Nanoindentation and *in situ* microcompression in different dose regimes of proton beam irradiated

304 SS

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Abstract

Recent developments in micromechanical testing have allowed for the efficient evaluation of radiation effects in micron-scale volumes of ion-irradiated materials. In this study, both nanoindentation and *in situ* SEM microcompression testing are carried out on 10 dpa proton beam irradiated 304 stainless steel to assess radiation hardening and radiation-induced deformation mechanisms in the material. Using a focused ion beam (FIB), arrays of 2 μm x 2 μm cross-section microcompression pillars are fabricated in multiple dose regimes within the same grain, providing dose-dependent behavior in a single crystal orientation. Analysis of the microcompression load-displacement data and real-time SEM imaging during testing indicates significant hardening, as well as increased localization of deformation in the irradiated material. Although nanoindentation results suggest that irradiation hardening saturates at low doses, microcompression results indicate that the pillar yield stress continues to rise with dose above 10 dpa in the tested orientation.

Keywords: microcompression, nanoindentation, ion irradiation, stainless steel

1. Introduction

Irradiation assisted stress corrosion cracking (IASCC) in austenitic stainless steels has become an increasing impediment to the long term integrity of light water reactor structural components [1]. Predictions of IASCC susceptibility continue to be hindered by poor understandings of the deformation mechanisms at hand, as well as the difficulties of

reproducing reactor conditions in laboratory tests. In the past several years, much research has been devoted to tackling both of these issues by performing standard mechanical testing on ion beam and neutron irradiated austenitic SS and correlating observed deformation mechanisms with crack initiation [2-4]. In 2011 Jiao & Was [2] demonstrated that a primary contributor to IASCC in SS is localized deformation via dislocation channeling, in which irradiation defects are cleared out in a narrow channel by gliding dislocations. This clearing of barriers to dislocation motion allows subsequent dislocations to easily follow the same path, causing strain to localize in these channels and reach values orders of magnitude higher than the bulk applied strain [5,6]. McMurtrey et al. [3,7,8] continued this line of investigation by characterizing the various mechanisms by which dislocation channels interact with grain boundaries. The authors found that in cases where dislocation pile-up at a grain boundary did not result in continuous slip into the neighboring grain, high levels of unrelieved stress near the grain boundary led to increased prevalence of cracking. It is proposed that such discontinuous channels could cause the oxide layer at the grain boundary to be ruptured, and thus promote localized attack that initiates IASCC.

Parallel studies have also investigated the role of deformation twinning, as well as phase transformations in the deformation of irradiated SS. In low stacking fault energy materials such as 300 series austenitic SS, deformation twinning is an alternative localized mechanism which may take place in addition to, or preferentially to, dislocation channeling at higher irradiation doses, lower temperatures, and faster strain rates [9]. Gussev et al. [4] observed deformation twinning within dislocation channels in particular grain orientations of neutron irradiated 304 SS. In an earlier study, the authors also noted the presence of small colonies of strain-induced martensite grains near the steps created by surfacing dislocation channels in these specimens, again in specific grain orientations [10].

These studies have revealed that deformation in irradiated austenitic SS can be a complex, multifaceted process which varies on a local microscopic scale in a grain orientation dependent manner. Several mechanisms of varying predominance can be involved, the contribution of each depending upon irradiation dose, temperature, and strain rate. Thus difficulties arise in determining the key factor(s) responsible for localized IASCC when using macroscopic mechanical testing paired with subsequent microstructural characterization, particularly when testing in conditions different from those in a reactor setting.

By contrast, micro-mechanical testing presents a unique opportunity to investigate deformation mechanisms on a single-grain level at known orientations, as well as at specific grain boundaries. Micromechanical testing, including nanoindentation, microcompression, microtensile, and other methods, has been employed as a means to reduce sample size and overcome the limited penetration depths of ion irradiation, as well as the cumbersome hot cell work typically required for neutron irradiated materials [11]. In ion irradiated materials, which experience a strongly varying dose profile over shallow depths (~1.0-20 μm), micromechanical tests can be used to probe multiple dose regimes of the same irradiated sample [12]. Furthermore, the tests can be conducted *in situ* in an SEM or TEM, allowing real time observations of deformation.

Much work has been devoted elsewhere to studying the intricacies of micromechanical testing and the associated challenges with extrapolating the results to obtain macro-scale mechanical property values [13,14]. The purpose of this work is rather to determine what information can be derived about the deformation of ion beam irradiated austenitic SS using two common micromechanical testing methods, nanoindentation and microcompression. Arrays of nanoindents are performed on the cross-sectional surface of 10 dpa proton beam irradiated 304 SS, measuring irradiation hardening as a function of distance from the sample surface. These results are compared with similar length-scale microcompression tests performed *in situ* in an SEM, providing near-uniaxial stress-strain behavior. The ability to probe discrete volumes of material with microcompression testing is also demonstrated by fabricating specimens in multiple dose regimes within the same grain. This allows for a direct comparison of irradiated and unirradiated deformation in a single grain orientation.

Figure 1: SRIM-calculated damage profile in 304 SS irradiated with 2 MeV protons to an average dose of ~10 dpa. Locations at which $2\mu\text{m} \times 2\mu\text{m}$ cross-section microcompression pillars were fabricated, with respect to the damage profile, are indicated in blue.

2. Methods

2.1 Sample Irradiation

The sample for this study consists of a ~3 mm bar of 304 SS prepared with standard metallographic methods and electropolished prior to irradiation. The sample was irradiated with 2 MeV protons at 360°C in a Tandetron accelerator at the Michigan Ion Beam Laboratory (MIBL). During irradiation, the sample temperature was monitored with a two-dimensional

thermal imager and maintained within $\pm 10^\circ\text{C}$ of the target value. Assuming a full cascade and displacement energy of 40 eV, SRIM [15] calculations indicate that the sample was irradiated to an average dose of 10 dpa at a dose rate of $\sim 8 \times 10^{-6}$ dpa/s. Based on the calculated dose profile shown in Figure 1, the proton stopping point is predicted to be at a depth of $\sim 19\mu\text{m}$, leading to a much larger peak dose of ~ 100 dpa at this depth. The chosen irradiation conditions have been shown in previous studies to closely emulate the microstructure, hardening, and susceptibility to IASCC induced in stainless steels by reactor neutron irradiation [16]. A more detailed description of the proton irradiation procedure is published elsewhere [17].

It is important to note that there are two options in SRIM for calculations of dose: “full cascade” and “Khinchin-Pease.” Unless otherwise specified, this study uses the full-cascade option in order to maintain consistency with a large number of prior publications across the years that use proton-irradiation to investigate radiation damage, including prior publications by one of the co-authors using the same heat of stainless steel as this study. At the same time, a recent publication by Stoller et al. [18] establishes that the Khinchin-Pease option is more appropriate when comparing ion and neutron doses. The Khinchin-Pease (K-P) value is a factor of 2 less than the full-cascade value; that is, 10 dpa (full-cascade) corresponds to 5 dpa (K-P). Therefore, when this study compares the mechanical properties of proton-irradiated to neutron-irradiated stainless steels, the K-P dose values will be used and will be designated clearly by the suffix (K-P).

Following irradiation, the sample was polished in cross section with respect to the irradiated surface. In order to reduce edge rounding, the sample was mounted directly next to a thin piece of steel during grinding and polishing. The cross sectional surface was polished with 300 - 4000 grit SiC grinding paper, followed by 0.3 and 0.1 μm alumina polishing solutions, and finally by 0.05 μm non crystallizing colloidal silica.

2.2 Nanoindentation

Cross sectional nanoindentation measurements were performed using a Hysitron TI 950 Triboindenter. Arrays of 50 nm and 200 nm depth indents were performed using a Berkovich indenter in depth controlled mode with a 5-2-5 second loading scheme. The arrays were tilted at a slight angle with respect to the sample edge to increase spatial resolution. Evaluation of hardness, H , and the reduced modulus, E_r , for this work was performed on the load-displacement curves using the Oliver-Pharr method [19]. Indent locations with respect to the sample edge were later measured in an SEM.

2.3 Microcompression

In order to identify a single-grain region for microcompression testing, electron backscatter diffraction (EBSD) was used to generate grain maps along the sample's irradiated edge. A large grain of $\sim 150\ \mu\text{m}$ in length was identified at the sample edge, sufficient in size for groups of 4 to 5 microcompression pillars to be fabricated in three different dose regimes within the same grain. These three regimes include (1) the 10 dpa irradiated region (within a few microns of the sample edge), (2) the ~ 100 dpa peak dose region (~ 19 - $21\ \mu\text{m}$ from the sample edge), and (3) the unirradiated region ($>25\ \mu\text{m}$ from the sample edge). A schematic representation of how this may be done is given in Figure 2a. The grain orientation in the grain identified in Figure 2b was measured to be [025] with respect to the pillar loading axis. Focused ion beam (FIB) milling techniques were then employed to fabricate the three arrays of $2\ \mu\text{m} \times 2\ \mu\text{m} \times 5\ \mu\text{m}$ pillars according to the procedure outlined in [20]. Rough cuts were performed with a 30 kV Ga-ion beam at currents of 1-7 nA, and final cleaning of the pillars was conducted at 0.1 nA to ensure smooth, level surfaces and minimal ion damage. Rectangular pillars were chosen rather than the more common cylindrical geometry as their fabrication achieves minimal sample taper while requiring only low-grazing angle milling, resulting in a more uniform stress state and decreased FIB damage [21]. A total of 12 microcompression pillars were fabricated and tested, as depicted in Figure 2b. Note that the pillars were placed to strategically avoid a twin that bisects the grain.

Prior to testing, all pillar dimensions were measured using a Scanning Electron Microscope (SEM). Compression of each pillar was then conducted *in situ* in a SEM using a flat tip indenter on a Hysitron PI-85 Picoindenter system. The pillars were compressed in displacement controlled mode at a strain rate of $\sim 10^{-3}\ \text{s}^{-1}$. Since there is no obvious failure point in compression testing, loading was manually halted for

Figure 2: Schematic drawing showing the method for fabricating microcompression pillars at three distinct depths in the sample within a single grain (a). SEM images of microcompression pillars fabricated with FIB milling within a single grain, identified with EBSD orientation mapping of the sample surface (b).

Figure 3: Hardness as a function of depth in the sample, measured with Berkovich nanoindentation to depths of 50 nm and 200 nm. The irradiation stopping point is measured to be at a depth of $\sim 20 \mu\text{m}$.

the majority of tests at a strain of $\sim 20\%$. However, earlier termination was occasionally performed in irradiated tests when it was noted that slipped pillar material began to make contact with the bulk material surrounding the pillar. Engineering stress versus strain curves were calculated based on the initial pillar dimensions and the load-displacement data recorded by the indenter system. A yield stress value for each pillar was obtained by performing a linear regression on data from the linear elastic regime, and finding the intersection point of the stress-strain curve with a 0.2% strain offset of the regression line.

3. Results

3.1 Nanoindentation Results

Nanoindentation hardness as a function of distance from the sample edge is plotted in Figure 3. Significantly more spread is seen in the 50 nm indents compared to the 200 nm depth indents due to the small local variations in surface hardness that are captured by shallower indentation. This spread is even

more significant in the irradiated region, indicating inhomogeneities in hardening features on a length scale of tens to hundreds of nanometers. For both indent depths, a marked drop in hardness occurs in the transition from the irradiated to unirradiated regimes at about 20 μm into the sample, a slightly larger depth than predicted. For 200 nm depth indents, the average hardness in the irradiated material is 5.95 ± 0.19 GPa, roughly double that of the unirradiated material, 3.04 ± 0.14 GPa. Despite the varying dose profile calculated by SRIM, the irradiated regime exhibits a relatively constant hardness until the ~ 20 μm stopping point, indicating that the irradiation hardening saturates at or below a dose of 10 dpa [5 dpa (K-P)]. This is consistent with other nanoindentation studies which have shown that irradiation hardening in

Table 1: 0.2% offset yield stress values for all microcompression tests

Dose Regime	Pillar Number	Yield Stress	Average Yield Stress
Unirradiated	1	307.5	272.3 ± 34.0
	2	223.6	
	3	257.5	
	4	300.6	
Irradiated (~ 10 dpa)	1	769.9	834.4 ± 39.4
	2	876.7	
	3	843.8	
	4	847.3	
Irradiated Peak dose (~ 100 dpa)	1	1092.9	1069.8 ± 13.6
	2	1063.7	
	3	1064.7	
	4	1058.0

Figure 4: Microcompression engineering stress-strain curves for tests performed in three different dose regimes within a single grain: (a) unirradiated, (b) 10 dpa irradiated, and (c) peak dose irradiated.

neutron-irradiated austenitic SS tends to saturate at doses above 1 dpa [22]. Similar measurements performed on identically prepared 304 samples as this study, with nominal proton-irradiated doses of 1 dpa and 10 dpa, also suggest that the hardness measured with 200 nm depth indents plateaus at a value of ~6 GPa; however, the precise saturation dose is difficult to determine [23].

A significant indentation size effect can be seen in the higher average hardness measurements obtained for 50 nm indents, 7.61 ± 0.75 GPa in the irradiated region and 4.52 ± 0.33 GPa in the unirradiated material. In both the unirradiated and irradiated region, and for both indent depths, no dependency on grain orientation was observed. However, the elastic modulus also shows an increase in the irradiated versus unirradiated regions, from 181 GPa to 205 GPa for the 50 nm indents, and 173 GPa to 187 GPa for the 200 nm indents. It has been suggested that such an increase may be the result of residual stresses introduced by ion irradiation [24]; however further work is needed to confirm this effect.

Figure 5: SEM images of representative compressed pillars in each dose regime: (a) unirradiated, (b) 10 dpa irradiated, and (c) peak dose irradiated, and the corresponding engineering stress-strain curves (d).

3.2 Microcompression Results

A complete set of engineering stress-strain curves for the microcompression tests is given in Figure 4a, and yield stress values are tabulated in Table 1. Commercially reported bulk 0.2% offset yield stress values for 304 SS range from 210 to 290 MPa. A comparison of the microcompression stress-strain behavior in different dose regimes indicates that the material's 0.2% offset yield stress increases significantly with dose, from 272 MPa in the unirradiated pillars to 834 MPa in the 10 dpa irradiated pillars. The yield stress continues to increase in the peak dose irradiated pillars to an average of 1070 MPa, indicating that unlike nanoindentation hardness, microcompression yield stress is not observed to saturate at doses of 10 dpa and below in these samples.

A key benefit of *in situ* testing is the ability to correlate the recorded stress-strain data with high resolution real-time imaging of each specimen. In this case, both mid-test movies and post-test SEM images reveal significant differences in deformation behavior between the irradiated and unirradiated regimes. Post-compression images of representative pillars from each dose regime are given in Figure 5. In all cases, the compressed pillars were observed to undergo plastic deformation via intermittent slip along one or two common slip systems. The activation of the same slip planes in each pillar confirm that all tests were conducted within a single grain. For an FCC crystal, the expected slip systems consist of the $\{111\}$ family of planes and $\langle 110 \rangle$ directions. A Schmid factor calculation for the $z[025]$ loading direction predicts that two of the twelve possible slip systems share the highest Schmid factor of 0.493, the (111) plane in the $[1-10]$ direction and the (-111) plane in the $[101]$ direction. To confirm that the observed slip planes match those with the highest predicted Schmid factor, post-test image analysis was performed using SEM images of a representative compressed pillar. This was accomplished by first creating a three-dimensional CAD

Figure 6: Demonstration of the use of post-compression image analysis with three-dimensional CAD modeling to identify the activated slip planes in a microcompression pillar. Slip was confirmed to occur along two unique planes: (111) and (-111), which correspond to those geometrically predicted with a Schmid factor of 0.493.

model of the pillar and its slip planes, and using this model to estimate the normal vector of the observed slip planes. The four unique $\{111\}$ slip planes of the FCC crystal structure were then mathematically rotated by the grain orientation Euler angles measured with EBSD using a rotation matrix, and their normal vectors were compared to the measured slip plane normal to identify which planes were equivalent. Using this method, it was determined that the two slip planes observed in the tests indeed correspond to the (111) and (-111) planes, as shown in Figure 6.

The post-test SEM images in Figure 5a and corresponding blue stress-strain curve in Figure 5d show that the unirradiated pillars deformed via the initiation of a large number of small slip events, corresponding to many small load drops in the stress-strain curve following yield. A comparison of the stress-strain results for the four unirradiated tests shows fairly consistent behavior from pillar to pillar, with the exception of Pillar 4 which reached much higher strengths in the plastic regime. Images recorded during the test indicate that the initial slip event in this pillar occurred very close to the pillar base. As the material above slipped below the base of the pillar, it began to push into the surrounding bulk material and increased the apparent strength of the pillar.

Although the 10 dpa irradiated pillars also underwent plastic deformation via slip, yield tended to occur via the initiation of one large slip event, accompanied by a sudden burst of strain (2-4%) (Figure 5b,d). Such an event typically appears in the loading curve as a flat plateau followed by a large load drop. These features are artifacts of the indenter system, resulting from the strain rate during the slip event exceeding the controlled displacement

rate, data acquisition rate, and load feedback loop of the indenter. This mechanism is further described in the Discussion. Once loading of a slipped pillar was resumed, new slip events were not typically initiated, but rather the material continued to slip further along the same initial plane. SEM imaging during the tests revealed that strain in the 10 dpa irradiated pillars was typically localized in only one or two discrete slip planes, particularly at total strains of less than 10%. Beyond this point, the pillars displayed deformation more representative of the unirradiated behavior: steadily increasing stress with many small intermittent load drops.

Similar behavior occurs in the peak dose irradiated pillars (Figure 5c,d), with the onset of plastic deformation marked by large, sudden slip events which accommodated large amounts of strain. Straining of the pillars beyond 10% also resulted in transitioning to a similar strain hardening effect and an increase in the number of slip steps initiated in the pillar volume. Overall, the four high dose pillars tested showed very consistent yield stress and deformation behavior.

4. Discussion

Deformation in single-crystal micron-scale pillars under compression has been characterized in depth in many past studies [13]. Whereas smoothly varying flow curves are expected for bulk deformation in polycrystalline materials, intermittency and stochastic flow are the hallmark behaviors exhibited in single crystal microcompression. Specimens tend to undergo periods of easy glide alternating with elastic or near-elastic loading, giving rise to characteristic steps in microcompression loading curves. The unirradiated specimens in this study clearly demonstrate this behavior with many small slip steps intermittently forming throughout the pillar volume during plastic deformation, as evident in SEM imaging (Figure 5a).

With the introduction of proton irradiation damage, however, obstacles to dislocation motion in the form of a dense population of nanometer-scale Frank loops induce hardening by impeding dislocation motion [24]. Higher stresses are therefore required to initiate plastic deformation, as dislocations must overcome irradiation-induced obstacles for slip to occur. In studies examining polycrystalline ion-irradiated austenitic stainless steels, this has been observed to result in the sudden formation of defect-free channels, in which dislocations clear out irradiation defects in a narrow channel, creating an easy path for additional dislocations to glide along. The result is heterogeneous plastic deformation, in which strain is localized in a series of channels spaced 1-3 μm apart in each grain [2]. The proton-irradiated microcompression specimens of this study display an undoubtedly similar localization of strain, with often only one or two major slip steps forming in each 5 μm tall single crystal pillar. During deformation of an irradiated pillar, each slip step forms suddenly and carries a large amount of strain. As the pillar is further deformed, strain tends to occur within these pre-existing slip steps, rather than initiating new ones. This ultimately leads to significantly larger step heights on the irradiated pillar surfaces than observed on the unirradiated pillars (Figure 5a and b).

The observed differences in slip behavior can be quantified by first tallying the number of load drops observed in the load-displacement curve for each pillar. Tests in this study were performed in displacement controlled mode using a fixed displacement rate and data acquisition rate. Following the initiation of a slip event, strain rates are typically so high that only one or two data points are collected during this time, resulting in a flat plateau in the load curve connecting the sparse data. However, the indenter itself is load-controlled, such that when a sudden deformation event occurs, a feedback loop detects the change in displacement and adjusts the applied indenter force accordingly. For an event which occurs more quickly than the feedback loop can respond, such as the formation of a new slip step, this

Table 2: Comparison of slip behavior among unirradiated and irradiated microcompression tests.

		Area below stress- strain curve (up to 10% strain)	Pillar cross sectional area	Pillar height	Total energy dissipated	Number of load drops (slip steps)	Average energy per load drop		Average number of dislocations per slip step	Average slip step height
		[MPa]	[μm^2]	[μm]	[10^{-9} Nm]		[10^{-9} Nm]			[nm]
Unirradiated	1	40	4.1	5.6	0.92	15	0.062	0.083 ± 0.016	508 $\pm$ 97	126 $\pm$ 24
	2	43	4.1	5.1	0.91	9	0.10			
	3	42	4.4	5.2	0.96	13	0.074			
	4	50	4.1	5.3	1.1	11	0.097			
10 dpa Irradiated	1	83	4.4	5.1	1.8	5	0.37	0.50 ± 0.17	3049 $\pm$ 1061	756 $\pm$ 263
	2	140	4.5	5.0	3.1	4	0.78			
	3	90	4.4	5.2	2.0	4	0.51			
	4	85	3.9	5.1	1.7	5	0.34			
Peak dose (stopping point) irradiated	1	120	3.8	5.1	2.3	6	0.39	0.49 ± 0.13	3003 $\pm$ 807	745 $\pm$ 200
	2	113	3.8	5.0	2.2	3	0.72			
	3	105	3.9	5.2	2.1	5	0.43			
	4	102	4.2	5.0	2.1	5	0.43			

then manifests as a steep load drop in the curve. Thus the number of load drops in a given load-displacement curve can be taken as an estimate of the number of slip steps in the pillar. It is important to note that since compression tests have no discrete failure point, the tests were halted at various strain values depending on real-time SEM observations. Therefore, only strains up to 10% were considered. The resulting values given in Table 2 confirm that below

10% strain, deformation in the unirradiated pillars occurred via a much larger number of slip steps.

Using the integrated area under the stress-strain curve, the average energy dissipated per slip step can also be calculated for each pillar. The total plastic energy dissipated during the test (again, up to 10% strain) is given by the area under the curve multiplied by the pillar volume. Dividing this value by the number of slip steps observed in the test gives the average energy released per slip step. The results given in Table 2 indicate significant spread from test to test; however, when averaged over all tests of a given irradiation condition, we find that the average energy per load drop of the irradiated pillars (including both the 10 dpa and peak dose stopping point pillars) is a factor of 6 higher than that of the unirradiated pillars. Again, this points to a larger amount of energy dissipated in each slip event, and a greater extent of deformation localization along a smaller number of slip planes in irradiated pillars.

These values can further be used to approximate the average number of dislocations that were moved through the pillar in a given slip step, as well as the slip step height. First we must determine the value of the Peierls stress for the material, or the stress required to move a dislocation by one Burgers vector in a perfect lattice. The Peierls stress is given by:

where G is the shear modulus, b is the Burgers vector, ν is Poisson's ratio, and d is the interplanar spacing. For austenitic stainless steel, the shear modulus in the (111) plane is 650 MPa [26] and the lattice constant is 0.351 nm [27], leading to a Burgers vector of 0.248 nm and a (111) interplanar spacing of 0.202 nm. This gives a Peierls stress of τ_p . The work a dislocation must perform in order to move through the entire pillar can then be calculated with

where L is the dislocation line length (equal to the pillar diameter in this case), and d is the dislocation travel distance (assumed to be the entire distance through the pillar as well). In a 2 μm diameter pillar for which the slip planes are at nearly 45 degree angles with respect to the compression axis, the travel distance will be roughly 2.8 μm . The work a dislocation must perform to travel through the pillar volume is, then, W Nm. Comparison of this value to the average energy released per slip event measured from the microcompression data indicates that an average of 3049 dislocations were moved through the 10 dpa irradiated pillars in a typical slip step, while only 508 dislocations were moved in the unirradiated pillars. This corresponds to a slip step height of 756 nm and 126 nm, for the irradiated and unirradiated pillars, respectively.

It is important to note that the above calculation includes several geometric and physical simplifications, and can therefore only be taken as an approximation. For instance, it does not take into account the precise slip plane angles, nor the surface energy created by a dislocation event. Nonetheless, the result agrees well with the magnitude of observed slip step heights on irradiated and unirradiated pillars based on post-test SEM images (Figure 5a-c). It is clear from the much larger number of dislocations involved in each slip step in the irradiated material that the energy required to initiate a new slip events in the irradiated

case exceeds that required for dislocation motion to continue along the existing plane. Although this behavior is strongly indicative of dislocation channeling, it does not rule out the presence of dislocation twinning and/or deformation martensite which occur on a similar length scale. A TEM investigation of pre- and post-compression irradiated pillars is necessary to confirm the exact deformation mechanism(s) at hand, and will be the subject of future work.

Another key observation of this study is that proton irradiation hardening measured via nanoindentation appears to saturate at low doses [≤ 10 dpa, or ≤ 5 dpa (K-P)], whereas microcompression yield stress continues to rise with dose beyond this point. It is informative to place this observation in the context of studies conducted on neutron-irradiated stainless steels; to do this, the dose value calculated with the Khinchin-Pease option is used, as discussed in the Methods section. Microstructural studies of 304 SS irradiated with reactor neutrons indicate that as irradiation dose is increased, the size and density of Frank loops increases rapidly for doses up to 5-10 dpa, and increases only slightly at doses exceeding this level [25]. In addition, as the size and density of Frank loops increases, the stress required to plastically deform the material reaches the point at which stress-induced defaulting of Frank loops can take place, thus maintaining this stress below a critical level. These two factors lead to the prediction that irradiation hardening should undergo saturation at a doses exceeding 5-10 dpa in neutron-irradiated 304 SS [25], which is in good agreement with the nanoindentation results of this study on 304 SS proton-irradiated to 5 dpa (K-P). Conventional tensile testing of reactor neutron irradiated 304 SS confirms this behavior, showing that tensile yield stress saturates at 5-10 dpa at a value ~ 600 MPa higher than that of the unirradiated material [28]. Microcompression results of this study agree up to this dose, with an increase in yield stress of ~ 560 MPa due to proton irradiation to 5 dpa (K-P). However, microcompression tests in the peak dose region indicate that the yield stress increases a further ~ 236 MPa at ~ 50 dpa (K-P) from proton irradiation.

Of course, fundamental differences in ion beam irradiation versus reactor neutron irradiation make a direct comparison of dpa thresholds difficult, particularly when testing is conducted in the ion beam stopping point region. Proton irradiation leads to a narrow region of hydrogen implantation, causing the formation of additional hardening features such as voids and bubbles at a defined depth in the sample along with regular irradiation point defects and Frank loops. Given that this region is only 1 to 2 microns wide, measuring its hardness with nanoindentation alone may be exacerbated by the large and poorly defined volume sampled by indents. It has been shown that the indentation plastic zone typically extends over a half-sphere volume of radius equal to 4-10 times the indent depth [19]. Therefore, it is expected that hardness measurements made with 50 nm and 200 nm depth indents correspond to material in diameters of 0.5-1.0 μm and 2.0-4.0 μm respectively. The peak dose region is therefore difficult to isolate with nanoindentation unless very shallow indent depths are employed. However, below indent depths of 200-300 nm, size effect mechanisms begin to dominate, and surface effects significantly increase [29]. Microcompression, by contrast, samples a discrete volume; thus fabricating a free-standing 2 μm diameter pillar may successfully probe the hydrogen implantation region and produce more accurate irradiation hardening measurements.

The observed dose dependence of pillar yield stress may also be a product of fundamental differences in sample geometry and scale in nanoindentation, microcompression, and conventional tensile testing. While microcompression induces a relatively uniaxial stress state in a single crystal specimen, nanoindentation requires that a minimum of five unique slip systems be active for the material to accommodate strain. Accordingly, microcompression results tend to be highly dependent on grain orientation, whereas many authors report comparatively small orientation-dependent differences for nanoindentation results of similar materials [24,30], as observed in this study. Although conventional tensile testing is uniaxial in nature, the elastic and plastic properties measured are effectively an average over all grain orientations in the sample. Thus in irradiated materials, plastic deformation may initiate locally in soft grains, giving rise to dislocation channeling and slip steps in particular grains well before the bulk yield, which in turn can lead to localized attack. In fact, this phenomenon has been observed in 4-point bend tests of neutron irradiated 304 SS, in which dislocation channels were shown to form in an orientation-dependent manner at as low as 72% of the bulk yield stress [9]. In addition, the presence of deformation twinning and martensite formation in irradiated 304 SS has been shown to have a strong orientation dependence [4,9,10,22]. Studies presently underway, utilizing micro Laue diffraction in an effort to “see inside” a pillar volume during microcompression, suggest that deformation induced martensitic phase transformations do not take place under the current test conditions. However, it remains a possibility that compression of irradiated single-crystal SS pillars may result in different yield stress values as well as different deformation mechanisms, depending upon the orientation tested. With increased dose, newly activated deformation mechanisms may manifest in certain grain orientations and not in others, hence the possibility of observing different doses at which irradiation effects appear to saturate. This makes microcompression a useful method for isolating and comparing the extent and nature of localized deformation in various grain orientations, or potentially at specific grain boundaries. Of course, it is important to take into account that such orientation dependence also leads to mechanical property measurements in single crystal microcompression which may be non-representative of bulk polycrystalline material. As demonstrated, the technique is ideally applied when seeking to compare deformation behavior in unirradiated and irradiated material within the same sample, in the same grains, or at the same grain boundaries.

Conclusion

In this study, a combination of nanoindentation and microcompression testing were applied to assess radiation hardening and deformation behavior in 10 dpa proton beam irradiated 304 SS. Of particular interest is the successful use of these methods to exploit the varying dose profile induced by ion beam irradiation to obtain mechanical property measurements at multiple doses in the material. Major findings can be summarized as follows:

- (1) *Irradiation hardening:* As expected, the increased defect density in the 10 dpa [5 dpa (K-P)] proton irradiated material resulted in significant increases in hardness and yield stress determined by both nanoindentation and microcompression testing. The hardness was measured to have doubled, and the microcompression yield stress increased by ~560 MPa. These results are closely aligned with existing tensile data for neutron irradiated 304 SS, which indicate a ~600 MPa increase in yield stress for 5-10 dpa irradiated specimens [28].
- (2) *Dose saturation:* Cross sectional nanoindentation measurements made at depths of 50 nm and 200 nm indicate that irradiation hardening saturates at doses at or below 10

dpa. By contrast, microcompression yield stress continues to rise above this dose in the peak dose stopping point region. It is believed that this effect can be attributed to the presence of orientation-dependent deformation mechanisms, as well as the differences in geometry of nanoindentation and microcompression tests.

- (3) *Localized deformation: In situ* microcompression testing enabled the observation of significant differences in deformation behavior in the unirradiated and irradiated stainless steel. Following yield, the unirradiated pillars plastically deformed via many small intermittent slip events, while the irradiated pillars consistently exhibited a small number of large, sudden slip events which accommodated large amounts of strain. The localization of strain along selected slip planes in the irradiated material suggests the formation of dislocation channels.

Overall the results of this study indicate that nanoindentation alone may not be insufficient to assess irradiation induced changes in a material's mechanical properties. Other forms of micromechanical testing, including microcompression, may provide additional information on phenomena such as localized deformation and orientation-dependent mechanisms. However, it is ultimately necessary to perform these tests in a variety of grain orientations at reactor operating temperature to obtain a complete picture.

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References

- [1] Y. Chen, O.K. Chopra, E.E. Gruber, W.J. Shack. Irradiation-assisted stress corrosion cracking of austenitic stainless steels in BWR environments. U.S. NRC Report NUREG/CR-7018 (2010).
- [2] Z. Jiao, G.S. Was. Impact of localized deformation on IASCC in austenitic stainless steels. *Journal of Nuclear Materials* 408 (2011) 246-256.
- [3] M.D. McMurtrey, B. Cui, I. Robertson, D. Farkas, G.S. Was. Mechanism of dislocation channel-induced irradiation assisted stress corrosion crack initiation in austenitic stainless steel. *Current Opinion in Solid State and Materials Science* 19 (2015) 305-314.
- [4] M.N. Gushev, K.G. Field, J.T. Busby. Deformation localization and dislocation channel dynamics in neutron-irradiated austenitic stainless steels. *Journal of Nuclear Materials* 460 (2015) 139-152.
- [5] K.G. Field, M.N. Gushev, J.T. Busby. Microstructural characterization of deformation localization at small strains in a neutron-irradiated 304 stainless steel. *Journal of Nuclear Materials* 452 (2014) 500-508.

- [6] N.M. Ghoniem, S.-H. Tong, B.N. Singh, L.Z. Sun. On dislocation interaction with radiation-induced defect clusters and plastic flow localization in fcc metals. *Philosophical Magazine A* 81 (2001) 2743-2764.
- [7] M.D. McMurtrey, G.S. Was, L. Patrick, D. Farkas. Relationship between localized strain and irradiation assisted stress corrosion cracking in an austenitic alloy. *Materials Science & Engineering A* 528 (2001) 219-236.
- [8] M.D. McMurtrey, et al. Strain localization at dislocation channel-grain boundary intersections in irradiated stainless steel. *International Journal of Plasticity* 56 (2014) 219-231.
- [9] T. Byun, N. Hashimoto. Strain localization in irradiated materials. *Nuclear Engineering and Technology* 38 (2006) 619-638.
- [10] M.N. Gussey, K.G. Field, J.T. Busby. Strain-induced phase transformation at the surface of an AISI-304 stainless steel irradiated to 4.4 dpa and deformed to 0.8% strain. *Journal of Nuclear Materials* 446 (2014) 187-192.
- [11] P. Hosemann, C. Shin, D. Kiener. Small scale mechanical testing of irradiated materials. *Journal of Materials Research* 30 (2015) 1231-1245.
- [12] A. Reichardt, et al. *In situ* micro tensile testing of He²⁺ ion irradiated and implanted single crystal nickel film. *Acta Materialia* 100 (2015) 147-154.
- [13] M.D. Uchic, P.A. Shade, D.M. Dimiduk. Plasticity of micrometer-scale single crystals in compression. *Annual Reviews in Materials Research* 39 (2009) 361-386.
- [14] H. Van Swygenhoven, S. Van Petegem. The use of Laue microdiffraction to study small-scale plasticity. *Journal of the Minerals, Metals, and Materials Society* 62 (2010) 36-43.
- [15] J.F. Ziegler, J.P. Biersack. SRIM Program. IBM Corp. Yorktown, NY (2008).
- [16] G.S. Was, J.T. Busby, et al. Emulation of neutron irradiation effects with protons: validation of principle. *Journal of Nuclear Materials* 300 (2002) 198-216.
- [17] G. Gupta, Z. Jiao, A.N. Ham, J.T. Busby, G.S. Was. Microstructural evolution of proton irradiated T91. *Journal of Nuclear Materials* 351 (2006) 162-173.
- [18] R.E. Stoller, et al. On the use of SRIM for computing radiation damage exposure. *Nuclear Instruments and Methods in Physics Research B* 310 (2013) 75-80.
- [19] W.C. Oliver, G.M. Pharr. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research* 7 (1992) 1564-1583.
- [20] D. Kiener, C. Motz, T. Schöberl, M. Jenko, G. Dehm. Determination of mechanical properties of copper at the micron scale. *Advanced Engineering Materials* 8 (2006) 1119-1125.
- [21] J. Hütsch, E.T. Lelliudden. The influence of focused-ion beam preparation technique on microcompression investigations: Lathe vs. annular milling. *Scripta Materialia* 77 (2014) 49-51.
- [22] C. Bailat, et al. The effects of irradiation and testing temperature on tensile behavior of stainless steels. *Journal of Nuclear Materials* 283-287, Part 1 (2000) 446-450.

- [23] A. Lupinacci, et al. Characterization of ion beam irradiated 304 stainless steel utilizing nanoindentation and Laue microdiffraction. *Journal of Nuclear Materials* 458 (2015) 70-76.
- [24] C.D. Hardie, S.G. Roberts. Nanoindentation of model Fe-Cr alloys with self-ion irradiation. *Journal of Nuclear Materials* 433 (2013) 174-179.
- [25] C. Pokor, Y. Brechet, P. Dubuisson, J.-P. Massoud, A. Barbu. Irradiation damage in 304 and 316 stainless steels: experimental investigation and modeling. Part I: Evolution of microstructure. *Journal of Nuclear Materials* 326 (2004) 19-29.
- [26] C. Sun, et al. Superior radiation-resistant nanoengineered austenitic 304L stainless steel for applications in extreme radiation environments. *Scientific reports* 5 (2015) 7801
- [27] *Program on Technology Innovation: Effects of Post Irradiation Annealing on IASCC*. EPRI, Palo Alto, CA: 2015. 3002005475.
- [28] C. Pokor, Y. Brechet, P. Dubuisson, J.-P. Massoud, A. Barbu. Irradiation damage in 304 and 316 stainless steels: experimental investigation and modeling. Part II: Irradiation induced hardening. *Journal of Nuclear Materials* 326 (2004) 30-37.
- [29] G.M. Pharr, E.G. Herbert, Y. Gao. The indentation size effect: A critical examination of experimental observations and mechanistic interpretations. *Annual Reviews in Materials Research* 40 (2010) 271-292.
- [30] J.J. Roa, G. Fargas, A. Mateo, E. Jiménez-Piqué. Dependence of nanoindentation hardness with crystallographic orientation of austenite grains in metastable stainless steels. *Materials Science & Engineering A* 645 (2015) 188-195.