

Examination of a Ferritic-Martensitic Steel following Irradiation and High Temperature Water Corrosion

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ABSTRACT

This paper focuses on the characterization of an advanced steel which has been developed for use as a structural material within future nuclear fusion reactors, including in irradiated water coolant-facing locations. In the paper an experimental plan is described which would allow both the corrosion and stress corrosion cracking susceptibility of irradiated Eurofer-97 to be studied. Also included are early results from characterization of self-ion irradiated (using Fe ions) Eurofer-97 following high temperature corrosion experiments using electron microscopy techniques. Field emission gun scanning electron microscopy (FEG SEM) images of the surfaces of unirradiated Eurofer-97 are compared to conventional unirradiated stainless steel types following a high temperature corrosion experiment. In a different, longer, high temperature corrosion experiment using ion-irradiated Eurofer-97, a focused ion beam scanning

electron microscope (FIB SEM) was used to prepare lamella for observation by high magnification transmission electron microscopy (TEM) and elemental analysis.

Key words: water coolant, ion irradiation, fusion, nuclear, microstructure, stress corrosion cracking, scanning electron microscopy, transmission electron microscopy

INTRODUCTION

Nuclear energy currently contributes approximately 10 % of the worldwide energy mix.¹ Nuclear energy generation is a form of low-carbon electricity, typically run as base-load, which alongside renewables can help nations toward climate change goals. Nuclear fission thermal reactors make up the majority of the reactors operating today. Nuclear fusion on the other hand is a promising alternative which produces less radioactive waste and does not have a reliance on the finite source of uranium fuel. Eurofer-97, a reduced activation ferritic-martensitic (RAFM) steel, will be used as a structural material for fusion reactors. The earliest literature reference to RAFM steels originated from 1994 by Abe et al.² One option for the European demonstration fusion reactor (DEMO) is to use a water-cooled lead-lithium (PbLi) breeder blanket (WCLL BB) design for heat extraction. Breeder blankets will be used to generate a source of tritium, for the fusion reaction with deuterium. Such a BB design will expose Eurofer-97 to high temperature water on the inside of cooling channels, and liquid PbLi on the outside.³ Several authors have already published details on the corrosion of Eurofer-97 in contact with the PbLi liquid metal eutectic,⁴⁻⁷ though comparably little published literature is available for Eurofer-97 in contact with high temperature water. Although limited work has been published on the corrosion of Eurofer-97 in water, a small body of work has been conducted at lower temperatures (60 °C) by Martin et al.⁸ to consider the fusion-specific impact of a magnetic field. These researchers found indications that the presence of a magnetic field could affect corrosion in aggressive solution chemistries, which is notable as toroidal-type fusion reactors control the hot plasma by means of magnetic confinement. Other researchers have published details on the WCLL BB water chemistry, temperature and pressure working specification, which leverages fission operating experience (pressurized water reactor (PWR) water temperatures (295 °C inlet to 328 °C outlet) and 15.5 MPa pressure).³ Along with the current lack of corrosion experiments being reported in the open literature for Eurofer-97 in high temperature water, there is also a corresponding lack of stress corrosion cracking (SCC) experiments for the alloy detailed in the open literature. An exception to this is the work by Dyck and Bosch⁹ who studied neutron irradiated Eurofer-97 in high-temperature water using slow strain rate testing (SSRT). In their work they found no instances of SCC when the water chemistry was well controlled.

Eurofer-97 will be used in the form of channels within the WCLL BB, which will contain a number of geometrical convolutions. Although the thermal design of the structure has been optimised, such features will inevitably experience elevated stresses within the material, and, in the presence of a corrosive electrolyte (high-temperature water), introduce the risk of SCC at these locations. Other residual stresses could also be present from manufacturing, e.g., welds, joining or machining processes, and therefore SCC experiments need to be conducted to evaluate susceptibility to this phenomenon. Eurofer-97 will be subjected to neutron irradiation during its service life. Irradiation of materials by neutrons leads to two broad effects, microstructural changes and transmutation of hydrogen and helium. Microstructural changes include, formation of point defects (vacancies, interstitials), precipitates, line defects (dislocation loops), and voids. These microstructural changes can then cause a reduction in bulk mechanical properties, which could include stress relaxation, swelling, or embrittlement. For some materials, such as 20Cr-25Ni-Nb stainless steel, used as fuel cladding within advanced gas-cooled (AGR) fission reactors, these irradiation-induced changes can lead to a change in grain boundary microchemistry. This occurs through the inverse Kirkendall effect (radiation induced segregation mechanism), effectively sensitising the steel, and thus the susceptibility to intergranular corrosion (IGC) and intergranular SCC (IGSCC) during aqueous storage.¹⁰⁻¹³ Transmutation of nickel can lead to the formation of helium, which can aggregate within the microstructure to form helium bubbles due to the low solubility within the matrix, which can then cause embrittlement at elevated temperature. Finally, irradiation by neutrons can lead to the formation of other radioisotopes, causing activation of the material which can cause high dose rates

to workers, which impacts future decommissioning of the reactor. Eurofer-97 is designed to limit the effects of neutron activation, through optimisation of the alloy composition.

In this paper an experimental procedure to investigate SCC on Eurofer-97 is outlined, and some early results are given. It is proposed that the viability of micro-mechanical experiments are explored to investigate susceptibility of Eurofer-97 to SCC. In this type of experiment 1-10 μm size specimens will be milled into the specimen using Ga^+ ions in a focussed ion beam (FIB) instrument. Micro-mechanical experiments using these micro-sized features are then conducted using a micromanipulator or nano indenter. Examples of this approach have been more prevalent over the past decade, owing to advances in focussed ion beam scanning electron microscope (FIB-SEM) apparatus, with micropillars,¹⁴ micro-cantilevers,¹⁵ and even micro dog-bone tensile specimens.¹⁶ By performing experiments at the micro-scale there is the potential to not only perform far greater numbers of experiments with a fixed volume of material, but also perform site-specific analyses. For example, single grain boundaries or precipitates can be studied, as opposed to conventional mechanical experiments which will sample many grains. The fact that these types of measurement can be performed on such a small volume of material is an advantage when studying irradiated materials. Neutron irradiation is often cost prohibitive and may not follow radiological safety principles⁽¹⁾ which would seek to mitigate risk at early developmental stages. Whilst the effects of this type of radiation are not the same, by performing proton or ion beam irradiation, the residual radioactivity from the specimen will be far lower, making experiments more practicable. Of course, later in development neutron irradiation is likely to be required for materials qualification / accreditation as this is the type of incident irradiation which will be present during service lifetime of the component. Micro-mechanical experiments are compatible with specimens having undergone either of these types of irradiation, i.e., size-reduced neutron irradiated specimens, and proton or ion irradiated specimens which have only a small zone of irradiation damage into the depth of the material.

EXPERIMENTAL PROCEDURE

Eurofer-97, a 9% Cr-W-V-Ta steel, was obtained from the United Kingdom Atomic Energy Authority (UKAEA)⁽²⁾ in the form of a block approximately 50 x 50 x 5 mm in size. The Eurofer-97 alloy specification can be found in Table 1. This was sectioned using a linear precision saw into sizes suitable for corrosion experiment ($\sim 4 \times 3 \times 1$ mm). Specimen faces and edges were ground to a surface finish of P1200 by grinding wheel using SiC paper and water lubricant. Two specimens were sent to Argonne National Laboratory⁽³⁾ for ion irradiation. One of the specimens received ion irradiation, whereas the other was masked during irradiation, which meant that the control specimen experienced the same heating conditions but was not irradiated. Self-ion irradiation using Fe ions was conducted isothermally at 340 °C (613.15 K) under vacuum at 89.73 MeV ion energy, with a peak fluence of $0.69 \times 10^{17} \text{ cm}^{-2}$ at the beam center. The current used was 173 p-nA (particle nano ampere) for a period of 4.5 h. Calculations with the SRIM (stopping range of ions in matter) software package¹⁷ estimated that the Bragg peak was located at a 7 μm depth.

Table 1: Eurofer-97 specification, square brackets denote target values¹⁸

Element	Specification, wt. %	Element	Specification, wt. %
Fe	Balance	W	1.0–1.2 [1.1]
Cr	8.5–9.5 [9.0]	Ta	0.06–0.09
C	0.09–0.12 [0.11]	Ti	<0.01

(1) See “as low as reasonably practicable”, ALARP for the UK, or “as low as reasonably achievable”, ALARA for the USA.

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Mn	0.20–0.60 [0.40]	Nb	<0.001
P	<0.005	Mo	<0.005
S	<0.005	Ni	<0.005
V	0.15–0.25	Cu	<0.005
B	<0.001	Al	<0.01
N	0.015–0.045 [0.030]	Si	<0.05
O	<0.01	Co	<0.005

Following the irradiation, the specimens were further size reduced to allow observation of the specimens before, and after a corrosion experiment. The high-temperature water corrosion experiment was performed using a bespoke once-through hot water loop at the University of Bristol, UK.⁽⁴⁾ Specimens were exposed to high purity water at 300 °C for a period of either 100 or 250 h. In the preliminary 100 h experiment, a 10% hydrogen in nitrogen gas mix was used in the autoclave head space to pressurize the system, and argon gas was used to sparge the fill and feed water. In the preliminary 100 h experiment multiple steels were exposed (Eurofer-97, and austenitic stainless steels: S31600 and thermally sensitized S30400). None of the materials used in the preliminary experiment were irradiated. Thermal sensitization of the S30400 was undertaken by heat treatment (60 h at 600 °C). Imaging of the preliminary 100 h post-corrosion surfaces was undertaken by FEG-SEM using secondary electron and in lens detectors. In the 250 h experiment, argon gas was used to pressurize the system (i.e., no hydrogen gas), and this experiment relates only to the TEM specimens.

A FIB-SEM instrument was used for transmission electron microscope (TEM) lamella preparation and imaging using the instrument scanning transmission electron microscopy (STEM) detector. Following the corrosion experiment the specimen was mounted on its side so that the lamella could be extracted in cross section. This is shown schematically in Figure 1. A rectangular ~12 x 2 x 3 µm (width x length x thickness) layer of Pt was deposited on the surface, close to the edge of the specimen, such that material within the Bragg peak could be extracted. Large trenches were milled around the Pt rectangle using an ion beam current of 21 nA by standard cross section cut. This current was then lowered to 9.3 nA, and cleaning cross sections used on the pillar and sides of the trench prior to extraction. Once extracted, the lamella was attached to a Cu grid holder by deposition of Pt at each side of the lamella, and then successively thinned to electron transparency using 0.92, 0.46 and finally 0.28 nA ion beam current using cleaning cross sections at varying angles (50° and 54°). The STEM detector within the FIB-SEM allowed imaging using the following modes: bright field (BF), annular dark field (ADF) and high-angle annular dark field (HAADF). TEM was performed using an instrument with STEM, BF, ADF, HAADF, energy dispersive X-ray spectroscopy (EDS), and selected area electron diffraction (SAED) capabilities.

It is proposed that a micropillar array be milled using a FIB-SEM on both the control and ion-irradiated Eurofer-97 specimens. The array would include pillars present in the area of greatest irradiation damage (Bragg peak). These micropillars would then be compression tested before and after the corrosion experiment using a nano indenter. This would allow the compressive strength to be compared for the following scenarios:

- unirradiated;
- unirradiated following high temperature corrosion;
- irradiated (but not at Bragg peak);
- irradiated (but not at Bragg peak) following high temperature corrosion;
- peak irradiation zone; and
- peak irradiation zone following high temperature corrosion.

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The limitations of the micropillar compression testing are that there is no simultaneous corrosion and application of strain, therefore true SCC experiments are not possible. In addition to this therefore, a possible secondary option would be to use micro-cantilevers. As shown by Holmes et al.¹⁹, and later disseminated by Clark et al.¹⁵ dual hexagonal cross section micro-cantilevers can be milled using a FIB-SEM and then self-strained in place by use of a micro-manipulator needle. This has the benefit of straining the cantilever elastically whilst the specimen is subject to high temperature water corrosion. A degree of further experimental development is required to ascertain the optimal length scale with high-temperature water SCC experiments as the past cantilever iterations were found to have been fused together by corrosion product.

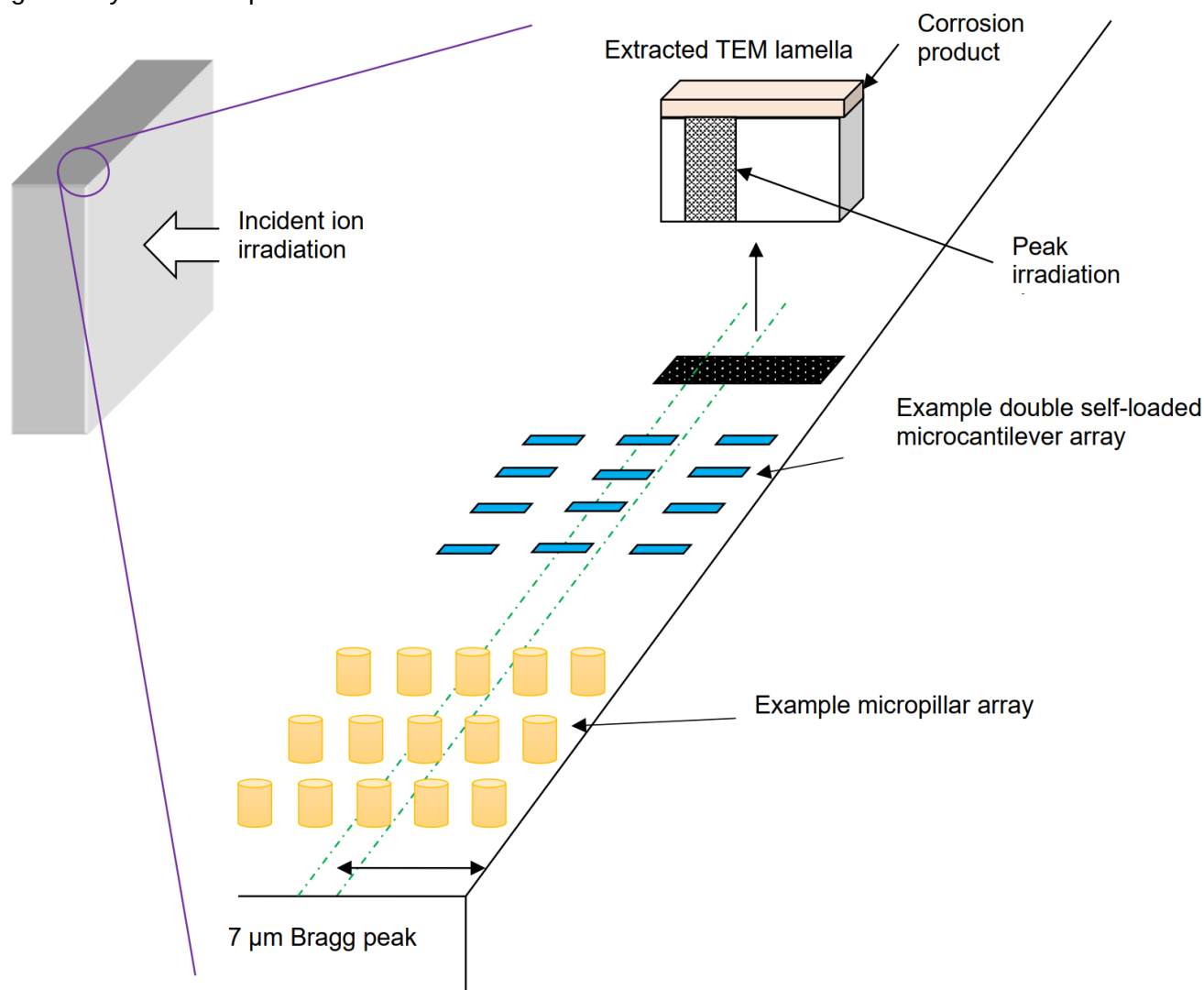


Figure 1: Schematic showing how both TEM lamella were extracted, and proposed methods for micropillar array and self-loaded cantilever array (not to scale)

RESULTS AND DISCUSSION

Preliminary Experiment (100 h Exposure)

In the short preliminary experiment, three different materials were exposed to high temperature water: Eurofer-97, S31600 and thermally sensitized S30400 for a period of 100 h. Following the high temperature corrosion experiment, the materials were imaged by use of SEM. The results of this are given in Figure 2. The images showed the presence of crystalline structures attributed to magnetite, which