SMALL SCALE MECHANICAL TESTING ON ION BEAM IRRADIATED 304SS

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ABSTRACT

Ion beam irradiation and small-scale mechanical testing can be a powerful combination for assessing the degradation of mechanical properties as a surrogate for the testing of reactor-irradiated bulk materials. In this work, 304SS irradiated with 2 MeV protons are used to assess mechanical property changes from room temperature to reactor operation temperature. Mechanical properties can be derived from small-scale mechanical test data and directly compared to macroscopic values. The irradiated material shows significantly stronger tendency for slip step formation than the unirradiated material at all test temperatures, and its yield stress decreases more quickly with temperature than the unirradiated material. Extending these techniques beyond basic investigations of model materials to reactor-relevant materials has several benefits. In principle (although not within the scope of this paper), because the measurements can be site specific, the impact of microstructural/microchemical changes in the grain interior can be investigated separately from those that occur at the grain boundary. For ion-irradiated materials, measurements can be conducted entirely within the thin damage layer, unaffected by the non-irradiated substrate; and parameters associated with plastic deformation can be obtained, in addition to hardness. For neutron-irradiated materials, the small amount of material translates into greater ease of material sampling and examination, with significantly reduced concern about dose.

Keywords: Stainless steel, radiation damage, small scale mechanical testing, nanoindentation, microcompression testing.

1. INTRODUCTION

Light water reactors produces 11% of the world’s electricity [1] and is an important electricity provider. However, most LWR’s are approaching the end of their operating license and because of barriers in the deployment of new reactors, among them the large initial capital costs of installation, utilities are interested in extending the operating life of current reactors. Therefore, age-related degradation is becoming an increasingly important. One of the main issues is irradiation assisted stress corrosion cracking (IASCC) of stainless steel reactor components. The aggressive environment of the reactor fostered by elevated temperature, neutron irradiation, radiolysis, in conjunction with imposed stresses and radiation damage and microstructural changes in the material, all contribute to IASCC susceptibility [2]. Although radiation-induced changes in mechanical properties and in microstructure and microchemistry are important and inter-related, a clear understanding of their contributions to IASCC susceptibility remains lacking [3]. Investigations using neutron-irradiated stainless steels, such as materials retrieved
from operating reactors, are difficult, expensive, and time-consuming because of the radioactivity; consequently ion-beams, at energies sufficiently low to avoid activation\(^1\), have been deployed to provide surrogate irradiation to study the effects of radiation damage in materials. However, the lower energies limit the penetration depth of the ions to tens of micrometers or less. At this length scale, although transmission electron microscopy (TEM) and atom probe tomography (APT) can characterize the radiation damage and microstructural changes, mechanical properties are not easily accessible and are generally limited to hardness measurements. Heavier ions (e.g. Ni\(^{2+}\), Fe\(^{2+}\)) are increasingly used in irradiations to achieve high dose rates, but they have shallower penetration depths, so the limitations on mechanical property measurements become even more acute. Small-scale mechanical testing can address this issue.

Micro compression and micro tensile techniques have been developed and have been, to-date, applied primarily to basic science investigations of model systems; but they are now sufficiently robust and flexible for engineering application. These techniques have well-defined geometry and sample volume that are subjected to uniaxial stress; their data is more easily interpreted to provide information about the plastic region of the stress-strain curve. Some of the advantages are described below.

- For ion-irradiated materials, dose vs. depth is not constant through the irradiation depth, as illustrated by Figure 1, in which the ion “stopping peak” is clearly evident, and the non-irradiated substrate lies deeper beyond it. Different parts of the ion-beam irradiation damage profile curve can be sampled separately to assess whether mechanical properties of the stopping peak are different than those of the “plateau” portion of the curve.

- “Site selection” offers important flexibility: grain interiors and grain boundaries can be investigated independently; or grains of different orientations; or the weld metal and heat affected zone (and base metal) of a weldment.

- For neutron-irradiated materials, because of the small volumes involved, small-scale mechanical testing allows the investigation of radioactive materials in facilities that would not otherwise be able to handle such materials, creating broader opportunities for research collaboration and contribution.

- Small volume mechanical characterization enables the assessment of mechanical properties over a range of temperature without requiring multiple macroscopic samples. Trends can be more easily ascertained to facilitate extrapolation.

This paper discusses small-scale mechanical testing on proton-irradiated 304SS and evaluates the mechanical properties of both the “plateau region” and the stopping peak, as well as their temperature dependence from room temperature to 300°C.

### 2. EXPERIMENTAL

Commercial available 304 SS was prepared with standard metallographic methods and electropolished prior to irradiation. The ion beam irradiation of the samples was conducted using 2 MeV protons in a

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\(^1\) Proton irradiation at energies below 2 MeV avoids excessive activation of steels and is therefore preferred. Higher-energy protons do cause the formation of Co-56 and Co-57; for example 6 MeV proton irradiation of 12\%Cr steel leads to significant activation [4, 5]. Heavier ions (e.g. Ni\(^{2+}\), Fe\(^{2+}\)) can be used at higher energies without activating the sample (but have shallower penetration depths); for example, 70 MeV Fe\(^{2+}\) irradiation of ferritic steels (at the CAMS facility at Lawrence Livermore National Laboratory) do not activate the sample.
Tandetron accelerator at the Michigan Ion Beam Laboratory (MIBL). The alloy was irradiated to 10 dpa at 360°C with a dose rate of ~8 x10⁻⁶ dpa/s based on SRIM calculation [6] (full cascade with a displacement energy of 40 eV). The sample temperature was monitored using a two-dimensional thermal imager and the variation was kept within ±10 °C during the course of the irradiation. These irradiation conditions have been previously reported in [7] to closely emulate the microstructure, hardening, and susceptibility to IASCC induced in stainless steels by LWR neutron irradiation. A detailed description of the proton irradiation procedure has been published elsewhere [8]. SRIM calculations provide the dose profile in Figure 1a, with a proton penetration depth of ~20 μm.

To obtain a smooth surface and sharp edge for measurements, each sample was mounted directly next to a thin piece of tool steel and polished in cross section with respect to the irradiated surface. The samples were wet-polished with 300-4000 grit SiC paper, followed by 0.3 μm and 0.1 μm alumina polishing solutions, and finally by 0.05 μm colloidal silica polishing solution [9].

A FEI Quanta 3D FEG dual beam instrument, which consists of a focused Gallium-69⁺ ion beam (FIB) and a SEM, was used to manufacture micro compression test samples in the irradiated and unirradiated regions of the specimen. The process of manufacturing the pillars followed a similar procedure as described in [10]. Figure 1b shows a schematic of the test configuration. SEM images of the pillars can be found in Figures 6 and 7. Although ion beam milling causes some surface damage on the pillars, the damaged layer was calculated by SRIM to be <10 nm for a 30 keV Ga-ion beam impinging on 304SS at a glancing angle. The damaged layer is thin compared to the total volume of the pillar, so FIB damage should not affect the test results. Electron backscattered diffraction (EBSD) was used to map the grains close to the edge in order to identify single-grain test regions so that irradiated and unirradiated pillars can be manufactured within the same grain, which makes critical resolved shear stress calculations (Schmid’s law) simpler, and tests better comparable.

Cross sectional nanoindentation measurements were performed using the Micro Materials NanoTest™ indenter at the University of California, Berkeley Nuclear Materials Laboratory. The machine is contained in an environmental chamber that can be purged with high purity Ar or Ar-H₂ mixtures to reduce the oxygen level below 2% for high temperature tests, to minimize oxidation of the samples. The limit of 2% is confirmed using a commercial handheld oxygen meter. The authors are evaluating the adoption of more accurate oxygen measurement methods. Indentations were performed at room temperature (25°C), 50 °C, 100 °C, 200 °C, and 300 °C in an argon atmosphere (oxygen content < 2% at test temperatures above 50°C) with a cubic boron nitride (cBN) Berkovich indenter. Indentations were performed in both the irradiated and non-irradiated regions. In order to minimize the interaction between neighboring indents, the distance between indents was set at 5 μm.

Values for the hardness (H) and Young’s modulus (E) of the steel were obtained with depth-controlled nanoindentations performed to 300 nm depth with a loading rate of 1 mNs⁻¹, unloading rate of 2 mNs⁻¹, and a dwell segment of 5 s. Arrays of a minimum of 50 indents per temperature were performed, at a slight angle to the edge to increase spatial resolution. The results are summarized in Figure 2. Thermal drift corrections were performed post-indentation at 10% of the maximum peak load (60-70 seconds). The last 60% of the recorded drift data was used for the thermal drift correction, which was below 0.3 nm/s for all measurements. The evaluation of hardness and the reduced modulus, Eᵣ, which is related to the elastic modulus, was performed based on the load-displacement curves according to the Oliver-Pharr method [12]. Distances between indent locations and the edge of the sample were later measured in an SEM.

2 Diamond (carbon) indenters are not ideal for elevated temperature testing because they react with steel at temperatures above 400°C [11]. Using one indenter material across the widest accessible temperature range is preferred.
The size effect measurements were performed using a Hysitron Triboindenter because at low loads this device has better resolution and therefore can cover a wider range of indentation depths, down to 50 nm. The procedure for conducting these tests is similar to that stated above for the Micro Materials NanoTest™ indenter.

A flat punch 10 μm diameter diamond indenter was used to conduct the micro compression tests at high temperatures using the Micro Materials NanoTest™ indenter. The major challenge of these measurements is to achieve proper alignment between the indenter tip and the axis of the micro pillars, since they were conducted ex-situ (i.e. not in the SEM), and direct observation of the alignment was not possible. Test indents were made on the surface to verify the alignment, as described in [13, 14]. The pillars were compressed using load control mode. The loading rate was between 0.02 mN/s and 0.05 mN/s, and the unloading rate was ~0.01 mN/s. Because strain rate is not an independent variable, the tests were stopped manually at an arbitrary strain after yielding. To ensure thermal stability between the indenter tip and the specimen, a waiting time of 10 minutes was set before each test. A total of 30-40 micro pillar compression tests were performed in non-irradiated and irradiated single-grain regions. Out of these, approximately 15 pillars were used to develop the alignment technique, and 2 to 5 pillars at each test condition (irradiated and unirradiated, at different temperatures) were tested.

A limited number of room temperature compression tests were performed in-situ (in the SEM) using a Hysitron PI85 indenter. This allows the recording of a movie during the actual tests, and the load-displacement curve can be directly correlated with the deformation processes recorded. Alignment is less of an issue for in-situ tests because the tip and sample can be directly observed, and misalignment can be corrected. Compared to ex-situ testing, in-situ testing leads to a higher proportion of successful tests.

In addition to the micro compression tests described above, bulk tensile testing of non-irradiated 304SS was performed over a similar temperature range as a reference. However, a different heat of 304SS was used since the amount of material available was not sufficient. The tensile testing was conducted by the University of South Carolina using a strain rate of 10⁻³ s⁻¹.

RESULTS AND DISCUSSION:

In Figure 2a, the first ~20 micrometers represent the ion-beam irradiated region and has higher hardness values; the unirradiated region lies deeper in the material and has significantly lower hardness values. The distance of ~20 microns corresponds nicely with the calculated stopping point of the protons (Figure 1). Despite the spatially varying dose profile in Figure 1, the irradiated region exhibits a relatively constant hardness up to and including the stopping peak at ~20 μm, indicating that for this irradiation condition, irradiation-induced hardening has saturated. Figure 3 illustrates an irradiation condition (lower dpa) where the hardness has not saturated, and the hardness profile follows the dose profile. It is obvious in Figure 2b that the lower-temperature indents give higher hardness values than higher-temperature indents. At room temperature (25°C), the irradiated region has an average hardness value of ~3.2 GPa greater than that of the non-irradiated region. As the temperature is elevated, this difference in hardness decreases to ~2.4 GPa at 300°C. Overall, hardness decreases at elevated temperatures in both the irradiated and unirradiated regions, with more significant decreases occurring in the irradiated region.

In Figure 4b, the nanoindentation hardness values obtained from the unirradiated region are transformed to yield stress and compared against bulk 2% offset yield stresses, at various temperatures, provided by the University of South Carolina (from tensile tests of a different heat of unirradiated 304SS) [15]. The nanohardness values are first converted to microhardness numbers using:
Hv=0.0947*Hnano

Equation 1

Subsequently the microhardness numbers are further converted to YS according to an empirical relationship outlined in Bruemmer et al. [16] for 300-series stainless steels [17] :

\[ \sigma_y = 2.5 \left( H_v - 68 \right) \]

Equation 2

In the equations, \( \sigma_y \) is the yield stress in MPa, \( H_v \) is the Vicker’s hardness number (MPa), while \( H_{nano} \) is the nanohardness in MPa. 3

Strictly speaking, the measured raw nanohardness values should be corrected for the size effect before they are used (e.g. in Equation 1). The size effect at room temperature is illustrated in Figure 4a using data from the irradiated (10 dpa) unirradiated (control) regions; hardness appears to increase as the indents become shallower, which is an artifact of the measurement. The inset of Figure 4a show the data as a Nix and Gao plot, \( H_0 \) vs. \( (1/h^*) \), where \( H_0 \) is the hardness at infinite indent depth and \( h^* \) is the characteristic (or measurement) indentation depth. For the unirradiated region, extrapolation of the line to \( (1/h^*) = 0 \) gives \( H_0 = \sqrt{3.6654} = 1.91 \) GPa. One can use Equation 1 to deduce that 1.91 GPa nanohardness and 180 Hv (MPa) microhardness are equivalent and find by Equation 2 that they correspond to 280 MPa yield strength, which is rather close to the bulk 2% offset yield stresses of 267 MPa measured by the University of South Carolina. The nanohardness measured at a particular indentation depth can then be corrected by at least two methods [18, 19]. The nanohardness measured at 300 nm is 2.73 GPa. Method 1 applies a constant offset of 2.73–1.91=0.82 GPa; that is \( H_{corrected}=H_{300nm}-0.82 \) (GPa). Method 2 applies a multiplicative correction factor of 0.82/2.73\( \approx \)0.3; that is \( H_{corrected}=H_{300nm}-0.3xH_{300nm}=0.7xH_{300nm} \) (GPa).

Extending the consideration outlined above over a range of temperatures would require a size effect curve at each temperature, and such curves have not been measured on 304SS across a range of temperatures; in fact, very little is known about indentation size effects as a function of temperature, and a study is needed. But one can attempt to apply the correction factors and relationships determined at room temperature to other temperatures. In this way, Method 1 and method 2 have been applied to correct measured nanohardness data for the size effect; the corrected nanohardness values were subsequently converted to YS by Equations 1 and 2 (Figure 4b). There is good agreement between nanohardness derived YS and bulk yield strength at lower temperatures; at higher temperatures, method 2 produces a reasonably good match between nanoscale and macroscale measurements. (Method 1 produced a match that was rather poor.) It is interesting to note in Figure 5, where data at different temperatures are plotted together, bulk YS vs. as-measured nanohardness and bulk UTS vs. as-measured nanohardness both have nearly linear relationships, suggesting also that nanoscale measurements over a temperature range could indeed be related straightforwardly to macroscale measurements.4

Micro compression testing conducted on the same sample as nanoindentation leads to additional insight. Prior room-temperature micro compression testing [20] confirmed, of course, that the proton-irradiated material had a markedly higher YS than the non-irradiated material. More importantly, the proton-irradiated micro compression sample experienced significantly fewer but more pronounced slip steps than the non-irradiated material, as can be seen by comparing the images of Figure 6a and Figure 6c. In addition the irradiated material experienced larger and more pronounced load drops than the non-irradiated materials (Figure 6d). Because these room-temperature micro compression tests (irradiated and non-irradiated) were carried out within the same grain, orientation-related differences are excluded.

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3 It should be noted that the use other empirical equations instead of Equations 1 and 2 leads to somewhat different results, as described in [9].

4 As noted in the Experimental section and earlier in this section, the tensile tests were conducted on a different heat of 304SS.
Since micro pillars can be fabricated by FIB at specific locations, it is possible to place a micropillar at the stopping-peak region of an ion-beam irradiated sample. For the proton-irradiated 304SS of this study, the dose at the stopping-peak region is ~8 time higher than at the flat “plateau” part of the dose profile (Figure 1), i.e. ~80 dpa vs. 10 dpa. Figure 6d shows that in initial tests carried out at room temperature, the yield stress is higher at the stopping-peak region than in the “plateau”, a result not observed by nanoindentation, even in cross-section. Since for an indent depth of 200 nm, the plastic zone expands underneath the indenter to dimensions of 3-4 µm laterally and in depth, we speculate that the property measured by nanoindentation is integrated over this volume and the higher yield strength of the stopping-peak region was “averaged out”. In contrast, the micro pillars can be placed at the location of the stopping peak and is, in fact, fabricated by cutting away the surrounding material. Although the 3 x 3 µm pillar used in this study does extend beyond the stopping-peak region, which is less than 1 µm in width, its volume is much better defined (Figure 1), which makes evident the different stress-strain behavior at the stopping-peak. Post compression, the micro pillar that contains the stopping-peak region (Figure 6b) displays pronounced slip steps, like the micro pillar from the irradiated plateau region (Figure 6a). While it might appear that the slip steps of the micro pillar that contains the stopping-peak region are slightly less pronounced than those of the plateau region, one should keep in mind that the micro pillar also contains some material from the non-irradiated region (Figure 1). Therefore, in addition to critical resolved shear stress, work hardening rate, and observations of load drops and slip band formation, micro pillar compression can provide information, from the same sample, about regions that represent different parts of the dose profile curve. Differences in properties along the dose rate curve and how they affect measured behavior will be the subject of future investigation.

The authors are extending micro compression testing to elevated temperatures (up to 300°C) to evaluate whether pronounced load drops and slip bands are still visible at reactor operating temperature and how the measured YS compares to macroscopic testing and to nanoindentation. Figure 7 shows deformed micro pillars tested at 100°C, and pronounced slip steps do form at this temperature. As noted in the Experimental section, elevated temperature measurements were conducted using an ex-situ instrument (i.e. not in the SEM). Although the test chamber’s oxygen concentration was reduced to ~2% and the samples were kept clean, surface contamination from the mounting agent or handling prevented good images of the post tested pillars. However, we do want to state that slip steps were also observed at higher temperatures (200°C and 300°C) in addition to localized contamination. Ex-situ measurements has two other significant disadvantages: (i) because the feed-back control is slower than the in-situ system, load drops cannot be observed clearly; and (ii) unlike measurements conducted in-situ, it is not possible to record movies to correlate visual observations with load and displacement. Therefore, in-situ measurements at elevated temperatures will be implemented.

Ex-situ stress (and strain) measurements remain informative and Figure 8 plots at different temperatures the YS and the critical resolved shear stress (CRSS) measured by micro pillar compression and hardness measured by nanoindentation. CRSS takes grain orientation into account and is a better measure for comparison among different grains. YS, CRSS, and hardness all follow the same trend. It is interesting compare the CRSS obtained by micro pillar compression and hardness obtained by nanoindentation, since both are micromechanical testing techniques. Figure 9 indicates that there is a nearly linear relationship between these two properties, which is not surprising. However, it also shows that the irradiated and non-irradiated materials have significantly different slopes, suggesting mechanistic changes in the deformation process.

The results of this study indicate that irradiation does lead to increased localized deformation within a single grain. Strong and localized slip events occur across the temperature range tested. It is plausible that the localized slip observed in the study is the result of formation of defect-free channels, and TEM work is underway. If so, in-situ micro pillar compression, in conjunction with video capture, can measure the stress (or the critical resolved shear stress) needed to form a defect free channel. Values at different doses or at different temperatures can be compared.
The micro pillars of this study were fabricated from grain interiors and are effectively single crystals. IA SCC is predominantly intergranular; therefore, the interaction of localized slip with grain boundaries is important. For example, if the slip impinging on a grain boundary cannot be transmitted, the local stress will increase, and the grain boundary may de-bond, contributing to crack initiation if at the surface. Alternatively, if grain boundary sliding accommodates the slip, it may disrupt the grain-boundary passive film at the surface, contributing to crack initiation. Small-scale mechanical testing can target grain boundaries in future investigation.

Different test geometries can be used in small-scale mechanical testing. The application of micro pillar compression and the information that can be obtained have been described. One drawback is that a definitive failure point cannot be determined in compression; the micro pillar can deform significantly in a localized fashion but still stay together. Therefore, the authors, as well as other researchers, are evaluating micro tensile testing as a complementary approach [21, 22].

**CONCLUSIONS**

This study demonstrates that quantitative mechanical test data are accessible even on rather shallow proton-irradiated (and more generally, ion-irradiated) samples. All region of the proton-irradiated samples can be accessed, including the stopping-peak and non-irradiated regions. The results provide insight about localized deformation over a range of temperature, up to 300°C; in particular, irradiation concentrates slip into a few but pronounced slip steps. Although the material of this study were irradiated with protons, the irradiation conditions were selected to simulate LWR neutron irradiation. But micromechanical techniques can be applied to neutron-irradiated material with comparatively minimal dose concerns.

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**REFERENCES:**


[15] D. Kaoumi private communications


Figure 1: SRIM calculated dose rate and H content in the as-irradiated sample a). Schematic sketch of the nanoindents traversing the proton-irradiated damage layer and the unirradiated substrate and of micro compression samples manufactured in the plateau region and at the stopping peak b).

Figure 2: Nano hardness profiles with respect to depth, measured over a wide temperature range (RT-300°C) across the damage layer and into the unirradiated substrate a). Nanohardness of irradiated and unirradiated areas over a range of temperatures b).
Figure 3: Cross-section nanoindentation results from proton-irradiated (1 dpa at 360°C) and unirradiated regions of the same sample; blue and red, respectively. Note the increase in hardness of the irradiated region associated with the stopping peak.

Figure 4: Size effect measured on 304SS sample at room temperature and related Nix and Gao fit a). Measured YS and YS calculated from nanoindentation of 304SS over a range of temperatures b); Method 1 applies a constant size-effect offset of 0.82 GPa and Method 2 applies a 30% offset to account for the size effect.
Figure 5: YS and UTS vs. as-measured nanohardness (YS and UTS are from the tensile test data) of non-irradiated material; data were obtained at different temperatures.

Figure 6: SEM image compressed micro pillars; from the irradiated region a); from the stopping-peak region b); and from the non-irradiated region c). Stress-strain curves obtained from the micro compression tests in the irradiated, stopping-peak, and non-irradiated regions d).
Figure 7: SEM images of deformed micro pillars tested at 100°C; non-irradiated a) and irradiated b).

Figure 8: Summary of micromechanical test data collected from room temperature to 300°C.
Figure 9: Normalized critical resolved shear stress from micro compression testing vs. normalized hardness from nanoindentation.