in the fossil power plants. However, operation temperature of power plant has been limited owing to the limited creep strength of these steels at elevated temperatures. These steels may suffer from grain boundary and/or matrix creep and loss of strength at high temperatures.

The creep strength of T91 has been reported as being determined by solid solution strengthening, by precipitation hardening (produced by normalizing and tempering treatment) and due to the high density of dislocations which are introduced into the matrix through martensitic transformations. Creep deformation is controlled at elevated temperatures by recovery and softening of the tempered martensite structure. In the initial service condition the microstructure is predominantly characterized by a relatively coarse dispersion of $M_{23}C_6$ and M_2X precipitates, together with a much finer scale dispersion of $M_{23}C_6$, M_2X , MX , M_6X , V_4C_3 , etc., precipitates. However, during creep the large precipitates coarsen and complex variations in the fine dispersion of precipitates occur [A.11-A.15]. The extent of coarsening increases with increasing temperature and stress [A.16-A.17]. The transformed microstructure in these steels consists of elongated subgrains that evolve during creep into coarse, equiaxed subgrains, while the dislocation density decreases [A.18-A.19]. The subgrain width is also substantially increased by creep deformation due to absorption of excess dislocations [A.20]. To achieve high creep strength, it is necessary to optimize the distribution of precipitates and dislocation structure and to retard microstructural degradation during creep.

Anderson et al. [A.11], Gianfrancesco et al. [A.12], Ennis et al. [A.13], Eberle et al. [A.14] and Spigarelli et al. [A.15] conducted creep tests on 9Cr-1Mo modified steels at several temperature-stress combinations. T91 exhibits a normal three-stage creep behavior, following a relatively small instantaneous elongation [A.1]. Orlova et al. [A.17], Anderson et al. [A.11], Gianfrancesco et al. [A.12], Eberle et al. [A.14] and Spigarelli et al. [A.15] have shown that a typical creep curve for T91 consists of a primary stage of a decreasing creep rate, a very short secondary region (or rather a minimum creep rate range) followed by a long tertiary stage.

Anderson et al. [A.11] assumed that the stress exponent n and the activation energy Q for creep were true constants independent of stress and temperature and obtained a value of the stress exponent of 15.25 and the activation energy for creep of 796 KJ mole⁻¹ after applying a multilinear curve fitting procedure to Norton's creep equation. The creep mechanism believed to be operating at this high value of stress exponent is power law breakdown. Ennis et al. [A.13] also suggested a stress exponent value of 16 at high stresses and temperatures. Eberle et al. [A.14] have developed two creep models for this alloy but at lower values of stress and higher temperature and their data doesn't fit for higher values of stress. Spigarelli et al. [A.15] have developed a creep model on the basis of the threshold concept and found the value of the stress exponent to be 5 for which dislocation-based creep is the more dominant mechanism. Sauzay et al [A.21] explained softening behavior during creep by lath and sub-grain boundary elimination. Dimmler et al [A.22] observed stress exponent values of greater than 20 at high stress and explained the behavior on the basis of power law break down or exponential creep.

Our strategy for improving creep resistance is via grain boundary structure engineering, in which the fraction of special boundaries is increased. Such increases in special boundaries have proven effective in reducing creep rates in ferritic and austenitic alloys [A.23-A.24]. Diffusional flow and power law are the two principal mechanisms of creep observed in alloy T91. Grain boundary diffusion has been shown to depend on the grain boundary structure, which also impacts its effectiveness as vacancy sinks and sources [A.25-A.29]. CSLBs have been shown to be more resistant to creep fracture under conditions where grain boundary diffusivity controls creep [A.26]. When power law creep is dominant, CSLBs will affect creep through dislocation adsorption as described by Thaveeprunsiorn et al [A.6]. In either case grain boundary structure engineering is expected to enhance the creep strength of this alloy.

A.1.1.4 Proton Irradiation of F-M alloys

Understanding radiation effects in these alloys is critical for their success in advanced reactor and transmutation systems. These steels have been used in the power-generation, chemical, petrochemical industries and fossil fired power plants at temperatures up to 550-600°C [A.30]. However, the effects of irradiation in the environments expected in Gen IV and ADS systems are only partially understood. The objective of this work is to evaluate the microstructural, microchemical, and mechanical property changes in irradiated ferritic-martensitic alloy T91 to provide a better understanding of their behavior in advanced reactor systems.

A limited number of studies of irradiation performance have been performed under fast reactor and low-temperature spallation environments [A.31-A.35]. Ferritic-martensitic steels are attractive because of their resistance to radiation-induced swelling. The maximum reported swelling for T91 is reported by Gelles [A.32] as 1.76% at just over 200 dpa at 420°C. However, fast-reactor irradiations do not produce the large amount of transmutation gases that are associated with fusion and spallation environments. Hashimoto and Klueh [A.34] irradiated T91 doped with 2% Ni in the High Flux Isotope Reactor (HFIR) to 12 dpa at 400°C. T91 and T91+2%Ni produced 30 and 161 appm He and exhibited swelling of 0.17% and 0.15%, respectively. Kai and Klueh [A.33] analyzed the microstructure of T91 irradiated in the Fast Flux Test Facility (FFTF) to 35 dpa at a temperature of 420°C. Post-irradiation microstructure showed a high density of fine voids and large dislocation loops. The $M_{23}C_6$ and MC precipitates were mostly unchanged; showing only a minor decrease in number density and an increase in diameter. However, the irradiated T91 formed a high density of very fine χ -phase precipitates.

Limited experiments have been performed on T91 under spallation conditions. However, the irradiation temperatures are lower than the expected operating temperatures of Generation IV, fusion and future ADS systems. Jai and Dai [A.35] analyzed T91 irradiated in SINQ Target-3 to doses ranging from 2.7 to 11.8 dpa at temperatures ranging from 90 to 360°C. The pre-irradiation dislocation density was approximately 10^{14} m^{-2} . $M_{23}C_6$ precipitates were observed primarily along prior austenite and lath boundaries. The precipitate sizes varied from a few tens of nm to $\sim 2 \text{ }\mu\text{m}$ in diameter. Due to the nature of the experiment, the fluence and He content increased with irradiation temperature, making it, difficult to determine the effects of each parameter individually. At He concentrations above 500 appm, high densities of very fine He bubbles were observed. While the changes were small, a trend of decreasing bubble density and increasing size was observed with increasing dose, He concentration and irradiation temperature. Additionally, dislocation loop size increased with dose/temperature. Jai and Dai observed amorphization of precipitates at temperatures below 250°C. This is consistent with the observations of Sencer et al. [A.36] for low-temperature irradiations of T91 at the LANSCE facility.

Several studies have been performed on the response of mechanical properties of T91 to irradiation [A.37-A.41]. General trends show an increase in yield strength and ultimate tensile strength and associated decrease in uniform elongation and total elongation with dose. The severity of these changes decrease with increasing temperature. The same trends have been observed with increasing He concentration in implanted samples [A.42]. Low level damage (≤ 0.8 dpa) occurred due to the He implantation process in the otherwise unirradiated samples.

In general irradiation enhances diffusion and/or precipitate redistribution, which can enhance recovery and coarsening, and thus, increase the rate of softening. The principal effects of irradiation include non-equilibrium segregation and physical changes to the microstructure (dislocation loops, dislocation network, voids, and precipitates). Hence an understanding of the effects of irradiation on the structure and chemistry of F-M alloys is critical for their success in advanced reactor and transmutation systems. To understand the effects of irradiation we need to study irradiated microstructure along with changes in hardening and radiation-induced segregation.

A.1.1.5 Stress Corrosion Cracking of F-M alloys in Supercritical Water

One of the most promising advanced reactor concepts for Generation IV nuclear reactors is the supercritical water reactor (SCWR). Operating above the thermodynamic critical point of water (374°C, 22.1 MPa), the SCWR offers many advantages compared to current LWRs including the use of a single phase coolant with high enthalpy, the elimination of components such as steam generators and steam separators and dryers, a low coolant mass inventory resulting in smaller components, and a much higher efficiency. Since supercritical water has never been used in nuclear power plant applications, there are numerous potential problems, particularly with materials. Depending upon what species are present and how much oxygen is present in the solution, SCW can become a very aggressive oxidizing environment. This is a cause of concern about the general corrosion and stress corrosion cracking (SCC) of the structural materials and fuel elements of the reactors.

F-M alloys have been identified as candidate core structural alloys in SCWR. Preliminary studies have shown that F-M alloys experience high corrosion rates in the SCWR. They generally exhibited low susceptibility to SCC, although HT-9 has shown evidence of IGSCC in SCW at 400°C and 500°C [A.43]. The effect of irradiation on SCC of F-M alloys is unknown. Service and laboratory experience have shown that irradiation enhances the stress corrosion cracking of austenitic alloys in high temperature water [A.44-A.52]. GBE is being explored as a means of reducing the susceptibility to IGSCC in SCW. It is envisaged that CSL enhancement would improve the SCC behavior of T91 in SCW both with and without the effect of irradiation.

A.1.2 Experiment, Results and Discussion

A.1.2.1 CSL Enhancement of F-M alloy T91

F-M alloys present a unique challenge to coincident site lattice enhancement due to their complicated microstructure. The challenge is to enhance the grain boundary CSL fraction without disturbing the original microstructure. Since the microstructure is critical to achieving high temperature properties, the heat treatment process requires strict control [A.53]. Higher austenitizing temperature will result in coarser prior austenite grain sizes and reduction in toughness and creep ductility. Depending upon the concentration levels of various elements the critical temperature (for austenite formation) can drop to as low as 815°C. If adequate control of temperature is not maintained during tempering then it is possible to form fresh austenite or ferrite during the process. The presence of either ferrite or untempered martensite will compromise both toughness and high temperature properties of the alloy [A.54].

Orientation imaging microscopy (OIM) was used to measure the fraction of CSLBs in T91. OIM scans were performed over a 25µm x 60µm area with a step size of 0.4µm. CSLB fractions are reported by length. The total length of the grain boundaries and of Σn boundaries in the scan area was measured. Their ratio gives the CSL fraction (where $n < 29$ is an odd

number). In the terminology of the CSL model the newly formed superlattice is Σn where Σ is the reciprocal of the coincident site lattice fraction [A.2-A.3]. Brandon's criterion was used to determine the CSL characteristics of a boundary [A.55].

A series of experiments was conducted to identify a treatment to optimize the CSLB fraction in T91. The annealing temperature required to achieve a high CSLB fraction is generally $\sim 0.7 T_M$ [A.56-A.57] or about 1050°C for T91. Annealing at that temperature will fully austenitize the microstructure and dissolve all carbides. Therefore, the first experiments subjected the as-received (A/R) sample to 5% compression deformation and annealing at 800°C for 2 hrs. However, this treatment did not result in CSL enhancement. Extending the annealing time was ineffective as well, Table A.1.

Another potential problem was the presence of grain boundary carbides that pin the boundaries and inhibit grain boundary movement during heat treatment. To address this issue, a second approach was developed in which the sample was annealed to dissolve the carbides and then air cooled prior to the compression and heat treating steps. But this process resulted in the formation of martensite, which is very hard and difficult to compress for CSL enhancement, Table A.1. The next strategy involved compression of the A/R sample, followed by annealing at $0.7 T_M$ for 1 hr, followed by tempering at 800°C for 40 min. The purpose of the annealing treatment was to dissolve the chromium carbides and the tempering treatment was conducted to re-precipitate them to recover this element of the original microstructure. The (Nb, V) carbides and carbonitrides which are very fine (10-50 nm) and difficult to detect do not dissolve on austenitization. They pin the dislocations and thus help in enhancing the creep strength. The T-91 samples were deformed to various percentages and then optimized at 5% compression. Table A.1 indicates that this two-step (annealing and tempering) heat treatment following 5% compression of the A/R material was most effective in enhancing the CSL fraction. This method was repeated on a different sample to demonstrate reproducibility.

The most significant result of the processing experiment was that the CSLB fraction of T91 was enhanced over the A/R case while maintaining the other critical features of the microstructure; grain size, carbide size and location, density and hardness, Table A.2. Preserving all the microstructural features (Fig. A.6) decisive for high creep strength in T-91, while increasing the fraction of low angle boundaries is expected to increase creep strength.

Due to the complex nature of the microstructure it is important to determine which boundaries are actually modified by CSL-Enhancement. There are actually three different types of boundaries in the tempered condition of T91; PAGBs, packet boundaries and the subgrain boundaries. Generally the PAGBs and the packet boundaries have a high misorientation between them and thus are the high angle boundaries. The subgrain boundaries are generally the low angle boundaries with small misorientation between them. OIM analysis shows an increase in the fraction of sigma $\Sigma 1$ boundaries from the A/R condition to the CSLE condition. These boundaries are the subgrain boundaries where subgrains refer to the tempered laths. Theoretically a $\Sigma 1$ boundary denotes a perfect (or nearly perfect) crystal; i.e. no boundary at all. However boundaries relatively close to the $\Sigma 1$ orientation are those with only small misorientations (less than 15°) called "small-angle grain boundaries" - and they are subsumed under the term $\Sigma 1$ boundaries. The fraction of these low angle boundaries with misorientation

less than 3° is higher in CSLE samples as compared to A/R samples by 35%. Fig A.7 shows the distribution of the fraction of $\Sigma 1$ boundaries in the two conditions with misorientation angle.

Condition: Thermal-Mechanical Processing	CSLB Fraction
As-Received	27.8
5% comp, 800°C, 2h (air cool)	29.7
1050°C, 1h (air cool), 5% comp, 800°C, 2h (air cool)	22.6
1050°C, 1h (air cool), 800°C, 0.66h (air cool)	27.2
13% comp, 1050°C, 1h (air cool), 800°C, 0.66h (air cool)	26.3
8% comp, 1050°C, 1h (air cool), 800°C, 0.66h (air cool)	29.6
5% comp, 1050°C, 1h (air cool), 800°C, 0.66h (air cool)	36.5/35.7

Table A.1 Summary of results of deformation-heat treatment trials to increase the CSL fraction in alloy T-91.

Property	As-Received	CSL Enhanced
CSL fraction	28%	37%
Grain size	9 μ m	10 μ m
Carbide size (diameter) $M_{23}C_6$	0.36 μ m	0.37 μ m
Linear GB carbide density $M_{23}C_6$	1.8/ μ m	1.7/ μ m
Hardness (HRB/HV)	97/225	97/225

Table A.2 Summary of microstructure for T-91

As Received condition

CSL-Enhanced condition

a

b

c

d

Figure A.6. Micrographs for T91 and CSLE T91 showing : a,b) grain size, c,d) carbide size and location.

Figure A.7 Plot of fraction of $\Sigma 1$ boundary for AR and CSL condition of T91 for misorientation angle between 0-15°.

A.1.2.1.1 Creep of T91

Tensile bars with a gage length of 21 mm, a gage diameter of 2.2 mm, and a gage thickness of 1.5 mm were used for creep experiments (Fig. A.8a). Figures A.8b and A.8c show the schematic of the compression technique for the deformation step in the CSL-enhancement process. The 5% compressive deformation was accomplished by compressing the sample perpendicular to its gauge length between two 14.3 mm square WC blocks (Figure A.8a) using an Instron machine. This deformation step produced two parallel flat surfaces on the initially round in cross section tensile specimens (Fig A.8b).

Creep tests were conducted in constant load test apparatus which consists of a four liter autoclave and a loading system, as shown schematically in Fig. A.9. The autoclave is a multisample system in which three samples can be loaded independently and in parallel. The autoclave was purged with argon for sufficient time prior to heating the vessel to eliminate oxygen in the vessel environment. The autoclave was heated using resistance heating bands until the desired temperature was reached. Load was applied to samples by means of a lever arm via a pull rod. The loads to be placed into the load pans were calculated based on the desired stress level for the test and the cross-section area of the sample. The amount of creep strains was measured outside the autoclave via external linear variable differential transformers (LVDT) attached to the pull rods.

Figure. A.8—a) Dimensions of the as-received tensile specimens, b) schematic illustrating the compression technique, and c) illustration showing the cross-sectional (shaded) area.

Figure. A.9—Schematic of the high temperature creep system and the load train assembly.

Creep experiments were conducted in argon environment on A/R T91 and CSLE T91 in the stress range of 140-235 MPa and in the temperature range of 500-600°C. Table A.3 gives results of the all the creep tests conducted on T91. The minimum creep rate for T91 CSLE samples was observed to be less than that of T91 A/R samples by a factor of 3-13. Figure A.10 shows a plot of minimum creep rate vs. applied stress for both A/R and CSLE conditions at 500°C and 600°C. The plot clearly shows the effect of CSL enhancement in reducing the minimum creep rate of A/R T91.

Table A.3 Results for Creep Experiments on A/R and CSLE T91

Temperature (°C)	Stress (MPa)	Min creep rate (s ⁻¹) for A/R	Min creep rate (s ⁻¹) for CSLE
500	255	1.34x10 ⁻⁷	6.61x10 ⁻⁸
500	250	1.29x10 ⁻⁷	6.2x10 ⁻⁸
500	245	6.09x10 ⁻⁹	2.58x10 ⁻⁹
500	235	2.06x10 ⁻⁸	1.57x10 ⁻⁹
500	220	2.56x10 ⁻⁸	6.46x10 ⁻⁹
550	245	5.44x10 ⁻⁶	1.75x10 ⁻⁶
550	235	7.94x10 ⁻⁷	9.81x10 ⁻⁸
550	220	1.06x10 ⁻⁷	3.01x10 ⁻⁸
600	235	2.39x10 ⁻⁵	7.56x10 ⁻⁶
600	220	1.41x10 ⁻⁵	2.67x10 ⁻⁶
600	200	4.25x10 ⁻⁶	2.18x10 ⁻⁶
600	180	7.64x10 ⁻⁷	3.45x10 ⁻⁷
600	170	3.33x10 ⁻⁷	1.57x10 ⁻⁷
600	165	3.16x10 ⁻⁷	9.8x10 ⁻⁸
600	160	1.06x10 ⁻⁷	3.10x10 ⁻⁸
600	155	5.03x10 ⁻⁸	2.14x10 ⁻⁸
600	150	2.57x10 ⁻⁸	2.08x10 ⁻⁹

Figure A.10 Plot of minimum creep rate vs. applied stress for creep tests done at 500°C and 600°C on both A/R and CSLE T91.

Figs. A.11-A.13 shows the plots of strain rate vs. strain and strain vs. time for creep tests at 500°C: 250MPa, at 550°C: 245MPa and at 600°C: 220MPa respectively. Note that the strains for both A/R T91 and CSLE T91 increase with stress in each case. Also the strain to failure for A/R T91 is greater than that for CSLE T91 for each case.

Figure A.11 Plot of a) strain vs. time and b) strain rate vs. strain for creep test of alloy T91 at 250MPa (500°C, argon).

Figure A.12 Plot of a) strain vs. time and b) strain rate vs. strain for creep test of alloy T91 at 245 MPa (550°C, argon).

Figure A.13 Plot of a) strain vs. time and b) strain rate vs. strain for creep test of alloy T91 at 220 MPa (600°C, argon).

Fig A.14 shows a plot of minimum creep rate vs. stress for T91 at 600°C. The plot contains data from the literature and also from this study for comparison. In general there is a good agreement of results of this study with what has been observed in the literature. Some scatter in the data is probably due to the slight difference in composition and heat treatment.

Figure A.14 Plot of minimum creep rate vs. stress at 600°C for T91.

During creep the subgrain width increases and the dislocation density decreases. The average subgrain size after creep for a T91 specimen under a load of 160MPa at 600°C was observed to be 0.9 μ m and 1.26 μ m for the CSLE and A/R condition respectively (Figure A.15). Similar analysis was done in the head or the grip region which was at temperature but without load and the average subgrain width was observed to be 0.65 μ m and 0.7 μ m in the CSLE and A/R conditions respectively (Figure A.16). This confirms the dependence of subgrain coarsening on load rather than just being an elevated temperature effect. The increase in subgrain width during creep has been attributed to the annihilation of mobile dislocations in the lattice (subgrain) with dislocations at the subgrain boundaries. Sawada et al. [A.58] have described the increase in lath width due to migration of lath boundaries and also unknitting of the dislocations that form lath boundaries. He conducted in-situ experiments during tempering to show the migration of the lath boundary and reasoned that the driving force was strain accumulated during martensitic transformation. The same mechanism governs the coarsening during creep. Igarashi et al. [A.59] described creep deformation due to annihilation and rearrangement of excess dislocations inside the lath-martensite, which causes coarsening of the lath and the formation of equi-axed subgrains. Maruyama et al. [A.60] explained two main processes which cause the recovery of the subgrain structure: a) disappearance of a sub-boundary by annihilation of dislocations constructing the sub-boundary and, b) mutual annihilation of two sub-boundaries with opposite sign. Both of these processes are diffusion controlled.

The ability to maintain a small subgrain size and a high density of dislocations for long times at high temperature and stress is important for high creep strength [A.12-A.15]. Subgrain boundaries consist of dislocation networks which, compared with the subgrain interiors are hard regions in the microstructure of ferritic steels. A small subgrain is equivalent to a high volume fraction of hard regions in the microstructure, and could thus be expected to be equivalent to high creep strength. Once formed, the boundaries of the subgrains lead to hardening as they induce long-range internal back stresses in the interior of the subgrains by forcing the mobile dislocations to take a bowed configuration [A.61].

a)

b)

Figure A.15 SEM scans of the gauge section of samples after creep test at 600°C:160MPa showing the subgrains for a) A/R and b) CSLE condition.

c)

d)

Figure A.16 SEM scans of the grip section of samples after creep test at 600°C:160MPa showing the subgrains for a) A/R and, b) CSLE condition.

A.1.2.1.2 Analysis of Creep Tests

The objective of the experiments is to understand the effect of CSLBs on the creep of F-M alloy, T91. We make use of the concept of internal stress to develop a mathematical model of creep for this alloy, in which creep rate depends on the effective stress rather than the applied stress. There are two major factors we consider here, inherent internal stress of the alloy and internal stress introduced due to coincident site lattice boundaries. The inherent internal stress is due to the precipitates which introduce the Orowan stresses, due to the free dislocations within the subgrains and due to the subgrain structure. It has already been mentioned earlier that the process of CSL enhancement increases the fraction of low energy subgrain boundaries. The effect of inherent internal stress on the creep rate was represented by introducing the constant, $\sigma_{0A/R}$ in the creep rate equation:

$$\dot{\epsilon}_{A/R} = A_{A/R} (\sigma - \sigma_0^{A/R})^{n_{A/R}}, \quad (A.1)$$

where $\sigma_0^{A/R}$ is the inherent internal stress and A is a temperature-dependent parameter. It was assumed that the effect of CSLBs on creep rate could be summed with the effect of inherent internal stress since they act independently of each other. Thus the creep rate equation was modified to:

$$\dot{\epsilon}_{CSL} = A_{CSL} (\sigma - \sigma_0^{CSL})^{n_{CSL}}, \quad (A.2)$$

where $A_{CSL} \neq A_{A/R}$, and σ_0^{CSL} represents the internal stress in CSL-enhanced samples. The values of $n_{A/R}$ and n_{CSL} were assumed to be equal to 5 ($n = 5$, when creep is controlled by dislocation climb). In order to obtain the values of the constants in eqns (A.1) and (A.2), we need to substitute the values of minimum creep rates corresponding to the values of applied stress. Since the creep test performed on T91 at 220MPa (500°C) did not reach steady state, it was not included in the regression analysis. The remaining experiments at 500°C were used in a regression analysis to obtain the values of the constants for eqns (1) and (2). Similar analysis was done for creep tests conducted at 600°C. Data for creep tests at 600°C in the stress range of 235-200 MPa was not considered for analysis as the samples failed very quickly. No analysis was performed for creep tests conducted at 550°C due to lack of sufficient data. Applied stress was taken as the independent (controlled) variable and the measured strain rate from experiment was considered as the dependent (random) variable. Optimal values of the constants were obtained when the sum of the squares of the vertical distances between the measured values and the regression line are minimized.

The values obtained were $A_{A/R} = 2.96 \times 10^{-16}$, $\sigma_{0A/R} = 203$ MPa for the as-received condition, and $A_{CSL} = 1.501 \times 10^{-15}$, $\sigma_{0CSL} = 221$ MPa, for the CSL-enhanced condition at 500°C. For creep tests conducted at 600°C values obtained were $A_{A/R} = 1.05 \times 10^{-15}$, $\sigma_{0A/R} = 120$ MPa for the A/R condition, and $A_{CSL} = 1.28 \times 10^{-15}$, $\sigma_{0CSL} = 130$ MPa, for the CSLE condition. That the value of σ_{0CSL} is greater than the value of $\sigma_{0A/R}$ for creep tests both at 500 and 600°C indicates that the

internal stress for the CSL-enhanced case is greater than that of the as-received condition. It is proposed that the difference, $\Delta\sigma = \sigma_{0\text{CSL}} - \sigma_{0\text{A/R}}$ represents the contribution of the CSLBs to the internal stress suggesting that the effect of the CSLBs is consistent with the mechanism of increased internal stress due to the higher CSLB fraction. Figures A.17b and A.17b show plot of minimum creep rate vs. effective stress at 500°C and 600°C respectively. Note that the minimum creep rate of A/R T91 and CSLE T91 would be same at the same effective stress. The data scatter at the lower temperature of 500°C has also been observed by Kimura et al [A.62]. The linear nature of the curves are indicative of minimum changes in the microstructure brought on by stress and elevated temperature exposure for the range in which these experiments have been conducted.

Fig A.17 Plot of a) minimum creep rate vs. effective stress at a) 500°C and at b) 600°C. [R^2 value here indicates how well the calculated curve fits the original data. This value ranges from zero to one. The closer to one, the better the fit.] $R^2 = 1 - [\sum \{(y_i - x_i)/\sigma_i\}^2 / \sum \sigma_i (y_i - \bar{y})^2]$, where y_i is the actual value, $\bar{y}$ is the mean of the actual value, x_i is the calculated value and σ_i is the weight. Here y_i is applied stress, x_i is the observed minimum creep rate and σ_i is the number of observations.

The mechanism of reduced creep rate due to CSLBs is believed to be associated with the limited mobility of extrinsic grain boundary dislocations in the special boundaries [A.6]. Thaveerungsriporn and Was [A.6] hypothesized that the reason for the difference in IGSCC (and creep) behavior of alloys containing high fractions of CSLBs is due to the difference in dislocation absorption at CSLBs versus high angle boundaries (HABs). The authors suggested that the increased structural order and reduced free volume of the CSL boundaries inhibits dislocation motion by vacancy diffusion and climb, as well as the absorption and dissociation of extrinsic dislocations in these boundaries. The reduced creep rate due to an increased CSLB fraction is attributed to the resistance of CSL boundaries to incorporation of dislocations.

The absorption of a lattice dislocation into a CSLB is a difficult process due to the highly ordered structure of this boundary type. Therefore, subsequent lattice dislocations approaching the CSLB during deformation will be opposed by the first dislocations trapped there [A.10]. A long-range internal stress thus arises due to the stress field of leading dislocations, which then inhibits the motion of following dislocations. On the contrary, the process of dislocation absorption in HABs can be considered equivalent to the total annihilation of dislocations, which

relaxes the boundaries and results in the disappearance of long range strain fields [A.10]. Pesicka et al [A.63] suggested that high initial density of free dislocations creates high initial back stresses which are required to impose a given amount of total strain. Since the CSL boundaries would have a higher dislocation density, thus they create high initial back stresses similar to what has been observed experimentally.

OIM analysis of T91 for A/R and CSLE condition has shown that the CSLE condition has a higher fraction of $\Sigma 1$ (low angle) boundary as compared to the A/R condition with a higher fraction of low angle boundaries with a misorientation angle less than 3 degrees. Huang et al [A.64] studied subgrain growth and low angle boundary mobility. They observed that subgrain growth tends to be discontinuous (certain subgrains may grow faster than others) and that discontinuously growing subgrains are generally more highly misoriented to their surroundings than the slower growing subgrains. Also boundary mobilities were found to increase rapidly with increasing misorientation. Since there is a higher fraction of low angle boundaries with low misorientation in the CSLE condition as compared to the A/R condition the coarsening of subgrains would be less in CSLE condition as compared to the A/R condition and this has been also observed experimentally. Since the smaller subgrains result in increased creep strength, the higher creep strength of the CSLE condition is understandable. Also since annihilation of dislocations at subgrain boundaries is controlled by diffusion processes and boundaries with low misorientation would have a smaller diffusivity it would be more difficult to annihilate the subgrain boundaries in CSLE condition as compared to A/R condition or, in other words, it would be easier to annihilate subgrain boundaries A/R condition as compared to CSLE condition. Finally, since the subgrain boundaries induce internal stresses inside the lattice the concept of increased internal stress in CSLE condition as compared to A/R condition is relevant for T91.

Another relevance of CSLE can be seen as a benefit in terms of temperature increment to achieve the same minimum creep rate. That is, with the CSLE condition, one can go higher in temperature and still have the same creep strength as an A/R sample. To evaluate this effect we need to observe the minimum creep rate at different temperatures and same stress level. From Table A.3 it is evident that at a stress level of 220MPa the creep strength of T91 in the CSLE condition at 550°C is similar to that in the A/R condition at 500°C. This benefit of temperature increment doesn't seem to be applicable at 220MPa between 550°C and 600°C. The lack of creep data at the same stress level for different temperatures makes it difficult to make a conclusive statement regarding a temperature benefit. The available data suggests that the beneficial effect of CSLE in terms of temperature is between 30 and 50°C.

A.1.2.2 Proton Irradiation of F-M alloys

F-M alloys T91, HCM12A, HT-9 and 9Cr-ODS were proton-irradiated at 400 and 500°C using 2 MeV protons. Table A.4 gives chemical composition in wt% of these F-M alloys. Table A.5 gives the details of the irradiations conducted using 2 MeV protons for these alloys. The stage temperature during each irradiation was maintained within $\pm 10^\circ\text{C}$ of the target irradiation

temperature. Post irradiation beta counting of samples was done after each irradiation to evaluate the dose uniformity between all the samples.

Proton irradiations were performed using a specially designed stage connected to the General Ionex Tandetron accelerator at the Michigan Ion Beam Laboratory. The irradiation stage was designed to control the sample temperature by controlling the stage temperature. The stage was heated using a resistive cartridge heater and cooled using room temperature air flowing through cooling lines that penetrated the back of the stage. The stage surface is made of copper to provide good heat conduction away from the samples. To provide effective thermal contact between the sample bars and the stage, a thin layer of either indium (400°C and 450°C irradiations) or tin (500°C irradiations) was placed between the samples and the stage surface. These metals are molten at the irradiation temperature, maximizing the thermal contact between samples and stage.

During irradiation, sample temperature was monitored continuously using a high-resolution two-dimensional, thermal imaging system (pyrometer) that was pre-calibrated with a set of thermocouples attached to the samples. During irradiation, the sample temperature was controlled to within $\pm 10^\circ\text{C}$ of the set point temperature by controlling the amount of heating and/or cooling provided to the stage. The irradiation stage was electrically isolated from the beam line and four rectangular tantalum apertures were used to define the area on the sample bars that was irradiated with the proton beam. The approximately 3 mm diameter proton beam was raster-scanned across the stage so that between one-half and two-thirds of the total beam current was deposited on the samples and the remainder on the apertures. Raster-scanning ensured that all regions of the samples received the same dose.

Irradiations were conducted using 2.0 MeV protons at a dose rate of approximately 2×10^{-5} dpa/s (the experimental doses and dose rates are calculated using the SRIM2003 simulation [A.65]), resulting in a nearly uniform damage rate through the first 15 μm of the proton range (20 μm), where dpa is calculated using SRIM with a displacement energy of 40 eV. The calculated dose rate is plotted as a function of depth in Fig. A.18.

Figure A.18 Damage rate depth profile for Fe irradiated with 2.0 MeV protons as modeled by SRIM2003.

Table A.4 Alloy compositions (wt%)-balance Fe

Alloy	C	Mn	P	S	Si	W	Al	Ni	Cr	Mo	Other
HCM12A	0.11	0.62	0.015	0.002	0.28	1.82	0.001	0.39	10.54	0.32	Cu_0.98, V_0.19, Nb_0.054, N_0.063,
9Cr-ODS	0.14	0.01	<0.01	<0.005	0.01	2.00	<0.008	0.02	9.19	<0.01	Ti_0.21, Y ₂ O ₃ _0.33, O_0.06
T91*	0.10	0.45	0.009	0.003	0.28	-	0.022	0.21	8.37	0.90	V_0.216, Cu_0.17, Nb_0.076, N_0.048
HT-9	0.20	0.52	0.02	0.006	0.22	0.52	<0.01	0.50	11.63	1.0	V_0.30, Cu_0.04, Co_0.08, N_0.047, Ti_<0.01

HCM12A- Normalized at 1050°C (air-cooled), Tempered at 770° (air-cooled)

9 Cr ODS- Normalized at 1050°C for 1 hr (air-cooled), tempered at 800°C followed by air-cooling for 1hr

T91 – Normalized for 46 min at 1066 °C (air cooled), tempered: 42 min at 790 °C (air cooled).

HT-9 – Normalized for 1 hr at 1040 °C (air cooled), tempered: 45 min at 740 °C (air cooled).

Table A.5 Details of irradiations conducted on F-M alloys using 2 MeV protons.

Temperature (°C)	Dose (dpa)	Alloy	Sample
400	10	HCM12A T91 HCM12A T91	6 x TEM bars 2 x TEM bars 3 x TEM bars + 3 x TEM bars 1 x TEM bar + 1 x TEM bar
500	3	T91 T91 CSL HCM12A	2 x TEM bars, 2 x SCC bars 2 x SCC bars 2 x TEM bars
400	7	ODS HT-9 T91 T91 CSL HCM12A	2 x TEM bar 2 x TEM bars, 1x SCC bar 1 x SCC bar 1 x SCC bar 1 x SCC bar
500	7	ODS T91 HT-9 HT-9 SM	2 x TEM bars 2 x TEM bars 2 x SCC bars 2 x SCC bars

A.1.2.2.1 Irradiation Induced Hardness

Microhardness testing is an efficient means of assessing the mechanical properties of many materials, and is especially convenient for irradiated samples because of the small sampling volume requirement. Microhardness was measured both prior to and after irradiation by protons. Vickers hardness was measured using a Vickers Microhardness Tester (Micromet-II). Indents were made with a load of 25g on a TEM bar in both the irradiated region and the unirradiated region. Since proton irradiation produces a fairly uniform damage layer over approximately the first 15 μm , a low load of 25g was applied over a period of 20 seconds to ensure that the unirradiated material below the damaged layer was not being sampled (the depth of indent with a 25g load is 7 μm).

Hardness measurements were performed on samples irradiated with protons to varying doses at temperatures of 400 and 500°C. The hardness results for T91, HCM12A, HT-9 and ODS 9Cr alloy are presented in Table A.6 (25 indents were measured for each condition). In addition to the measured hardness level, Table A.6 also contains the standard deviation and standard deviation of the mean associated with the measurement. Note that while the standard deviation indicates the variability in the individual hardness measurements, the standard deviation of the mean indicates the variability in the mean sample hardness.

Table A.6 Summary of results for hardness measurements on proton-irradiated T91, HCM12A and HT-9 (25 indents were measured for each condition).

Alloy	Dose (dpa)	Irradiation Temp (°C)	Hardness (HV)	Std. Dev	Std. Dev of Mean
T91	0	-	211.25	4.24	0.85
T91	3	400	238.95	8.35	1.67
T91	5	400	366.20	5.32	1.06
T91	7	400	374.40	8.57	1.70
T91	8	400	370.40	7.37	1.47
T91	10	400	374.30	9.94	1.98
T91	3	500	225.60	7.23	1.45
T91	7	500	241.40	6.63	1.30
HCM12A	0	-	252.85	9.23	1.84
HCM12A	3	400	298.16	6.75	1.35
HCM12A	5	400	413.50	8.34	1.67
HCM12A	7	400	437.83	6.49	1.30
HCM12A	8	400	416.80	8.10	1.62
HCM12A	10	400	432.86	5.76	1.15
HCM12A	3	500	262.10	8.35	1.67
HCM12A	7	500	276.00	7.29	1.46
HT-9	0	-	263.20	9.16	1.83
HT-9	7	400	458.30	8.57	1.71
HT-9	7	500	284.40	6.25	1.25
9Cr-ODS	0	-	339.70	8.34	1.67
9Cr-ODS	7	400	471.80	6.78	1.36
9Cr-ODS	7	500	385.40	5.38	1.08

The hardness results for T91, HCM12A and HT-9 are plotted in Fig. A.19. For T91 and HCM12A irradiated at 400°C, the hardness increases at low dose and tends to saturate near 7 dpa. Hardness increase for all three alloys is more pronounced at 400°C than at 500°C. At 500°C T91, HCM12A and HT-9 show a slight, but similar increase in hardness by 7 dpa indicating that the temperature dependence of hardening is similar between the three alloys. Also note that at both temperatures, HT-9 hardens more than HCM12A which hardens more than T91.

Figure A.19 Average hardness as a function of dose for T91, HCM12A and HT-9 irradiated at 400°C-500°C with 2 MeV protons.

The difference in hardening behavior for F-M alloys at 400°C and 500°C can be attributed to the difference in microstructure. Hardness increase for all three alloys is more pronounced at 400°C than at 500°C, consistent with the literature [A.66-A.70]. For F-M alloys irradiated at high temperature, diffusion is such that the irradiation induced defects anneal out and precipitates that can form coarsen rapidly (i.e., normal thermal processes are enhanced by irradiation) [A.67]. At 500°C T91, HCM12A and HT-9 show a slight, but similar increase in hardness by 7 dpa indicating that the temperature dependence of hardening is similar between the three alloys. The hardening varies between alloys in the same way that it does at 400°C. This is consistent with the work of Klueh and Bullough et al who show that hardening increases with increasing bulk Cr concentration [A.39, A.71].

Figure A.20 plots the change in yield strength vs. dose for various F-M alloys irradiated between 300 and 500°C. Data from this study is shown in solid symbols and color is used to denote temperature ranges: $T < 400^\circ\text{C}$: blue, $400 < T < 500^\circ\text{C}$: green and $T > 500^\circ\text{C}$: red. Because hardening due to neutron irradiation is generally determined from changes in yield strength, the hardening from microhardness measurements was compared to that from tensile tests using the relation $\Delta\sigma_y = 3.06\Delta H_y$ [A.72]. Note that hardening tends to saturate between 5 and 10 dpa for all of the alloys shown in Figure A.20.

Figure A.20 Plot of change in yield strength vs. dose for various F-M alloys (solid symbols denote data in this study).

A.1.2.2.2 Microstructure of unirradiated and irradiated F-M alloys

An understanding of the irradiated microstructure is critical to understanding the effects of irradiation on mechanical properties. Microstructural characterization for F-M alloy T91 was conducted on a JEOL 2010F analytical TEM (FEG-STEM, 200keV). Two-beam conditions with $\mathbf{g} = [002]$ and $[112]$ near $\langle 110 \rangle$ zone axis were set up for bright field imaging of dislocations. The combination of these two conditions should reveal all dislocations with $\mathbf{b} = a_0/2\langle 111 \rangle$ and $\mathbf{b} = a_0\langle 100 \rangle$. The radiation-induced cavities were examined in conventional bright field mode under slightly underfocused conditions. Dislocation loop size and number density and dislocation network density were examined in bright-field mode, lath and precipitate sizes were measured, and STEM/EDS analysis of the grain boundaries for the irradiated/unirradiated T91 was done [A.73]. Microstructural and microchemical analysis for F-M alloy HCM12A was done by Allen et al [A.74]. No microstructural or microchemical analysis was done on HT-9.

There were six sample conditions analyzed for alloy T91; unirradiated; irradiated to 3 dpa, 7 dpa and 10 dpa at 400°C; and irradiated to 3 dpa and 7 dpa at 500°C. Note that microstructural characterization was also performed on T91 irradiated using 2MeV protons at 450°C to doses of 3 and 10 dpa in a previous study. Although a different heat of material (referred to as Heat A) was used, the irradiation conditions (dose and temperature) are close to those used in this study the results are relevant for comparison. The composition of F-M alloy T91 alloy irradiated at 450°C is given in Table A.7 below.

Table A.7 Composition of T91 in wt%.

Heat	Cr	Mo	Mn	V	Nb	Ni	Si	Cu	C	P	Al	S	N	Fe
A*	8.13	0.98	0.43	0.24	0.24	0.22	0.27	0.16	0.09	0.09	0.015	<0.01	<0.005	Bal.

* Normalization: 1038°C: 1 hr, Temper: 740°C: 45 min [2]

The microstructure of unirradiated T91 contains martensite laths (Fig A.21a), precipitates and dislocation cells (Fig A.21b), and a sparse dislocation network (Fig A.21c). Precipitates are located preferentially on grain boundaries, and also on lath boundaries and in the matrix. Dislocation density varied dramatically, ranging from dislocation-free areas to dense tangles in dislocation cell walls that contain a dislocation density of approximately $5.6 \times 10^{13} \text{ m}^{-2}$.

Figure A.21. TEM micrograph of unirradiated T91 showing a) lath structure, b) dislocation cells and carbides, and c) dislocations (Diffraction condition of $g=110$ near zone $[001]$ was used).

The irradiated microstructure consisted of a high density of black dots and dislocation loops of type $a_0\langle 100 \rangle$, for irradiation temperatures of 400°C and 450°C. No black dot damage was evident for an irradiation temperature of 500°C. Also large loops of type $a_0\langle 100 \rangle$ were present even at a low dose of 3 dpa. No cavities or voids were observed which confirms the swelling resistance of these alloys to 10 dpa. No significant change was observed in the precipitate size and density following proton irradiation up to 10 dpa. Lath size also remained the same. Fig A.22 presents irradiation-induced defect structures in T91 steel irradiated to different doses. Irradiation conditions and defect data obtained from TEM investigations of the samples are listed in Table A.8.

Figures A.23a and A.23b show the plots of loop size and loop density with dose. At each irradiation temperature, the dislocation loop size and density and dislocation network increase with dose. For the sample irradiated to 3 dpa at 450°C the most prominent microstructural changes were the high density of dislocation loops and the increase of the network dislocation density, shown in Figs A.24a and A.25a. The dislocation microstructure at 10 dpa (Fig A.24b) is very similar to that at 3 dpa but with an increase in loop size and loop density. Similar trends were observed for samples at 400°C and 500°C with increasing dose. The only difference is the large loop sizes obtained at 500°C even at low doses. With an increase in irradiation temperature at the same dose, dislocation loop density and network density decrease while the loop size increases. It should be noted that the dislocation loop network features for the 450°C irradiation (conducted on a different heat with a different heat treatment than the 400°C and 500°C irradiations), follow the same dose dependence, but have magnitudes that are considerably smaller.

Figure A.22. Defect cluster structure of T91 samples irradiated at different conditions: a) 3dpa, 450°C b) 10 dpa, 450°C c) 3dpa, 400°C, d) 7 dpa, 400°C.

Figure A.23a) plot of loop size vs. dose and b) plot of loop density vs. dose.

Figure A.24. TEM micrograph showing laths in T91 irradiated to 3dpa at a) 450°C, and b) 400°C.

Table A.8. Irradiation conditions and defect data obtained from TEM investigation.

Irradiation temperature (°C)	Dose (dpa)	Dislocation loop density ($\times 10^{21} \text{ m}^{-3}$)	Dislocation loop size (nm)	Dislocation network density ($\times 10^{14} \text{ m}^{-2}$)
400	3	9.10	28.5	8.14
400	7	13.93	31.8	13.90
400	10	14.00	49.0	21.50
450	3	1.30	10.5	0.45
450	10	1.73	12.8	0.72
500	3	3.60	60.0	6.78
500	7	4.10	64.5	8.30

Figure A.25 Plot of a) Dislocation loop size as a function of dose b) Dislocation loop density as a function of dose.

The dislocation densities observed are comparable to those recently reported by Hashimoto and Klueh [A.34]. T91 samples irradiated with 800 MeV protons in the SINQ-3 spallation neutron source at PSI [A.35] to a dose of 11.8 dpa at 360°C resulted in the mean loop diameter and density of 8.9 nm and $1.3 \times 10^{22} \text{ cm}^{-3}$, respectively. This is close to the dislocation density observed in T91 at 400°C. The higher loop density and reduced diameter are consistent with the lower irradiation temperature. The presence of large loops at 500°C in T91 is similar to what was observed by Gan et.al [A.75] for Ni ion irradiated T91 at 500°C. Loops with sizes up to 100 nm have been observed in work by Gelles [A.32] on FFTF neutron irradiated T9 (similar to T91) at 420°C to 200 dpa and also in 9Cr-2WV steels irradiated to 38 dpa at 420°C by Klueh et.al [A.37]. Figures A.25a and A.25b plots our results and data from literature for dislocation loop size and loop density as a function of dose.

While the dependence of loop size, loop density and network density on dose for the 450°C irradiation matches those for the 400 and 500°C irradiations, the magnitudes are not consistent. This is likely due to the different heat treatment for Heat A irradiated to 450°C as compared to that given Heat B for 400 and 500°C irradiations. Heat A was tempered at a lower temperature, leading to reduced lath size, lower by a factor of 2.5 than that for Heat B. The reduced lath size means higher grain boundary area, which serves as a sink for irradiation-induced defects, suppressing initiation and slowing the growth of dislocation loops. Zinkle et al. [A.76] conducted similar studies on austenitic alloys and observed significant differences between dislocation evolution in cold worked and solution annealed steels at low doses (< 10 dpa). They observed a lower loop density for the cold worked specimen. A reduced tempering temperature for Heat A would correspond to a state of higher degree of cold work from the standpoint of defect sinks. Note that Jia et al [A.35] and Hashimoto et al [A.34] irradiated T91 which was initially tempered at relatively lower temperatures of 760 and 700°C respectively and their data for dislocation loop density and size matches with that for 450°C irradiation in this study (Figures A.25a and A.25b).

No cavities have been observed in the T91 irradiated with protons up to 10 dpa. Hashimoto and Klueh [A.34] report a population of 9 nm voids at a density of $3 \times 10^{21} \text{ m}^{-3}$ (0.17% swelling) in T91 irradiated in HFIR to 12 dpa at 400°C (with 35 appm He). While this would appear to contradict the results from the proton irradiated alloys, swelling in F-M steels can also depend on heat treatment and tempering. He gas would also help stabilize void nuclei. Further, 10 dpa is still a relatively low dose for swelling in ferritic-martensitic stainless steels. Data compiled by Klueh and Harries [A.70] shows that void swelling in neutron irradiated commercial T91 steels ranges from 0.85 % (~ 35 dpa at 420°C) up to only 2% after over 200 dpa at 420°C.

No significant change was observed in the precipitate size and density following proton irradiation up to 10 dpa. This is consistent with the results from T91 alloys irradiated in HFIR [A.34] to 12 dpa at 400°C where no difference in the size or distribution was measured in the M_{23}C_6 precipitates after irradiation. Was et al [A.77] also confirmed that there was no change in precipitate size, distribution and structure after proton irradiation at 450°C to 10 dpa.

For F-M alloy HCM12A microstructural characterization has been done only for a specimen irradiated with 2.0 MeV protons at 400°C to 10 dpa by Allen et al [A.74]. Dislocation loops, microvoids, and finely distributed small precipitates were observed in addition to the dislocations and M_{23}C_6 present in the unirradiated condition. The loops were identified as $a_0[100]$ type (a_0 is lattice constant), with an average size of 34 nm and density of $3.2 \times 10^4 \text{ cm}^{-2}$. Microvoids and radiation-induced small precipitates were also imaged, Figure A.26. The average size and volume for voids was observed to be 6.2 nm and 154 nm^3 , respectively. The void density was calculated to be $9.4 \times 10^{20} \text{ cm}^{-3}$ and the calculated void swelling was 0.015%. The small precipitates had an average size of 5.7 nm with a density of $3.9 \times 10^{21} \text{ cm}^{-3}$.

Figure A.26 HCM12A irradiated with 2 MeV protons at 400°C to 10 dpa showing a) overview b) voids and small precipitates in the same area [A.74].

A.1.2.2.3 Correlation of Hardening with Irradiated Microstructure of F-M alloy, T91

Since voids were not observed and precipitate size distribution did not change, the observed irradiation hardening was due to the formation of dislocation loops that impede the motion of dislocation lines. The evolution of dislocation loops induced by irradiation can be rationalized by the formation of small glissile $1/2a_0 \langle 111 \rangle$ loops that, with increasing dose, will form sessile $a_0 \langle 100 \rangle$ loops that decorate the dislocation lines and eventually fill the matrix

[A.78-A.83]. In the bcc lattice, the $a_0 \langle 100 \rangle$ loops are formed on the (001) plane which is not a close-packed slip plane in the bcc lattice, resulting in immobile dislocation loops.

Microhardness values can be compared to calculations of the expected amount of hardening due to irradiated microstructure using the dispersed barrier hardening model. In this model, the hardening produced by a dispersion of obstacles in the glide plane is described by the relation between increase in yield strength induced by the irradiation $\Delta\sigma = \sigma_{irr} - \sigma_{unirr}$ and a density of defect clusters N of diameter d according to $\Delta\sigma = M\mu\alpha b(Nd)^{1/2}$, [A.79] where (μ is the shear modulus, b the burgers vector, M is the Taylor factor ($M=3$ for bcc alloys [A.84]) and α is a parameter that describes the strength of the obstacle). For loops and other defect clusters, $\alpha \sim 0.2-0.3$.

Calculated hardening is compared with hardening from microhardness measurements by converting the increase in measured hardness to increase in yield strength using the relation $\Delta\sigma_y = 3.06\Delta H_y$ [A.72]. Fig A.27a shows a plot of measured and calculated hardening for the irradiations. The calculated values are based on the dislocation loop density. Note that while the trends are the same, the magnitudes of the measured hardening at 400°C and 450°C far exceed that calculated from the microstructure at higher dose. At 500°C the magnitude of the calculated hardening matches that of measured hardening even at higher dose. Figure A.27b accounts for the various microstructure contributions to hardness for the case of 450°C. Note that on top of the hardness of the unirradiated matrix, the visible dislocation loops structure and the dislocation network add nearly equal increments of hardening that increase rapidly with dose to 3 dpa. At 3 dpa, the hardening accounted for by the observed dislocation loop and network structure exceeds the measured hardening. However, above 3 dpa, the measured hardening increases linearly with dose while the hardening accounted for by the observable dislocation structure has nearly saturated. By 10 dpa, the observable dislocation structure accounts for only half of the measured hardening, indicating that additional microstructure changes have occurred that are not visible in the TEM. Likely candidates are nano-sized precipitates that can significantly harden the matrix and also nano-sized black dots. Hardening due to black dots seems to increase with dose up to a dose of around 0.1 dpa and then saturates with dose [A.85-A.86].

a)

(b)

Figure A.27 a) Plot of irradiation hardenings determined by microhardness indentation (closed symbols) and calculated from the dispersed barrier hardening model (open symbols). b) Schematic showing various microstructure contributions to hardness for the alloy irradiated at 450°C.

A.1.2.2.4 Grain boundary microchemical analysis

Microchemical analysis was performed on unirradiated T91 and a sample irradiated to 10 dpa at 450°C. Analysis was conducted on a scanning transmission electron microscope with

energy-dispersive X-ray analysis (STEM/EDS). The STEM/EDS analysis of the grain boundaries for the irradiated sample was performed on a Philips CM200/FEG at Oak Ridge National Laboratory, which produces a probe approximately 0.9-1.0 nm in diameter (full-width, half-maximum) while operating at 200 kV. STEM/EDS analysis for the unirradiated sample and the lath boundaries for a sample irradiated at 450°C to 10 dpa were performed on a JEOL 2010F at the University of Michigan Electron Microbeam Analysis Laboratory, which produces a probe approximately 0.5 nm in diameter (full-width, half-maximum) while operating at 200 kV. STEM/EDX profiles for the same grain boundary of the 10 dpa sample were collected using both microscopes and compared to verify equivalency, allowing comparison of data between the two instruments.

STEM/EDS measurements were performed on ‘edge-on’ grain boundaries so as to minimize broadening of the boundary profile. Details of the grain boundary measurement technique are given in Reference [A.82]. Measurements were made at 1.5 nm increments along a 45 nm line perpendicular to the grain boundary. Three line measurements were performed on one grain boundary (GB). *K*-factors [A.85] were determined by using 6 points on either end of the line scan and the bulk composition of the alloy (determined using electron microprobe) and averaged. Concentrations of Fe, Cr, Mo, Mn and V were calculated at each point along the line scans from these *k*-factors.

Figure A.28a presents a representative grain boundary composition profile for a sample irradiated at 450°C to 10 dpa. On average, Cr enriched by 4.7 wt%, V by 0.6 wt% (an enrichment by nearly 300%), and Fe depleted by 5.3 wt% over the bulk values. The full width at half maximum of the profiles is about 12 nm, which is very narrow and indicative of radiation induced segregation (RIS). Results for Mn and Mo showed no significant variation in concentration across the GB, as shown in Fig. A.28b. The known bulk composition, calculated *k* factors, and average measured GB compositions are presented in Table A.9. No changes in composition were observed near the grain boundary in the unirradiated condition, which verifies that the segregation presented in Figure A.28a is fully due to radiation (RIS). Additionally, the RIS phenomenon appears to be confined to prior austenite grain boundaries as no segregation was observed across the lath boundaries of the 10 dpa sample.

Figure A.28 Change in concentrations with distance from the GB for T91 irradiated to 10 dpa at 450°C with 2.0 MeV protons. a) Fe, Cr and V. b) Mn and Mo.

Table A.9 Average measured matrix and grain boundary concentrations for T91 irradiated to 10 dpa at 450°C.

Matrix Concentrations (wt %)					
	Fe	Cr	V	Mo	Mn
Bulk Composition	90.22	8.13	0.24	0.98	0.43
Calculated <i>k</i> factors	1.45	1.00	0.24	0.94	0.47
Grain Boundary Concentrations (wt %)					
	Fe	Cr	V	Mo	Mn
Average Measured Composition	84.97	12.71	0.91	1.00	0.41
Standard Deviation	0.13	0.23	0.05	0.28	0.00
Standard Deviation of Mean	0.08	0.13	0.03	0.16	0.00

The inverse Kirkendall effect [A.86-A.87] has been used to successfully describe RIS in austenitic stainless steels under irradiation, in which Ni enriches and Cr depletes at grain boundaries and Fe either enriches or depletes depending on the bulk alloy composition. Ohnuki et al. observed Cr enrichment in Fe-13Cr and Fe-13Cr-1Si irradiated to 57 dpa with 200 keV C⁺ ions [A.88]. However, they observed Cr depletion in Fe-13Cr-1Ti in the same study and in electron irradiated Fe-13Cr (without the presence of additional C) [A.89]. Allen et al. [A.90] have observed significant chromium enrichment in HCM12A irradiated with protons at 400°C and at 500°C to doses between 3 and 10 dpa that increased with dose. Segregation is greatest at grain boundaries but is also observed on cleavage facets created by fracture in an Auger Electron Spectrometer (AES) chamber. Additionally, Allen observed GB enrichment of chromium in the unirradiated condition. However, AES measurements also include pre-existing grain boundary carbides which are a likely the source of this apparent enrichment. Our results show that in the unirradiated condition, T91 exhibits no grain boundary enrichment or depletion of Cr or Fe. Therefore, any changes measured after irradiation are due to RIS.

Since Cr and V generally act as oversized solutes in the Fe one expects the inverse Kirkendall effect would predict that Cr and V should deplete at the grain boundary by preferential exchange with vacancies. The results of the present work, that of Allen et al., and that of Ohnuki et al. suggest that either a mechanism other than Inverse Kirkendall is controlling segregation in this alloy or the difference in migration energies for BCC dictates that Fe diffuses away from the GB at a faster rate than Cr. Ohnuki et al. suggested that a Cr-interstitial solute (such as C)-vacancy complex could lead to the enrichment of chromium at the grain boundary in Fe-13Cr and Fe-13Cr-1Si. Ohnuki's C+ irradiation resulted in the implantation of about 0.024wt% C at a dose (57 dpa) at which they observed Cr enrichment. The C content of T91 Heat A was 0.09wt% which is significant compared to the implanted C level in Ohnuki's experiment. Ohnuki explains the depletion of Cr in Fe-13Cr-Ti as being due to the addition of Ti that acted to suppress segregation.

However, Brimhall et al. observed no measurable segregation in any major or minor alloying element, apart from phosphorus, in HT-9 (Fe-12Cr-1Mo-0.2C) irradiated with 5 MeV Ni^{++} [A.91] to doses <1 dpa. Also, the chromium enrichment profiles observed by Ohnuki are 100-200 nm wide, which is an order of magnitude greater than those generally observed for RIS. The electron irradiation experiment is also suspect as there is significant evidence of unusual behavior in electron irradiation experiments due to the intense damage zone created by the electron beam.

Allen et al. [A.90] have applied the modified inverse Kirkendall (MIK) model to Fe-10.5Cr-0.4Ni (HCM12a) and predicted Cr enrichment, which is consistent with both the present work and their RIS measurements. However, several of the parameters of the MIK model pertain to FCC austenitic stainless steels. It is not clear what effect, if any, would occur if data were available to benchmark the model for BCC F-M alloys. Clearly, further study is necessary to fully understand RIS in F-M alloys.

A.1.2.3 Stress Corrosion Cracking of F-M alloys at 400°C in deaerated SCW

Constant extension rate tensile (CERT) tests were performed in the multi-sample supercritical water system. Table A.10 gives a summary of the CERT tests conducted on F-M alloys. The tensile samples were strained at a rate of $3 \times 10^{-7} \text{ s}^{-1}$. During exposure, the temperature inside autoclave was controlled to within $\pm 5^\circ\text{C}$ of the 400°C test temperature. The pressure was maintained at $3,655 \pm 15$ psig. High purity water was used as test solution and the dissolved oxygen (DO) content was maintained below 10 ppb at inlet and outlet lines by purging argon gas continuously. The inlet conductivity and the outlet conductivities were less than $0.1 \mu\text{S/cm}$. The flow rate was maintained at around 75 ml/min.

Table A.11 gives a summary of the results obtained in the three CERT tests. For both irradiation temperatures at the same dose HT-9 has a higher maximum stress and a lower strain to failure as compared to T91 and HCM12A. It also has the lowest values for reduction in area which indicates relatively poor impact properties and less ductility. This is similar to what was observed by Alamo et al [A.92]. One of the most important things to note is that the strains to

failure are almost similar in all the F-M alloys irrespective of the dose which is a likely a sign of the absence of any SCC, which was confirmed by cross-section analysis. In austenitic alloys [A.93], there is quite a decrease in strain to failure due to irradiation and that is accompanied by significant IG cracking.

Table A.10 Summary of the CERT tests performed at 400°C

Test #	Temperature (°C) Irradiation	CERT	Alloy Condition
1	500	400	T91 (3dpa), T91 CSL (3dpa), T91 (7dpa), HT-9 (7dpa)
2	400	400	T91, T91 CSL, HCM12A, HT-9, (all at 7dpa)
3	None	400	T91, HCM12A, HT9 and T91CSL

Table A.11 Summary of results of the two CERT tests conducted in deaerated SCW at 400°C.

Temperature (°C) CERT	Irr	Alloy	Dose (dpa)	ϵ_t (%)	R.A (%)	Max Stress (MPa)	Y.S (MPa)
400	500	T91	7	12.5	77.5	470	410
		T91	3	12.4	72.9	450	385
		T91 CSL	3	13.1	75.5	425	365
		HCM12A	7	11.0	50.1	590	495
400	400	T91	7	11.2	69.1	475	405
		T91 CSL	7	11.5	73.6	545	470
		HCM12A	7	12.4	45.8	635	515
		HT-9	7	10.1	34.3	640	520
400	None	T91	0	12.6	73.4	405	355
		T91 CSL	0	13.5	76.8	410	355
		HCM12A	0	12.2	53.7	540	460
		HT-9	0	12.1	51.5	575	490

A.1.2.3.1 Fractography

After completion of the experiments, the samples were examined using Philips XL-30 scanning electron microscope (SEM). The fracture surface and the faces of the sample gage sections were analyzed. Figure A.29 shows the images of the fracture surface of F-M alloys irradiated at 400°C using 2 MeV protons and CERT tested at 400°C in deaerated SCW. These figures were used to evaluate the percentage reduction in area (Table A.11). Note that all the surfaces give indication of fracture which is ductile in nature. Similar observation was made for fracture surfaces of F-M alloys irradiated at 500°C and tested at 400°C in deaerated SCW. Examination of the side surface of the fracture area did not give any evidence of cracking for both irradiation temperatures except in HT-9. Figures A.30a and A.30b show the image of the side surface of the fracture area for HT-9 irradiated at 500°C and 400°C respectively to a dose of 7 dpa and CERT tested at 400°C in deaerated SCW.

Figure A.29 SEM images of the top of the fracture surfaces of F-M alloys irradiated to a dose of 7dpa at 400°C and tested at 400°C Deaerated SCW, (a) T91 CSL, (b) T91, (c) HCM12A, and (d) HT-9.

Figure A.30 SEM image of the fracture surface of F-M alloy HT-9 tested at 400°C in deaerated SCW a) irradiated at 400°C to a dose of 7dpa and , b) irradiated at 500°C to a dose of 7dpa

Cracking analysis was done on cross-section of SCC samples which were prepared by mounting in epoxy resin and then mechanically polished. The mounted specimens were etched in 25% HCL and 75% HNO₃ in order to observe the grain boundary. The cracks were investigated in SEM with both secondary-electron (SE) mode and back scattered-electron (BSE) mode. The crack depth is accounted from the deepest part of crack to the outer oxide layer. Analysis of cracks on F-M alloys was performed on three areas of SCC bars; marked as A, B and C. Areas A, B, and C are defined by the ratio of width at a particular point to the width of flat area (un-necked width). Area A is from gage fracture to 80% of original width, area B is from 80% to 90%, and area C is from 90% to un-necked area (Figure A.31). Area A is highly deformed with localized plastic deformation so no crack analysis was performed in this region. So cracks were recorded only in areas B and C. Cross-section analysis was done for all the fractured F-M alloys according to the process described above. Fig A.32 displays intergranular cracking in HT-9 for both irradiation temperatures.

Figure A.31 Low magnification image of Fractured HT-9, irradiated to a dose of 7 dpa at 400°C with 2 MeV protons and CERT tested at 400°C in deaerated SCW.

Figure A.32 Cross-section images of F-M alloy HT-9 irradiated to a dose of 7 dpa tested at 400°C in deaerated SCW, displaying evidence of IG cracking. a) Irradiated side at 400°C, and b) Irradiated side at 500°C. (Note that all the images were taken from section B).

Figure A.33a shows a plot of the number of cracks for all three conditions of F-M alloy HT-9. Note that for the proton irradiated samples both the irradiated and the unirradiated sides were analyzed. Both the irradiated samples have more cracks on the irradiated side as compared to the unirradiated side thus establishing the effect of irradiation on the cracking susceptibility of HT-9. Also the sample irradiated at a lower temperature of 400°C has more cracks than the sample irradiated to the same dose at 500°C. Figure A.33b shows a plot of the maximum crack depth for the all conditions for HT-9 tested at 400°C in deaerated SCW. The sample irradiated to a lower temperature of 400°C has deeper cracks as compared to the sample irradiated to the same dose at 500°C on the irradiated side. The maximum depth of crack on the unirradiated side for the two samples is similar to each other and to the unirradiated sample, as expected.

Figure A.33 Analysis on the cross-section of F-M alloy HT-9 tested at 400°C in deaerated SCW at all three conditions showing plots of a) number of cracks and b) average depth of cracks.

The enhanced cracking behavior of HT-9 samples irradiated at the lower temperature of 400°C as compared to 500°C might be explained by the increased hardening at the lower irradiation temperature which causes ductility degradation.

Alamo et al [A.92] also observed intergranular fracture besides some ductile regions with dimples in HT9 irradiated to a dose of 3.4 dpa at 325°C in the Osiris reactor and tested at 20°C. Evidence of IG fracture in HT-9 might be explained on the basis that the 12Cr-1MoVW (HT-9) steel contains twice as much carbon as does T91 and HCM12A steel, and in the normalized-and-tempered condition, it contains almost twice as much volume fraction of precipitates [A.94]. Fracture in steels is generally initiated at carbide particles or inclusions [A.95-A.96].

A.1.2.3.2 Effect of Irradiation and GBE on CERT Behavior

The effect of irradiation on the tensile behavior of F-M alloys in SCW can be observed by comparing the results from the two CERT tests conducted on irradiated F-M alloys with those conducted on unirradiated F-M alloys. Figure A.34a shows the plot of stress vs. strain for F-M alloy HT-9 tested in deaerated SCW at 400°C for three conditions; unirradiated, irradiated to a dose of 7 dpa at 400°C and at 500°C. All the curves are typical stress-strain curves with an elastic region where stress is directly proportional to strain, followed by work hardening and saturation where work hardening is balanced by softening finally leading to fracture. The stresses for the two irradiated samples are higher than the unirradiated one, with the sample irradiated at 400°C having higher values of stresses than the one irradiated at 500°C, though lower total and uniform elongation (Note here that the irradiated samples are basically composite samples with a thin irradiated region and the bulk of the sample being unirradiated). This is consistent with the increased hardening observed in HT-9 at lower irradiation temperature. Basically during plastic deformation as the degree of deformation increases generation and interaction between dislocations changes. As dislocation loop density and dislocation network density are higher at lower irradiation temperature they have greater interaction and thus higher

stresses are required for yielding. Klueh et al [A.97] irradiated modified 9Cr-1Mo steel in EBR-II to 9 dpa and observed that the total and uniform elongation increases with increasing irradiation temperature and maximum stress decreases with increasing irradiation temperature. Shiba et al [A.98] conducted tensile tests on irradiated F82H, a F-M alloy and observed that the yield strength decreases with increasing test temperature from 400°C to 500°C while the total elongation increases. Note that the strain to failure of the unirradiated sample is more than the irradiated ones which is expected and similar to what has been observed by various researchers. Similar trends were observed for HCM12A, T91 and T91 CSL. The effect of irradiation on SCC behavior of F-M alloys is discussed later in the section on fractography.

Figure A.34 Plot of stress vs. strain for F-M alloy a) HT-9 tested in deaerated SCW at 400°C for all three conditions, b) T91 and T91 CSL CERT tested in deaerated SCW at 400°C.

The effect of GBE on F-M alloys in SCW can be understood by comparing the tensile behavior of T91 and T91 CSL. Figure A.34b shows the plot of stress vs. strain for irradiated T91 and T91-CSL samples CERT tested at 400°C in deaerated SCW. T91 irradiated at 500°C to a higher dose of 7 dpa has slightly higher stresses than the one irradiated to a dose of 3 dpa, though almost similar strain to failure values. Toloczko et al [A.99] conducted tensile tests at 164°C and at 500°C on irradiated T91 and he observed an increase in stress with dose at 500°C and also almost similar values of total elongation between 3 and 7 dpa. At both temperatures and similar doses the CSL condition has a higher strain to failure and similar values of stresses thus exhibiting enhanced ductility. Similar improvement in ductility was observed due to CSL enhancement in the unirradiated condition by Ampornrat et al [A.43]. They conducted CERT tests on T91 AR and T91 CSL at 400°C in deaerated SCW and at 500°C in 300ppb oxygen. For both test conditions the CSL condition had a much higher strain to failure (Figure A.35).

The stresses at similar values of strains are higher in the CSL condition. This is similar to what has been observed in creep tests conducted at 500°C-600°C in argon on T91 AR and T91 CSL [A.100]. Since the dislocation behavior is inherent to both creep and tensile tests, this behavior can be speculated to be associated with the limited mobility of extrinsic GB dislocations in the special boundaries. That is, if two of the three grain boundaries meeting at a triple point are special boundaries, then intrinsic dislocations cannot move from one boundary to

the next. Thaveeprungsriporn and Was [A.6] hypothesized that the reason for the difference in IGSCC (and creep) behavior of alloys containing high fractions of coincident site lattice boundaries (CSLBs) is due to the difference in dislocation absorption at CSLBs versus high angle boundaries (HABs). The absorption of a lattice dislocation into a CSLB is a difficult process due to the highly ordered structure of this boundary type. Therefore, subsequent lattice dislocations approaching the CSLB during deformation will be opposed by the first dislocations trapped there. A long-range internal stress thus arises due to the stress field of leading dislocations, which then inhibits the motion of following dislocations. On the contrary, the process of dislocation absorption in HABs can be considered equivalent to the total annihilation of dislocations, which relaxes the boundaries and results in the disappearance of long range strain fields [A.101].

Figure A.35 Plot of stress vs. strain for F-M alloys T91 and T91 CSL CERT tested in deaerated SCW at 400°C and at 500°C with 300 ppb oxygen (From reference A.13).

A1.3 Conclusions

The fraction of CSL boundaries in the alloy, T91 can be increased by about 32% by a thermo-mechanical process involving by 5% strain, 1040°C:1h + 800°C:0.66h, air cool without changing the microstructural features like hardness, grain size, carbide size, location and number density. OIM analysis has shown that the CSLE condition has a higher percentage of $\Sigma 1$ boundaries as compared to A/R condition along with a higher fraction of these low angle boundaries with lower misorientation.

Experimental analysis shows that the CSL-enhanced condition results in a lower minimum creep rate by a factor of 3-13 as-compared to A/R condition for T91 at a temperature range of 500-600°C and in the stress range of 140-235MPa. Preliminary investigations have shown that coarsening of the subgrains is reduced in the CSLE condition relative to the A/R condition. Subgrain coarsening affects creep strength and since the subgrain width of the CSLE condition was observed to be less than A/R condition after creep, it is likely explanation for the

better creep strength. Preliminary analysis has given evidence that the benefit of CSLE as a temperature increment to achieve the same minimum creep rate is in the range 30 - 50°C, though this increment decreases at higher temperature. Preliminary analysis shows that the effect of CSL-enhancement is consistent with a model in which CSLBs add to the internal stress. There may be other factors too. This has been reasoned due to the difference in the misorientation and thus mobilities and diffusivities of these subgrain boundaries in the two conditions.

The observed dislocation loop size and loop density increased with increasing proton irradiation dose at constant temperature. For a given dose, the observed dislocation loop size increased with increasing temperature, while the loop density decreased. No change in precipitate size occurred with irradiation and no voids were observed. The evolution of the irradiated microstructure is highly dependent upon the alloy heat treatment. Lower tempering temperature reduces the defect sink density that suppresses both nucleation and growth of dislocation loops. The change in hardness increases with increasing dose and decreases with increasing irradiation temperature. For low temperature, the change in hardness saturates by 7 dpa. Measured hardening is greater than that expected based on the observed microstructure changes. The difference between measured and calculated hardening is likely due to irradiation-induced black dot damage and fine precipitates that are below the resolution limits of TEM imaging. Grain boundary microchemistry measurements show substantial enrichment of Cr and V and depletion of Fe in proton irradiated T91. This is opposite of the trend observed for FCC austenitic stainless steels. There is some indication that advanced inverse Kirkendall models may predict this, but these models are not optimized for BCC F-M steels.

In CERT tests conducted in 400°C, deaerated supercritical water, most of the alloys had a high reduction in area thus exhibiting good ductility properties. HT-9 had the highest hardness after irradiation and lowest values of reduction in area and strain to failure among all the alloys thus exhibiting maximum ductility degradation. Only HT-9 displayed evidence of intergranular cracking. For both irradiation temperatures of 400°C and 500°C the number of cracks and maximum crack depth was more than those found on the unirradiated sample. The degree of cracking increased with irradiation and was greater at 400°C than at 500°C. While cracking was not observed in T91, the CSL condition had higher values of strain to failure and uniform elongation than the as-received condition. CSL enhancement enabled samples to bear higher stresses at the same value of strain, thus improving the strength.

A.2 Response of the 12Cr steel HCM12A to Proton and Heavy Ion Irradiation

A.2.1 Background

Because of their improved swelling resistance at high dose, ferritic-martensitic steels are favored as cladding and duct material for fast reactor systems. The 12Cr alloy HT9 was used as the most advanced cladding and duct material for both FFTF and EBR-II [A.102]. Many Generation IV reactor systems are conceptualized such that they would operate at higher temperature than was achieved in these first generation sodium-cooled systems. The sodium-cooled fast reactor (SFR), the lead-cooled fast reactor (LFR), and the supercritical water-cooled reactor (SCWR) all include advanced ferritic-martensitic steels in the list of potential candidates [A.103]. HCM12A was developed as a third generation 12 Cr steel with an upper temperature limit approximately 55°C higher than HT9 [A.104]. Because of the potential improvement in cycle efficiency allowed by operating at higher temperature, the possibility of replacing HT9 with HCM12A is of interest to Generation IV reactor designers. Because no information exists on the radiation response of HCM12A, this work examined the hardness changes as well as the microstructural and microchemical changes of HCM12A irradiated with 2.0 MeV protons at 400°C and 5 MeV Ni-ions at 500°C.

These ion irradiations are not substitutes for neutron irradiation, but are a complementary tool for understanding the microstructural changes that will occur under radiation. Because ion irradiation occurs at much higher displacement rates than experienced in a typical reactor environment, a shift in temperature is required to obtain microstructures similar to that expected in a neutron environment [A.105]. A detailed study on using ion irradiation to understand radiation response in austenitic stainless steels under light water reactor conditions has shown the utility of the ion irradiation technique [A.106]. Because HCM12A could be used across a wide range of temperatures in Gen IV systems, these experiments provide a first look at possible microstructural changes. HCM12A is also being irradiated in the ATR reactor to obtain low dose thermal spectrum response. Plans exist to irradiate HCM12A in the PHENIX reactor to get high dose, fast spectrum response. Concurrent testing of the corrosion response of HCM12A in both supercritical water and lead-alloys is also underway. Early experiments indicate a similar corrosion response between HCM12A and HT9 in supercritical water.

A.2.2 Experiment

HCM12A was obtained in plate form from Sumitomo Metal Industries, Kashima Steel Works. The composition, as reported in the manufacturer's check chemistry, of the HCM12A is listed in Table A.12. An independent measurement indicated that the Cr concentration was higher, at 11.3 wt. %. The plate was normalized at 1050°C followed by air-cooling and then tempered at 770°C followed by air-cooling. Following the temper, the average grain size of the prior austenite grains is $14.3 \pm 3.3 \mu\text{m}$.

TABLE A.12—Composition of HCM12A (wt%)-balance Fe

C	Si	Mn	P	S	Cu	Ni	W	Cr	Mo	V	Nb	Al	N	B
.11	.28	.62	.015	.002	.98	.39	1.82	10.54	.32	.19	.054	.001	.063	32 ^a
^a ppm														

Proton irradiation was performed on 2 mm thick bars at the Michigan Ion Beam Laboratory using 2.0 MeV protons at a temperature of 400°C to doses of 3, 7 and 10 dpa and 500°C to 3 dpa. Ni-ion irradiation were conducted at the Environmental and Molecular Science Laboratory at Pacific Northwest National Laboratory using 5 MeV Ni ions at 500°C and 1×10^{-7} torr with a damage rate of 1.4×10^{-3} dpa/s. The material was irradiated with Ni-ions to doses of 5 and 50 dpa.

Microhardness was measured both prior to and after irradiation by protons. Vickers hardness was measured using a Vickers Microhardness Tester (Micromet-II). Indents at a load of 25 g were applied on a TEM bar in both the irradiated region and the unirradiated region. Since proton irradiation produces a fairly uniform damage layer over only the first 30 μm , a low load of 25g with load time of 20 seconds was applied to ensure that the unirradiated material below the damaged layer was not being sampled. The center-to-center spacing of indents is approximately 100 μm , so that specimen deformation from an indent does not affect results of subsequent indentations.

For Ni-ion irradiated samples, TEM discs were punched from the irradiated sheet using a disc punch to a diameter of 2.3 mm. The discs were then mechanically wet polished from the unirradiated side down to roughly 70 μm to minimize the magnetic interference with the electron beam in the microscope. A 5 MeV Ni ion has a maximum penetration depth approximately 1.5 μm into stainless steels. A thin layer of approximately 0.5 μm depth was removed from the irradiated side using a 5-second jet electro-polishing with a solution of 2% perchloric acid and 15% ethylene glycol in methanol at a polishing condition of 25V and -65°C. TEM discs were then jet-polished from the unirradiated side to perforation. The 2.3 mm disc sample was mounted to a 50 μm thick and 3-mm diameter Cu slot grid using epoxy to provide a 3 mm diameter TEM disc. Microstructure characterization was carried out using a JEOL 2010 200KV transmission electron microscope equipped with EDS for chemical analysis.

A PHI 670 scanning Auger electron spectroscopy was used to analyze microchemistry at interfaces. To promote intergranular fracture, samples were cathodically charged with hydrogen in a solution of 0.1N sulphuric acid with the addition of As_2O_3 as a poison for recombination of hydrogen. Samples were fractured in situ at a pressure of 1×10^{-9} Torr by bending with a special fracture stage attached to the Auger vacuum chamber. Once the fracture was achieved, a secondary electron image of the fracture surface was obtained to identify the areas of the sample that failed intergranularly. Analyses in an area of about 1 μm^2 were performed on grain boundary facets, channeled fracture areas, and on ductile fractures for comparison. Auger spectra from 30 to 1000 eV were recorded from every point analyzed at a beam energy of 10 keV. Results of chemical composition are reported as atomic concentration calculated following Davis et al. [A.108]. Sensitivity factors of iron, chromium, copper and nickel have been obtained

by comparing calculated concentration at the ductile areas of as-received sample to the composition of the material.

A.2.3 Results

The microstructure of normalized and tempered HCM12A is shown in Fig A.36. The sample was etched using a solution of HNO_3 , H_2O and HCl with a ratio of 1:1:1. The microstructure shows martensite laths within the prior austenite boundaries. Although not shown in this micrograph, limited ferrite stringers were also observed.

Fig. A.36. Microstructure of normalized and tempered HCM12A

Microhardness is used to estimate changes in mechanical properties during irradiation. Hardness measurements were performed on samples irradiated with protons to varying doses. The hardness results for HCM12A are presented in Fig. A.37 along with those for alloy T91 for comparison. For both alloys, the hardness increases at low dose and appears to saturate near 5 dpa. Klueh and Alexander performed tensile tests on 9Cr-1MoVNb (corresponding to T91) and 12Cr-1MoVW (corresponding to HT9) in both HFIR (doses of 8-11 dpa and 37-72 dpa) and EBR-II (doses of ~16 dpa) [A.122]. The HFIR experiments showed that the yield strength increases occurred early in the radiation with only small changes occurring between 8-11 and 37-72 dpa. Yield strength changes were larger for the higher Cr concentration alloy and larger in the thermal spectrum reactor HFIR. As changes in hardness and yield strength are typically proportional for metals, the hardness data of this work is consistent with the work of Klueh with hardening increasing with bulk chromium concentration.

The microstructure of unirradiated HCM12A consists mainly of precipitates that are distributed both at prior austenite grain boundaries, lath boundaries, and in the matrix. The

dislocation density is not uniform from grain to grain. The diffraction pattern and EDS analysis of the precipitates revealed nearly all the precipitates in the unirradiated case are $M_{23}C_6$ with an FCC lattice parameter of 1.06 nm. Although compositions varied, precipitates are typically rich in Cr and W. Dislocation density varied dramatically, ranging from dislocation free areas to areas dense with a tangled and complex dislocation configuration. The general views of unirradiated microstructure and the detailed arrangement of dislocations are shown in Figure A.38 (a) and Figure A.39(a).

Fig. A.37. Hardness for HCM12A and T91 irradiated with protons at 400°C.

For the sample irradiated to 5 dpa with Ni-ions, there is no significant change in microstructure, as shown in Figures A.38(b) and A.39(b). Neither cavities nor dislocation loops were observed. The precipitates examined were still dominated by $M_{23}C_6$, but a few bulk vanadium-chromium-niobium precipitates were identified from EDS analysis, with a typical composition of approximately 50%V, 17%Cr, 17% Fe, 12%Nb. Figure A.40 shows various precipitates suspended on a film (and therefore independent of the matrix composition) formed during jet-polishing. Among the precipitates in Fig. A.40, those marked p04, p08 and p11 are V-Cr-Nb precipitates with a typical composition of approximately 52%V, 18%Cr, 18% Fe, 12%Nb and the rest are mostly $M_{23}C_6$ precipitates. The inserts in Figure A.40 show the EDS spectrum of $M_{23}C_6$ and V-Cr-Nb precipitates suspended on a film. In figure A.40, the size of the $M_{23}C_6$ and V-Cr-Nb precipitates appears similar. Typically, the $M_{23}C_6$ precipitates in 9-12 Cr steels are

coarser [A.123]. More detailed microscopy, with greater statistical basis, is required before making definitive conclusions on precipitate formation under irradiation. The overall dislocation density appears to increase with dose as shown in Figures A.38 and A.39. No quantitative measurement on dislocation density was attempted due to its non-uniform distribution and extremely high density in the dense dislocation areas.

The bulk microstructure of HCM12A irradiated to 50 dpa is similar to that at 5 dpa as demonstrated in Figure A.38 (c) and A.39(c). No voids were found at 50 dpa. However some dislocation loops were found in the dense dislocation areas. The microstructure at 50 dpa is still dominated by dense dislocation network and $M_{23}C_6$ precipitates. The major difference between the unirradiated and 50 dpa microstructure is the presence of fine precipitates in the matrix. These precipitates are V-Cr-Nb precipitates and, as the new microstructural feature not present in the unirradiated alloy, are the likely major source of hardening. As mentioned previously, the copper additions to this alloy may also lead to fine precipitates and affect the hardening, similar to the hardening that occurs in reactor pressure vessel steels. These fine precipitates are likely to be smaller than the TEM resolution and attempts to locate them were not attempted in this work.

Fig. A.38. Low magnification overview of microstructure for alloy HCM12A irradiated with Ni ions at 500°C to (a) unirradiated, (b) 5 dpa and (c) 50 dpa

Fig.A.39. Dislocation microstructure for alloy HCM12A irradiated with Ni ion at 500°C to (a) unirradiated, (b) 5 dpa and (c) 50 dpa

Fig. A.40. Precipitates in HCM12A irradiated with Ni ions at 500°C to 5 dpa. Those marked p04, p08 and p11 are V-Nb precipitates. The rest are $M_{23}C_6$ type precipitates.

The prior austenite grain boundary composition was measured using Auger electron spectroscopy. For the AES analysis, intergranular fracture was obtained under all conditions although the area that fractured intergranularly was low. The percentage of intergranular features exposed in the proton-irradiated samples is lower than that of the normalized and tempered material. Figure A.41 shows, as an example, secondary electron images of a fracture surface obtained from the normalized and tempered material. In general, the fracture surfaces showed ductile areas (Fig. A.41(b)) in the inner part of the sample away from the fracture initiation side, and intergranular areas (Fig. A.41(c)) close to the fracture initiation side. Closer to the fracture initiation side of the sample, areas of cleavage were also exposed during fracture of the proton irradiated samples.

Fig. A.41. SEM images of (a) overview, (b) ductile area and (c) intergranular area of the fracture surface of an as-received sample obtained in the Auger vacuum chamber.

Figure A.42 shows, as an example, Auger spectra of a proton irradiated sample obtained from a ductile area and from an intergranular facet. The intergranular facets are likely to correspond to prior austenite boundaries. In ductile areas, the main alloying elements, iron and chromium, and also copper, nickel and oxygen were identified. Spectra from areas of intergranular fracture show the same elements as the ductile areas plus the presence of silicon and phosphorus. The phosphorous was not detectable at all intergranular facets. In addition to the spectra from ductile and intergranular areas, spectra were analyzed from areas of cleavage as shown in Fig. A.42(c). One of the images of the cleavage area is shown as an inset of Fig. A.42(c). The elements present on the cleavage area are similar to the intergranular area but without the presence of phosphorus. Compared to intergranular areas, a higher oxygen signal was measured in the ductile and cleavage areas. The higher oxygen concentration may be caused by the larger surface area at the rough ductile area that promotes the adsorption of oxygen more readily than the smooth intergranular facets.

Fig. A.42. Auger spectra obtained from a sample with proton irradiated at a dose of 7 dpa: (a) ductile area, (b) intergranular facet and (c) cleavage area.

Quantitative analysis results of the elements of Cr, Fe, Ni and Cu are listed in Table A.13. Oxygen and carbon were not included in the quantitative analysis because they are subject to errors due to environmental contamination during long-time examination. The Ni concentration is likely overestimated although the Auger peak range of Ni1 for semi-quantitative analysis was selected carefully to minimize the influence of the partial overlap of the Auger peak of Cu2 on Ni1. Phosphorus was determined to be ~0.13 at.% and ~0.08 at.% enhanced at intergranular and cleavage areas, respectively. The cleavage areas may correspond to partial IG fracture and thus the phosphorous increase. The segregation of Cr, Fe, Ni and Cu at intergranular and cleavage areas compared to the ductile area is shown in Fig. A.43. In addition to the data from the 3dpa irradiation at 500°C, the data from a previous 3, 7 and 10 dpa irradiation at 400°C are included in Fig. A.43. It is clear that the segregation of Cr and Fe increases with irradiation dose and temperature. The irradiation effect on the segregation of Cu and Ni is complex. Since the function of Cu in alloy HCM12A is to substitute for Ni as an austenite forming element while minimizing δ -ferrite harmful to toughness, and since Cu and Ni have similar crystallographic properties, similar segregation behavior of Cu and Ni is expected. This is confirmed by the same segregation trend of Cu and Ni due to irradiation observed at intergranular areas. Different radiation-induced segregation trends of Cu and Ni observed at cleavage areas indicates cleavage occurs by a different mechanism than that seen in the intergranular area or is a mixture of IG and ductile areas.

Table A.13: Average atomic concentration calculated from Auger spectra

			Cr	Fe	Ni	Cu	P
As-received		D	11.7±0.7	85.7±0.8	0.5±0.1	0.9±0.1	0.03
		IG	17.6±2.1	79.2±2.2	0.6±0.2	1.1±0.2	0.04
3 dpa	400°C	D	11.9±0.9	85.2±1.8	0.6±0.1	1.0±0.2	0.03
		C	12.2±0.9	83.3±1.0	0.8±0.1	1.2±0.2	0.06
		IG	19.1±1.6	75.6±2.3	0.9±0.3	2.0±0.3	0.07
	500°C	D	11.9±1.0	86.4±2.2	0.4±0.1	0.9±0.3	0.03
		C	14.6±1.5	80.9±2.5	0.5±0.1	1.3±0.1	0.11
		IG	21.5±1.2	71.7±1.8	0.5±0.1	1.4±0.2	0.16
7 dpa (400°C)		D	11.8±1.4	85.3±1.5	0.6±0.1	1.0±0.2	0.03
		C	13.4±1.5	82.8±2.2	0.7±0.3	1.2±0.3	0.08
		IG	24.8±2.4	69.9±2.0	0.8±0.2	1.9±0.4	0.11
10 dpa (400°C)		D	11.9±0.9	85.3±0.9	0.5±0.1	1.0±0.2	0.03
		C	16.2±2.1	79.8±2.5	0.5±0.2	1.3±0.3	0.10
		IG	25.9±2.6	69.5±2.6	0.4±0.2	1.5±0.3	0.14

Note: Characters D, C and IG denote ductile, cleavage, and intergranular areas, respectively.

Uncertainty is the standard deviation of the measurements.

Auger peak overlaps, such as O on Cr and Cu on Ni, exist during the analysis of this material. Many efforts have been devoted to determining the effect of resolving the overlap between the 515 eV O peak and the 529 eV Cr peak [A.110-112] on the calculation of chromium concentration. A study by Damcott et. al. [A.113] indicated that the calculated Cr is not significantly affected if the measured O concentration is less than 25 at%. The oxygen peak was not considered in the overall composition calculation since the measured oxygen concentration is less than 15 at% during quantitative analysis. The calculated Ni concentrations listed in Table A.13 are likely overestimates caused by the contribution of the 849 eV Cu peak overlap with the 848 eV Ni peak. The low-energy portion of the Auger peak of silicon is affected by the Auger peaks of Fe, Cr, Ni and Cu with kinetic energies below 80 eV, which may influence the concentration difference of Si at areas of intergranular and cleavage

Fig. A.43. Irradiation effect on the segregation of HCM12A.

A.2.4 Discussion

Correlations are typically used to estimate yield strength change from hardness change. Rice and Stoller [A.107] developed a correlation for model ferritic alloys and two commercial steels for nano-indentation with loads between 0.05 and 1.0 g. Their correlation is provided in Eq. (1). They also determined the correlation between the same nano-hardness measurements and

hardness measured using a Vickers indenter with loads of 200g and 500g. The ratio between Vickers and nano-hardness was 0.937. For the microhardness measurements of HCM12A in this study, which used a load of 25 g, the yield strength increase associated with proton irradiation can be estimated roughly as 520 MPa.

$$\Delta\sigma_y(\text{MPa}) = 274\Delta H_N(\text{GPa}) \quad (1)$$

Busby et al. have recently developed a correlation between yield strength and hardness for ferritic steels [A.121]. The relation is shown in Eq. 2. Using the correlation from Busby, a change in yield strength of 550 MPa is calculated, within about 6% of the correlation in equation (1).

$$\Delta\sigma_y(\text{MPa}) = 3.06\Delta H_v\left(\frac{\text{kg}}{\text{mm}^2}\right) \quad (2)$$

The hardness change at 400°C was also measured in T91, a 9Cr ferritic-martensitic steel. The unirradiated hardness of the T91 is less than the HCM12A. Like the HCM12A, the hardness increase saturates near 5 dpa and the hardness increase in T91 is similar in magnitude to the hardness increase in HCM12A. Because both saturate near 5 dpa, the mechanical property change due to irradiation for either alloy will saturate early in life for any Generation IV concept. The increase in hardness is similar for the two alloys indicating the irradiation induced increase in yield strength is similar. Although there was some concern that the copper additions to HCM12A may lead to larger hardening than in earlier generations of 9-12 Cr ferritic-martensitic steels, these initial hardness results do not indicate this to be a problem. Verification with analysis of the neutron-irradiated samples will be presented in future work. The neutron irradiation will also determine if ductility saturates at the same dpa as the strength.

The presence of V-Cr-Nb precipitates is likely to be primarily responsible for the radiation hardening in alloy HCM12A. Very limited dislocation loops and voids were noted in the 50 dpa sample, so features typically associated with hardening of austenitic steels have not developed by 50 dpa in HCM12A. The microstructural development of the Ni-ion irradiated HCM12A was very similar to that of T91 irradiated at 500°C to 50 dpa [A.119]. This correlates well with the change in hardness that showed similar increases with radiation dose. Neither of these alloys appears to undergo unacceptable microstructural changes during irradiation at 500°C.

For austenitic stainless steels, chromium is depleted at the grain boundary during radiation. As discussed above, the TEM analysis showed Cr-rich grain boundary carbides in the unirradiated HCM12A. Chromium concentration was observed to further increase with irradiation in this study. The enrichment of chromium could be related to the formation of new chromium-rich precipitates, e.g., carbides and phosphides [A.114-A.117], or the growth of existing carbides, possibly enhanced by radiation. This is consistent with the review of Maziasz [A.118] that indicated that the irradiation-induced phases in martensitic/ferritic steels are all Cr-rich, in contrast to the Cr-poor phases induced in the austenitic steels.

Boundaries could also be enriched in chromium during irradiation as part of a radiation-induced segregation (RIS). In austenitic stainless steels, Cr always depletes during radiation. Models have been developed for predicting RIS in austenitic stainless steels. The most advanced models (known as modified inverse Kirkendall (MIK) models) take into account local composition when calculating diffusional energies [A.120]. Although these models have not been optimized for BCC steels, a model calculation using a base composition of Fe-10.5Cr-0.4Ni (corresponding to HCM12A) does predict Cr enrichment during radiation. Future work will use STEM-EDS to provide a better analysis of the local composition and precipitates in the vicinity of the grain boundaries. This should elucidate the Cr enrichment seen in the AES measurements of this study.

The enriched chromium at the grain boundaries has potential implication for Generation IV lead-cooled fast reactors as well as supercritical water-cooled reactors. Sensitization issues experienced in light water reactors due to carbide precipitation would also be possibilities in supercritical water or in lead-alloy coolants as chromium depletion could lead to corrosion or stress corrosion cracking susceptibility.

A.2.5 Conclusions

The ferritic-martensitic steel HCM12A was irradiated with 3.2 MeV protons at 400°C to a dose of 10 dpa and with 5 MeV nickel ions at 500°C to 50 dpa. The hardness of HCM12A increases with dose, saturating after approximately 5 dpa with an approximate 70% increase of hardness. Using hardness-yield strength correlations, this corresponds roughly to a 520-550 MPa yield strength increase. Dislocation loops and voids do not form in significant quantities so the increase in hardness appears to be attributable primarily to precipitate formation. Chromium is enriched at boundaries and iron is depleted in the unirradiated state. The higher chromium concentration at the boundaries is likely due to chromium carbides. Irradiation causes further increases in chromium concentration and decreases in iron concentration at the boundaries. This could be due to coarsening of existing carbide particles, nucleation of new carbide particles, or radiation-induced segregation of chromium to the boundary away from carbides. Further TEM studies should elucidate the mechanism for the changes in grain boundary concentration as measured using AES.

A.3 Radiation Response of a 9 Cr Oxide Dispersion Strengthened ODS to Heavy Ion Irradiation

A.3.1 Background

Advanced nuclear energy systems proposed under the Generation IV initiative are aimed at making revolutionary improvements in economics, safety and reliability, and sustainability. To achieve these advancements, Generation IV systems anticipate operating at much higher temperatures and in higher radiation fields than current light water reactors. Of the candidate alloy systems being considered, ferritic-martensitic alloys are expected to play an important role as cladding or structural components in Generation IV systems operating in the temperature range 350-700°C and to doses up to 200 dpa. Ferritic-martensitic steels are expected to be used as high dose components in sodium- and lead-cooled reactors, low-temperature components in gas-cooled reactors, and possibly components in supercritical water reactors.

Ferritic-martensitic steels offer better swelling resistance but may suffer from grain boundary and/or matrix creep and loss of strength at temperatures above ~600°C and unacceptably low toughness at lower temperatures [A.124]. However, the growing body of data on ferritic-martensitic steels, combined with specific, tailored microstructure modifications may be able to address the deficiencies at high temperature/dose. The martensitic 9Cr-ODS steel, oxide-dispersion-strengthened by using Y_2O_3 particles, is expected to have high creep strength for application at even higher temperature. However, the stability of the Y_2O_3 particles under irradiation to very high dose needs to be investigated for its potential use in the high temperature reactors. Heavy-ion irradiation provides a unique approach in this exploratory task to evaluate material tolerance to radiation up to very high doses.

A.3.2 Experiment

The composition of 9Cr-ODS is listed in Table C.9. Thin sheet samples with a size roughly at $1.5 \times 1.5 \text{ mm}^2$ and a thickness approximately 200 μm were prepared, with a final surface finish of 0.1 micron diamond paste polishing. The Ni ion irradiations were conducted at the Environmental and Molecular Science Laboratory at Pacific Northwest National Laboratory using 5 MeV Ni ions at 500°C, 600°C, and 700°C and 1×10^{-7} torr with a damage rate of 1.4×10^{-3} dpa/s. The samples were mounted on a radiation stage that allows temperature control through heating with electron beam and cooling with liquid nitrogen flow in the cooling channel. The ion beam was rastered over an irradiated area of $8 \times 8 \text{ mm}^2$ on the sample. Irradiation temperature was monitored using both a pyrometer and a thermocouple. The material was irradiated to doses of 150 dpa.

Table C.9 Composition for 9Cr-ODS (Fe balance)

Alloy	C	Mn	P	S	Si	Ni	Cr	Mo	Other
9Cr-ODS	0.14	0.01	<0.01	<0.005	0.01	0.02	9.19	<0.01	W_2.00, Ti_0.21, Al_<0.008, Y_2O_3 _0.33, O_0.06

TEM discs were punched using a disc punch to a diameter of 2.3 mm. The discs were then mechanically wet polished from the unirradiated side down to roughly 70 μm to minimize the magnetic interference with the electron beam in the microscope. A 5 MeV Ni ion has a maximum penetration depth approximately 1.5 μm into stainless steels. A thin layer of approximately 0.5 μm depth was removed from the irradiated side using a 5-second jet electro-polishing with a solution of 2% perchloric acid and 15% ethylene glycol in methanol at a polishing condition of 25V and -65°C. TEM discs were then jet-polished from the unirradiated side to perforation. The 2.3 mm disc sample was mounted to a 50 μm thick and 3-mm diameter Cu slot grid using epoxy to provide a 3 mm diameter TEM disc. Grain boundary microstructure was examined using backscattering electron imaging on a SEM. Microstructure characterization was carried out using a 200KV transmission electron microscope equipped with EDS for chemical analysis.

A.3.3 Results

Low magnification views of the 9Cr-ODS alloy in the unirradiated condition as well as in the Ni ion irradiated condition to 150 dpa at 500°C are shown in Figures A.44 (a) to (d). The unirradiated microstructure in alloy 9Cr-ODS contains a very high dislocation density, submicron size grains with many under bending due to the internal stress, precipitates (54%Cr+10%W), and fine oxide strengthening particles. In both the unirradiated and irradiated conditions, all the oxide particles were associated with Ti at an atomic ratio close to 1:1 with yttrium. The high Ti content detected at the oxide particles suggested that Y_2O_3 and TiO_2 are closely associated in this 9Cr-ODS. Both types of particles are used for ODS materials [A.125]. Therefore, the oxide particles described further in this summary are Y-Ti-O particles. These microstructural features underwent no significant change up to the doses of 150 dpa. No voids were found in 9Cr-ODS for Ni ion irradiation to 150 dpa, which is consistent with the work by Gelles on a 13Cr-ODS alloy (MA957) irradiated with neutrons in FFTF to 200 dpa at 420°C [A.126]. The results of oxide particle measurement are summarized in Table A.14.

Table A.14. Summary of Y-Ti-O oxide particle measurements for alloy 9Cr-ODS

Dose (dpa)	Mean size (nm)	Size stdev. $\pm$ (nm)	Density (10^{15} cm^{-3})	Particle counts	Mean vol. (nm^3)	Oxide vol. fraction (%)
0	11.7	5.0	3.4	505	1392	0.47
T=500 °C						
5	10.5	5.4	4.1	469	1301	0.54
50	10.1	4.8	4.7	295	984	0.46
150	9.3	4.6	5.5	423	820	0.45
T=600 °C						
5	7.3	3.8	12	1146	417	0.48
50	4.8	2.3	19	1009	122	0.23
T=700 °C						
5	6.9	3.6	6.7	445	358	0.24
50	4.9	2.3	7.5	887	118	0.09
150	4.9	2.6	16	601	147	0.23

A.3.4 Discussion

A.3.4.1 Microstructural stability at 500 °C

For an irradiation temperature of 500°C, there is no significant change in the microstructural overview as shown in the Figures A.44 (a) to (d). The details of the dislocation microstructural evolution are shown in Figures A.45 (a) to (d). The dislocations formed tangled networks with no clear sign of the presence of loops. There are small and high-density spot features shown in all 4 micrographs. The determination of the composition and structure of these small spot features was not successful due to the tiny size. One assumption is that these particles could be fine oxides. The variation of the dislocation configuration from grain to grain is greater than the changes due to irradiation. The lack of dislocation microstructural changes under irradiation to very high doses is clearly demonstrated in Figures A.45 (a) to (d), probably due to the large concentration of point defect sinks created by the dislocations and high-density oxide particles.

The oxide dispersions of Y-Ti-O play a key role for application to high temperature. The micrographs of the oxide particles for the unirradiated and the irradiated conditions at 500°C are shown in Figures A.46 (a) to (d). The oxide particles, mostly round in shape, varied in size from a few nanometers to several tens of nanometers. Size distributions for the 4 conditions are shown in Figures A.47 (a) to (d). The average size of oxide particles are 11.8 ± 0.5 nm, 11.0 ± 0.5 nm, 10.2 ± 0.4 nm and 9.1 ± 0.3 nm for the unirradiated, the irradiated to 5 dpa, 50 dpa and 150 dpa, respectively (uncertainty listed is the standard deviation of the mean). All the distributions have a positive skew caused by the distribution of larger size particles. The average volume of the oxide particles are 1618 nm^3 , 1805 nm^3 , 1117 nm^3 and 890 nm^3 for the unirradiated, the

irradiated to 5 dpa, 50 dpa and 150 dpa, respectively. The oxide particles show a decrease in size and an increase in density as dose increased up to 50 and 150 dpa.

Figures A.48 and A.49 plot the oxide size distributions versus normal and lognormal distributions. The size distributions are reasonably described by the lognormal distribution, even after irradiation.

Both the unirradiated and the irradiated microstructure in 9Cr-ODS consists of high-density dislocation segments with no clear sign of dislocation loops. It appeared the internal stress is very high for this alloy since most of the submicron-size crystals are bent, making it difficult to image the dislocation structure with a uniform contrast even for a small area as shown in Figures A.45 (a) to (d). The very high initial density of the dislocation structure may act as a strong sink for the radiation induced point defects, making it hard to form loops.

At an irradiation temperature of 500 °C, the minor change in the size of oxide particles, shown in Figure A.47, is not expected to change their role in maintaining the material strength. There were areas in the 9Cr-ODS where the Y_2O_3 particle distribution is not uniform. However, no voids were found in those areas free of Y-Ti-O particles, suggesting the suppression of void swelling in this alloy is mainly due to its ferritic microstructure, not the oxide particles. While the 9Cr-ODS alloy showed excellent resistance to radiation damage in the microstructure, several unique problems were found with this material. Alloy 9Cr-ODS appeared to have a stronger magnetic strength than alloy T91 (based on difficulties in performing an analysis in the transmission electron microscope). The irradiated sample also showed a much more severe oxidation than alloy T91 under a vacuum of 1×10^{-7} torr during the irradiation, forming a dark-brown layer on the sample surface. The severe oxidation may limit its application in a high temperature and corrosive environment.

Figure A.44. Microstructural overview of the alloy 9Cr-ODS irradiated with Ni ions at 500°C to various doses: (a) unirradiated, (b) 5 dpa, (c) 50 dpa and (d) 150 dpa. No significant changes between the unirradiated and the 150 dpa condition is noted in the overviews.

Figure A.45. Details of the dislocation arrangement in 9Cr-ODS irradiated with Ni ions at 500°C to various doses: (a) unirradiated, (b) 5 dpa, (c) 50 dpa and (d) 150 dpa. No voids were present in all the conditions. No significant changes can be identified between the unirradiated and the 150dpa conditions.

Figure A.46. The Y_2O_3 microstructural features in the 9Cr-ODS alloy irradiated with Ni ions at 500°C to various conditions: (a) unirradiated, (b) 5 dpa, (c) 50 dpa and (d) 150 dpa. The yttrium-oxide particles appeared an increase in density and decrease in size as dose increases.

Figure A.47. The size distribution of oxide particles in alloy 9Cr-ODS under the (a) unirradiated condition, and (b) irradiated with Ni ion at 500°C to 5 dpa, (c) 50 dpa and (d) 150 dpa. The particle size and volume decreased at high doses compared to the unirradiated case.

Figure A.48 Oxide distributions compared to a normal distribution

Figure A.49 Oxide distributions compared to a lognormal distribution

A.3.4.2 Microstructural Stability at 600 °C

Similar to the irradiation at 500 °C, the network dislocation shows no significant change by irradiation at 600°C up to 50 dpa and the dislocation loops are not identified, as shown in Figures A.50 and A.51. The pinning of dislocations by oxide particles appears to still be effective at this temperature. However, a change in the oxide particles is more evident in the samples irradiated at 600°C than at 500°C. The population of large oxide particles is reduced and the density of small oxide particles increased with dose, shown in Figure A.52. The size distributions of the Y-Ti-O particles in samples irradiated at 600°C in comparison to the unirradiated samples are shown in Figure A.53.

At 50 dpa and 600°C, the average oxide particle size decreased by 59% compared to only 14% at the same dose at 500°C. This leads to an average particle size of 4.8 nm at 600°C, half of the size at 500°C. The particle density at 600°C, 50 dpa is about 4 times the particle density at 500°C, 50 dpa. The enhanced irradiation effects on oxide particles at higher irradiation temperature may be attributed to shrinkage of large oxide particles and reformation of smaller particles. Since the densely populated fine oxide particles are more effective in pinning dislocations than the large particles for the same particle volume fraction, the observed changes in particle size distribution may not cause a severe degradation in mechanical strength at high temperature. The presence of voids cannot be confirmed.

Figure A.50. Microstructural overview of the alloy 9Cr-ODS irradiated with Ni ions at 600°C to various doses: (a) unirradiated, (b) 5 dpa and (c) 50 dpa. No significant change between the unirradiated and the 50 dpa condition is noted in the overviews.

Figure A.51. Network dislocation in the alloy 9Cr-ODS irradiated with Ni ions at 600°C to various doses: (a) unirradiated, (b) 5 dpa and (c) 50 dpa. No significant change between the unirradiated and the 50 dpa condition is noted in the overviews.

Figure A.52. Oxide particles in the alloy 9Cr-ODS irradiated with Ni ions at 600°C to various doses: (a) unirradiated, (b) 5 dpa and (c) 50 dpa. A decrease in size and an increase in density is observed between the unirradiated and the irradiated samples.

Figure A.53. The size distribution of oxide particles in alloy 9Cr-ODS under the (a) unirradiated condition, and (b) irradiated with Ni ion at 600°C to 5 dpa and (c) 50 dpa. The particle size decreased at high doses compared to the unirradiated case.

A.3.4.3 Microstructural Stability at 700 °C

At 700 °C irradiation, the dislocation density still remains high with little evidence of annealing effect, shown in Figures C54 and C55. Similar to irradiation at 600 °C, the oxide particle size significantly reduced comparing to irradiation at 500 °C. However, the particle size appears no change between 600°C and 700°C at doses of 5 and 50 dpa, although the oxide particle densities at 700°C is about half of that at 600°. The micrographs of oxide particle evolution as a function of dose at 700°C are shown in Figure C56. The comparison of particle size distributions is shown in Figure C57. The particle size and its distribution between 50 dpa and 150 dpa show no difference. The drop in particle density at 700°C may affect the effectiveness of the oxide particles to provide high temperature mechanical strength. The significant reduction in alloy mechanical strength is not expected since the particle density is still quite comparable to the density at 500°C.

Figure A.54. Microstructural overview of the alloy 9Cr-ODS irradiated with Ni ions at 700°C to various doses: (a) unirradiated, (b) 5 dpa, (c) 50 dpa and (d) 150 dpa. No significant change between the unirradiated and the 150 dpa condition is noted in the overviews.

Figure A.55. Network dislocation in the alloy 9Cr-ODS irradiated with Ni ions at 700°C to various doses: (a) unirradiated, (b) 5 dpa, (c) 50 dpa and (d) 150 dpa. No significant change between the unirradiated and the 150 dpa condition is noted in the overviews.

Figure A.56. Oxide particles in the alloy 9Cr-ODS irradiated with Ni ions at 700°C to various doses: (a) unirradiated, (b) 5 dpa, (c) 50 dpa and (d) 150 dpa. A decrease in size and an increase in density is observed between the unirradiated and the irradiated samples.

Figure A.57. The size distribution of oxide particles in alloy 9Cr-ODS under the (a) unirradiated condition, (b) irradiated with Ni ion at 700°C to 5 dpa, (c) 50 dpa and (d) 150 dpa. The particle size decreased at high doses compared to the unirradiated case

A.3.4.4 Comparison of Oxide Stability at Varying Irradiation Temperatures

The size, density, mean particle volume and particle volume fraction of the Y-Ti-O oxide particles as a function of irradiation temperature and dose are shown in Figures A.58 and A.59. The size change as a function of dose appears fast at doses up to 5 dpa and then stabilizes at higher doses. The particle density is the highest in the samples irradiated at 600°C. The large fluctuation in particle volume fraction reflects the large uncertainty associated with this parameter since it is the product of particle density and mean particle volume. There is no clear evidence of loops and voids in the Ni ion irradiated 9Cr-ODS under irradiation conditions investigated.

The quantitative characterization using TEM for small oxide particles carries large uncertainty due to limitation on resolution power, foil thickness determination, the uniformity of particle distribution, the total sample volume examined, the difficulty in distinguishing the other small features at comparable sizes with oxide particles, and the unique problem due to magnetic field distortion to the electron beam from ferretic-martensitic alloy. The high internal stress and local bending in 9Cr-ODS and the weak image contrast from small Y-Ti-O particles impose great technical challenges to take decent TEM images for quantitative analysis. All these can ultimately affect the measurement results presented in this summary.

Using dispersed barrier hardening theory, the contribution of the oxide precipitates to the yield strength is determined by the mean spacing between particle faces. Specifically, the yield stress associated with dislocation bowing is inversely proportional to the mean spacing between particle faces [A.127],

$$\sigma_B \cong \frac{Gb}{(L - 2r)}, \text{ eq (1)}$$

where

G is the shear modulus

b is the Burger's vector

L is the average distance between particle centers

r is the average particle radius.

The interparticle spacing depends on the particle density N and the average particle diameter d. Specifically

$$L \cong \frac{1}{\sqrt{Nd}}, \quad \text{eq. (2)}$$

where N is the particle number density. The yield stress associated with bowing is then

$$\sigma_B \cong Gb \frac{1}{\left(\frac{1}{\sqrt{2Nr}} - 2r \right)} \quad \text{eq. (3)}$$

Figure A.58 plots the relative strength calculated using equation 3 and the data from Table A.14. The radiation-induced formation of a larger density of smaller oxide particles should lead to an increased strength with increased radiation dose. Ukai et al. obtained a similar result in a more detailed analysis [A.128].

Figure A.58. Oxide particle (a) size and (b) density for alloy 9Cr-ODS irradiated with Ni ions at 500, 600 and 700 °C to various doses.

Figure A.59. Oxide particle (a) the average particle volume and (b) the volume fraction of the particles in alloy 9Cr-ODS irradiated with Ni ions at 500, 600 and 700 °C to various doses.

Figure A.58. Relative strength calculated from the measured oxide density and size.

A.3.5 Conclusions

An examination of the microstructural stability of a 9 Cr ODS alloy irradiated with 5 MeV Ni-ions at 500°C, 600°C, and 700°C to doses of 150 dpa showed that irradiation causes the fine oxide particle distributions to shift toward a higher density of smaller particles with little associated change in the dislocation microstructure, and no void formation. The shift towards a finer oxide particle size distribution occurs more rapidly at higher irradiation temperatures. Simple calculations based on the oxide size and density indicates that the microstructural changes are likely to improve the strength of the alloy during radiation.

B. Evaluation of Austenitic Steels

Austenitic stainless steels are widely used in current light water reactors and are expected to be used in many Generation IV concepts. These steels are also expected to be used as vessel and support components in sodium-cooled, lead-cooled, and supercritical-water-cooled reactors, and as high-temperature components in gas-cooled reactors. These steels offer better high temperature strength and corrosion resistance as compared to F-M steels but suffer from stress corrosion cracking and void swelling. The evaluations of austenitic stainless steels in this report are described in three major sections:

1. The Effect of Oversized Element Addition on Radiation Stability
2. Grain Boundary Engineering of Alloy 800H

B.1 Oversize Element Effects on Irradiated Microstructures & IASCC

This task is focused on the development of damage-resistant alloys using oversized solute additions to reduce radiation damage. Selected oversized solutes such as hafnium (Hf) and zirconium (Zr) have been shown to restrict the evolution of deleterious microstructural features in austenitic stainless steels. Research has improved mechanistic understanding of interactions between these solutes and radiation-induced defects. Key proton and Ni-ion irradiations have been completed on specially tailored alloys and examinations performed on fast-reactor-irradiated (FFTF and Bor-60) stainless steels with single element additions. Comparisons are made to LWR-irradiated materials in order to make important assessments of dose rate, spectrum and temperature effects. Modeling studies were performed to elucidate mechanisms of radiation-induced microstructure and microchemistry evolution in reactor structural materials.

B.1.1 Background

Material degradation is a primary limitation for the safe and economical operation of commercial nuclear power reactors. Traditional approaches for alloy development have emphasized minor modifications in alloys (predominantly austenitic stainless steels) that were developed for use in non-irradiation environments. As problems were discovered during service, alloy characteristics or service conditions were adjusted to provide modest improvements in performance and hopefully achieve adequate component lifetimes. However, it is now clearly recognized that such minor traditional alterations are not sufficient to mitigate radiation-induced property degradation (loss in ductility and toughness, void swelling and embrittlement) and environmental cracking referred to as irradiation-assisted stress corrosion cracking (IASCC). Therefore, unconventional metallurgical approaches and alloys outside standard stainless steels

must be adopted to optimize performance in the radiation and corrosive environments of next generation nuclear reactors.

Radiation-induced degradation is driven by the displacement of atoms from their lattice sites and the subsequent creation of interstitial and vacancy defects as shown in Figure B1. Defect recombination, migration and their annihilation at sinks promotes a wide variety of potentially detrimental material changes including dislocation loop formation that leads to extensive hardening and limited uniform ductility, segregation of alloying and impurity elements to grain boundaries and other sinks, and void swelling. These changes are inevitable in standard stainless steels during LWR irradiation and result in an increasing susceptibility to failure with core component exposure. Displacement of atoms from irradiation cannot be avoided; they are the result of fundamental Newtonian mechanics. The path for aggregation of defects into detrimental microstructures can be altered, however. The processes of migration and aggregation of displacement defects are illustrated in Figure B2. Atoms of large size or mass misfit and fine-scale precipitate distributions interfere with the processes of recombination, migration and aggregation.

Figure B1. Schematic showing the influence of a large size or mass solute on the damage process. The primary knock-on atom can be created with ions, protons or neutrons. Minor additions of oversized solute are explored. Large elements in solution perturb the cascade production of defects and subsequent irradiation damage.

Figure B2. The fundamental products of displacement damage are interstitials (I) and vacancies (V). These point defects migrate and collect in components of radiation damage. Interstitials collect preferentially in interstitial loops and the remaining supersaturation of vacancies collects in voids. Solute atoms of large size or mass misfit can disturb the migration and aggregation of these point defects. Damage is induced using ions, protons or neutrons in this research and characterized by transmission electron microscopy.

Displacement events are created by ion, proton or neutron particles. Heavy ions and protons have the advantage of producing damage at high rates and therefore are commonly used for fundamental studies of damage mechanisms. Neutrons have the advantage of producing damage in bulk materials and therefore can be used for studies of bulk properties that are relevant to assessment of structural integrity. In this research, heavy-ion irradiation is used first as a screening tool to assess damage microstructures in candidate alloys to high doses. Protons are used for similar microstructural evaluations at lower doses and for studies of mechanical behavior and stress corrosion cracking. Finally, neutron-irradiated materials are investigated from industry collaborative research programs enabling access to both LWR- and fast-reactor-irradiated stainless steels. Fast-reactor examples were from the fast-flux test facility (FFTF) and from the Bor-60 reactor in Dimitrovgrad, Russia. The interdependence of damage rate, temperature and particle types employed in this project are shown in Figure B3. Damage from different particles can be related by using a higher temperature for higher-rate processes.

Figure B3. Increasing the rate of damage requires using a higher temperature to obtain equivalent damage microstructures. The lower temperature range is limited by mutual recombination and the upper temperature range is limited by the energy for vacancy formation. Equivalent ranges for neutrons, protons and ions are shown along with specific irradiation temperature and flux regions examined in this project.

Figure B4. Irradiation Dose Effects on Measured Tensile Yield Strength for Several 300-Series Stainless Steels reported in the literature near 288°C.

The development of radiation damage microstructures has two primary effects on components: (1) swelling and (2) mechanical behavior. Swelling is detrimental because the component dimensions change during service that affect stresses and core component dimensional tolerances. A primary concern in the present research is the affect on mechanical behavior and IGSCC. The effect of displacement damage on interstitial loop development, and on the increase in yield strength, for LWR-irradiated components has been documented. The measured increase in tensile yield strength is shown in Figure B4. A four-fold increase in yield strength occurs over the first few dpa of irradiation.

The critical links between damage processes, materials characterization and property measurements are highlighted in Figure B5. Although the primary components of irradiation damage (vacancies and interstitials) are simple, their aggregation into the microstructure and influence on deformation, void swelling and fracture are complex processes requiring a complementary mix of experiments being conducted on this NERI program.