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The effects of long-time irradiation and thermal aging on 304 stainless steel

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Abstract

The effect of long-time irradiation and thermal aging on the tensile, fracture, and swelling properties of 304 stainless steel were studied. Samples of cold-worked and annealed 304 were irradiated in EBR-II at temperatures between 371–400°C or thermally aged in the EBR-II primary core basket at 371°C for times up to 18 years. Samples of annealed steel were irradiated in rows 4 and 12 of EBR-II to determine the effect of dose rate. No significant changes in tensile properties or density occurred in cold-worked thermally aged steel. For samples irradiated near 370°C, decreasing the dose rate caused an increase in swelling and had no measurable effect on tensile properties.

1. Introduction

A large number of nuclear reactor core components are constructed from 304 stainless steel [1]. Therefore, performance of 304 stainless steel under long-time, low dose rate irradiation is important to extended life operation. As part of EBR-II reactor materials surveillance (SURV) program [2–6], test samples of 304 stainless steel were placed into EBR-II in 1965, with the intention of determining microstructural, corrosion, and mechanical property changes due to irradiation and thermal aging. This work reports on the swelling, tensile properties, fracture modes, and microstructural changes that occur in 304 stainless steel irradiated at temperatures from 371–400°C or thermally aged at 371°C over an 18-year period.

The peak displacement rate for the materials in the SURV subassemblies was approximately 6.5×10^{-8} dpa/s. This displacement rate is about two orders of magnitude lower than used in a typical accelerated reactor materials test but within the range of displacement rates experienced by commerical light-water reactor (LWR) core components [7]. While significant data on the mechanical properties of irradiated structural alloys exist in the literature (for reviews see [8,9]), the data typically come from high displacement rate experiments. Since some material properties are known to be displacement-rate dependent, the effect of low dose rate irradiation on swelling and mechanical properties needs to be determined. Additionally, by comparing the changes in mechanical properties caused by low dose rate irradiation to the changes in mechanical properties caused by thermal aging, the temperature effects can be isolated from the radiation effects. Both the response to displacement rate and the effect of irradiation as compared to thermal aging are analyzed in this paper.

2. Experiment

Two different lots of 304, two different processing histories (stress relieved and annealed), and two different core locations (rows 4 and 12) were used in these tests. The annealed material was the same used in constructing the EBR-II cover plate. Throughout this paper, the stress relieved samples will be designated as surveillance (SURV) material and the annealed samples will be designated cover plate material. Surveillance samples were 20% cold-worked with a stress relief heat treatment

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Table 1
Composition of test samples (wt%)

Material	C	Cr	Cu	Fe	Mn	Mo	Ni	P	S	Si	Other
SURV 304	0.08	18.38	0.18	Bal.	0.89	0.21	10.0	0.018	0.020	0.68	
EBR-II cover plate 304	0.06	18.57	–	Bal.	1.17	0.16	9.46	0.015	0.009	0.57	0.013 Sn, 0.003 Pb

of 468–496°C for 2 h following machining. Stress relieved SURV samples that were irradiated in row 12 of EBR-II will be designated S12. Some additional SURV material was thermally aged in the EBR-II primary core basket at 371°C. Cover plate material was solution annealed, machined, and then given a stress relief heat treatment of 468–496°C for 2 h. Cover plate samples were irradiated in rows 4 and 12 and will be designated CP4 and CP12, respectively. Table 1 lists the bulk composition of the two different lots of 304 stainless steel.

Samples from eight different SURV subassemblies were examined. Six of the SURV subassemblies were irradiated in row 12 at temperatures ranging from 371–400°C to peak doses of ~20 dpa. Two subassemblies were thermally aged, one at 371°C for 2994 days and a second at 371°C for 6525 days. Although displacement rates varied along the length of each subassembly, the peak displacement rate was approximately 6.5×10^{-8} dpa/s in row 12 and 1×10^{-6} dpa/s in row 4. Samples taken above and below the core centerline displacement rates as low as about half the peak displacement rate.

For these experiments, density, tensile properties, fracture mode, and microstructure were examined. Fig. 1 presents the dimensions of the tensile and density samples. Density was measured using an immersion density technique. To determine tensile properties, stress–strain curves were obtained at room temperature and at 371°C. Yield strength (0.5% offset), ultimate tensile strength, reduction in area, and uniform elongation were determined. Tensile tests were performed on multiple samples from each subassembly at a strain rate of 3×10^{-4} s^{-1}. Fracture surfaces of the failed tensile specimens were examined in a scanning electron microscope. Microstructure was examined by preparing transmission electron microscopy (TEM) foils from either density samples or from material retrieved from tensile specimens. The experimental conditions are listed in Table 2.

3. Results

The results of the density, tensile property, microstructure, and fractography measurements are presented in the sections below.

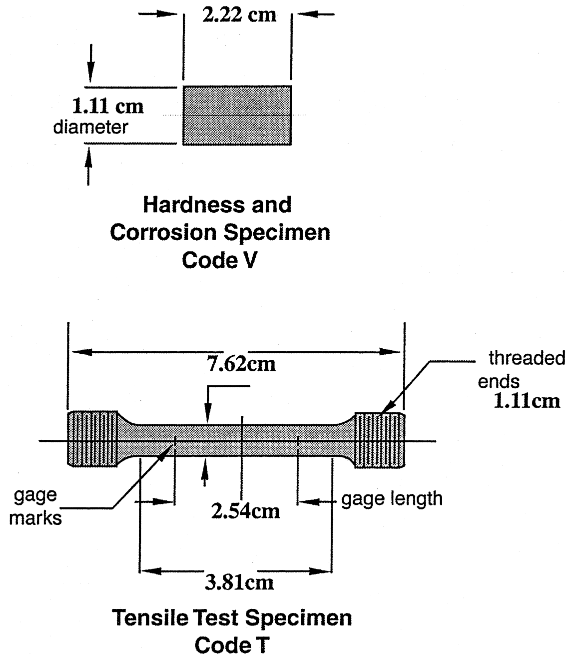

Fig. 1. Design of experimental tensile and hardness SURV samples. Density and microstructural samples were prepared from the hardness samples.

3.1. Density

Fig. 2 compares the effects of irradiation and thermal aging on the density of 304 stainless steel. Swelling of row 12 surveillance samples (S12) is shown for two exposure times. The uncertainty of the immersion swelling density measurements is 0.25%. Samples were irradiated for 2994 and 6525 days or thermally aged for 2994 and 6525 days. In the irradiated samples, the swelling increases with irradiation dose, reaching 2% by 19.6 dpa. No significant densification of 304 stainless steel is seen at low dose. This differs from 316 stainless steel where significant densification is seen under similar irradiation conditions [10]. For the thermally aged samples, no significant change (swelling or densification) in density occurs over the 18-year period.

Fig. 3 further amplifies the effect of irradiation on swelling. Swelling is plotted as a function of dose for row 12 surveillance samples and the row 12 cover plate samples. The swelling of the cover plate material was

Table 2
Experimental samples

Designation	Treatment	Irradiated tensile	Thermally aged tensile	Irradiated density	Thermally aged density
SURV-row 12 (S12)	Stress relieved	0–14 dpa 371–400°C		0–20 dpa 371–400°C	
SURV-core basket	Stress relieved		0–6525 days 371°C		0–6525 days 371°C
Cover plate-row 12 (CP 12)	Solution annealed	0–18 dpa 371–400°C		16 dpa 395–404°C	
Cover plate-row 4 (CP 4)	Solution annealed	0–11 dpa 371–400°C			

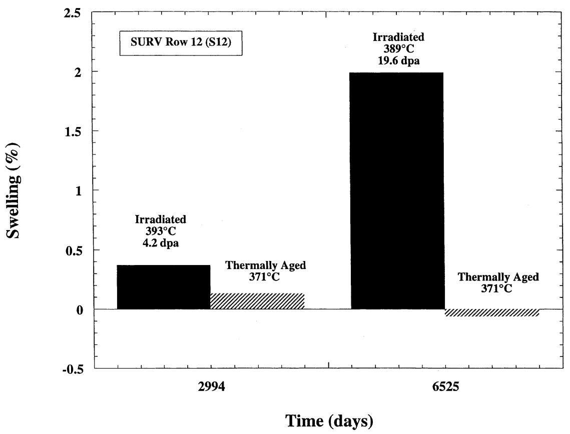

Fig. 2. Swelling due to irradiation and thermal aging near 371°C. Thermal aging has little effect on the density of 304 stainless steel.

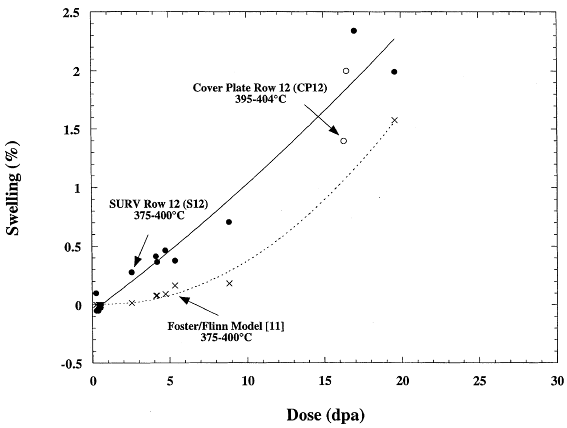

Fig. 3. Swelling as a function of dose for surveillance (cold-worked) and cover plate (annealed) material. No difference in swelling is noted between the two different sample materials.

measured by sectioning a piece from tensile specimens following tensile testing and was only measured at higher dose. The swelling increases continually with increasing dose, reaching 2% by 19.6 dpa. While austenitic stainless steel alloys eventually reach a terminal swelling rate of 1% dpa^{-1} [9], the swelling of the SURV 304 samples at 20 dpa is near 0.1% dpa^{-1} and therefore is still early in the transient portion of the swelling versus dose behavior.

3.2. Tensile properties

Analysis of the row 12 surveillance samples (S12) provides a comparison of the effects of thermal aging and irradiation on yield strength of stress relieved 304 stainless steel. Fig. 4 shows the room temperature yield strength for samples either irradiated or thermally aged for 2994 and 6525 days. Neither irradiation nor thermal aging increases the yield strength significantly over the non-irradiated/non-aged material. For dose up to 13 dpa and aging times of 6525 days, the yield strength does not vary significantly between the irradiated and thermally aged conditions.

The effect of cold-work on room temperature yield strength can be seen by contrasting the stress relieved

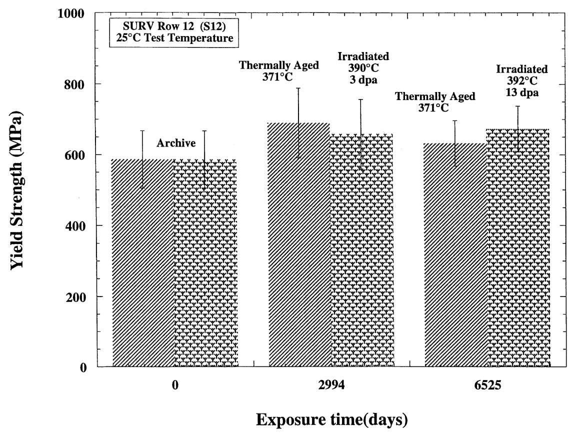

Fig. 4. Yield strength changes as a function of exposure time for irradiation and thermal aging near 371°C. The uncertainty is the SD of the yield strength.

and annealed samples irradiated in row 12, as seen in Fig. 5. The yield strength of the stress relieved material (S12), which started with considerable cold-work, does not change significantly with radiation dose. The yield of the annealed cover plate material increases by a factor of about three over a dose of about 5 dpa.

The effect of displacement rate on yield strength can be examined by comparing cover plate samples irradiated in rows 4 and 12. Fig. 6 compares the yield strength at 371°C (also the irradiation temperature) for the row 12 cover plate material (CP12) and the row 4 cover plate material (CP4). The yield strength of the row 12 cover plate material increases by about a factor of three over a dose of about 5 dpa. Even though the dose rate in row 4 is about two orders of magnitude larger than that in row 12, the yield strength of the material irradiated in row 4 is similar to that irradiated in row 12. No measurable effect of displacement rate on dose rate on the yield strength is evident.

The irradiation hardening can be examined by comparing the ratio of the yield strength (σ_y) to the ultimate tensile strength (σ_u) as a function of dose. As $1-(\sigma_y/\sigma_u)$ approaches zero, the material becomes harder. Fig. 7 plots $1-(\sigma_y/\sigma_u)$ for the row 12 surveillance material (S12) tested at room temperature, the row 12 cover plate material (CP12) tested at 371°C, and the row 4 cover plate material (CP4) tested at 371°C. The cold-worked surveillance material (S12) does not significantly harden, while the annealed cover plate material does (the yield strength approaches the ultimate tensile strength). The hardening occurs over about the first 4 dpa. The hardening can also be seen by analyzing the total elongation as a function of irradiation dose. Fig. 8 plots the uniform elongation for the row 12 cover plate material (CP12) and the row 4 cover plate material (CP4) for tensile tests at 371°C . The total elongation for the cover plate

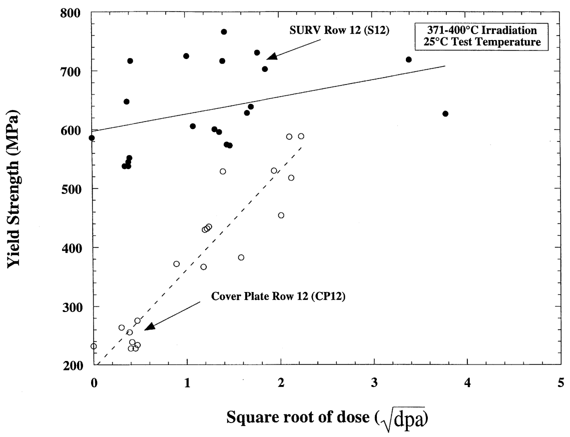

Fig. 5. Yield strength as a function of dose for annealed (CP12) and cold-worked (S12) 304 irradiated in row 12.

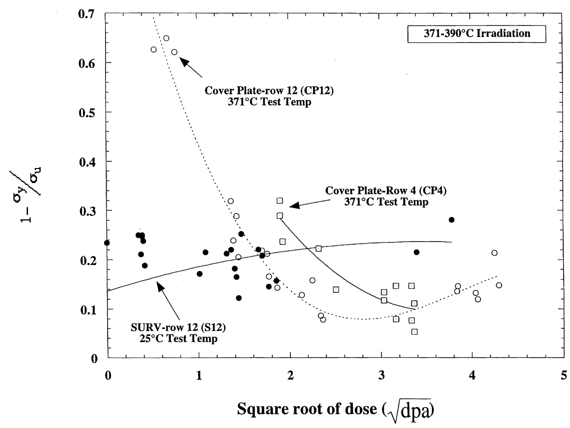

Fig. 7. Strength ratios as a function of irradiation dose.

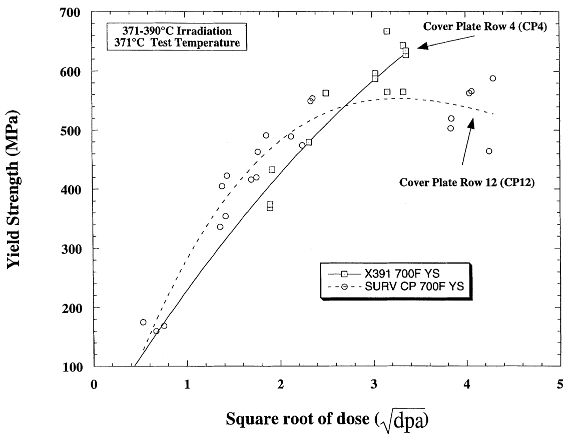

Fig. 6. Yield strength as a function of dose for annealed 304 irradiated in rows 4 and 12 (CP4 and CP12).

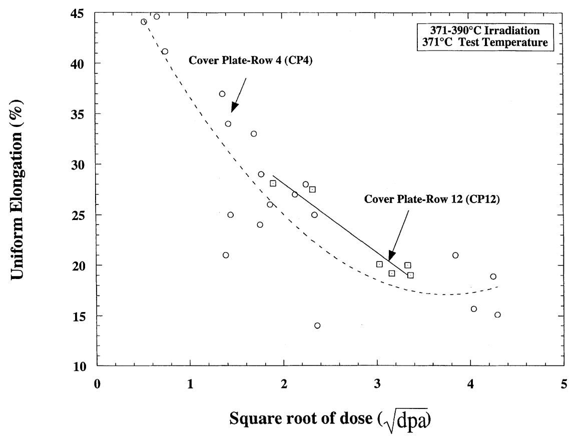

Fig. 8. Uniform elongation as a function of irradiation dose for annealed 304 irradiated in rows 4 and 12 (CP4 and CP12).

material in rows 4 and 12 decreases with increasing dose. No difference is seen in the total elongation between the material irradiated in row 4 and in row 12.

The ductility of 304 stainless steel decreases with increasing hardening. The uniform elongation as a function of irradiation hardening is shown in Fig. 9 for the row 12 surveillance material (S12), the row 12 cover plate material (CP12), and the row 4 cover plate material (CP4) tested at 371°C. For all three materials, as the yield strength approaches the ultimate tensile strength ($1 - (\sigma_y/\sigma_u)$ approaches zero), the total elongation decreases. In Figs. 7–9, the row 4 cover plate, row 12 cover plate, and row 12 surveillance material all have similar behavior at higher dose. Neither the initial cold-work composition, nor irradiation damage rate significantly affects the material hardening. Fig. 10 groups all of the 304 total elongation data from Fig. 9 into a single group and plots it versus $1 - (\sigma_y/\sigma_u)$. A best linear fit to the data is plotted along with the 95% confidence limits. As $1 - (\sigma_y/\sigma_u)$ approaches zero, the total elongation extrapolates to 15.2 ± 8.9. Therefore, 304 stainless steel irradiated at 371–390°C and tested at 371°C maintains significant residual ductility.

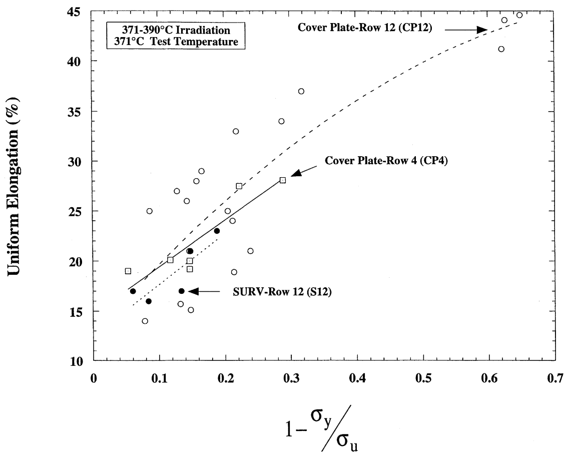

Fig. 9. Uniform elongation as a function of strength ratios for cover plate and surveillance materials.

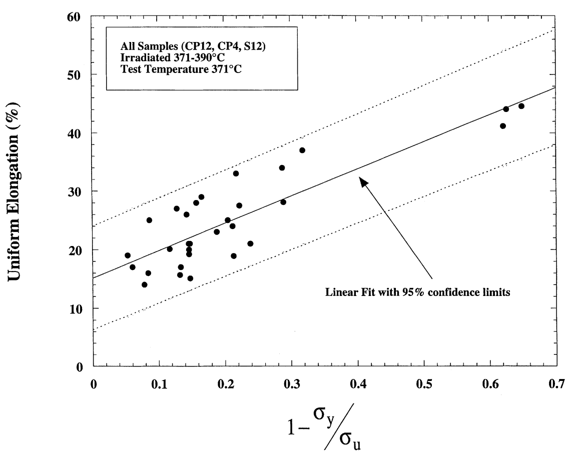

Fig. 10. Uniform elongation as a function of strength ratios for cover plate and surveillance materials, all data grouped as a single data set.

3.3. Fractography

Even though samples irradiated at different dose rates showed similar tensile properties, the fracture mode was slightly different. Figs. 11 and 12 show the fracture morphology at two different magnifications for cover plate samples irradiated to 8 dpa in rows 4 (CP4) and 12 (CP12) and tested at 371°C. The row 12 sample (low dose rate) displayed less fine-scale dimpling and more tearing while the row 4 sample (high dose rate) had a dimpled fracture surface typical of ductile failure.

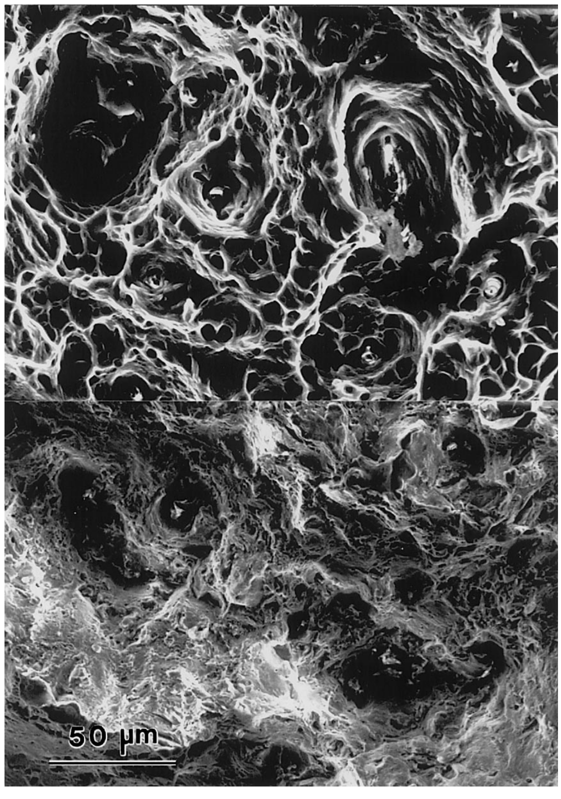

Fig. 11. Fracture surfaces from cover plate specimens irradiated to 8 dpa and tested at 371°C.

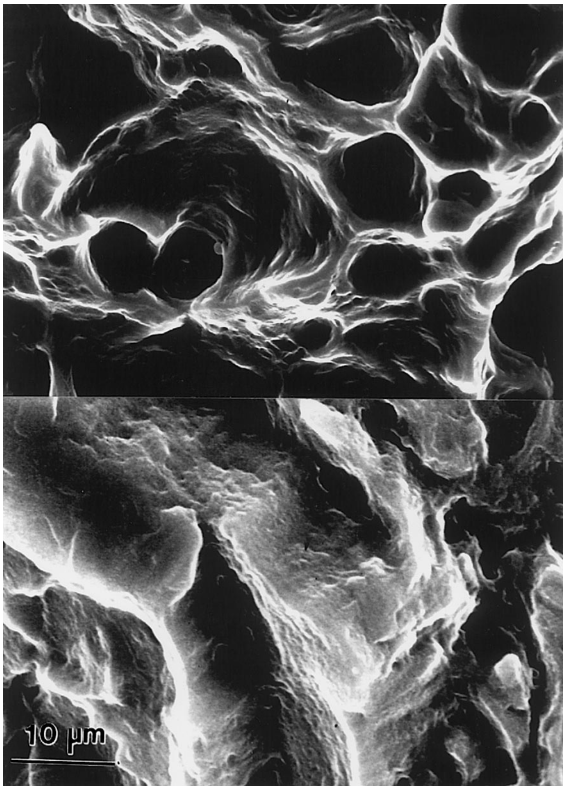

Fig. 12. Fracture surfaces from cover plate specimens irradiated to 8 dpa and tested at 371°C.

3.4. Microstructure

TEM samples were made from SURV density specimens or by cutting material from cover plate tensile specimens. The cover plate samples were taken from an area approximately 3.2 mm from the fracture surface. Fig. 13 shows the evolution of void size as a function of dose for the row 12 cover plate material. With increasing dose, the mean void diameter increases and the void size distribution widens. The density of voids decreases slightly.

The effect of dose rate on void size distribution can be seen in Fig. 14 which shows the void size distributions from samples of cover plate material irradiated in rows 4 and 12. For two samples irradiated to approximately the same dose, the voids are larger in the lower dose rate sample (row 12). In addition to having larger voids, the distribution is wider in the row 12 sample.

The effect of initial microstructure and cold-work is demonstrated in Fig. 15. The void distributions for cold-worked and stress relieved surveillance (S12) and annealed cover plate (CP12) row 12 samples are shown. The void distributions were taken from samples irradiated at nearly the same temperature but to different doses. The void microstructures are significantly differ-

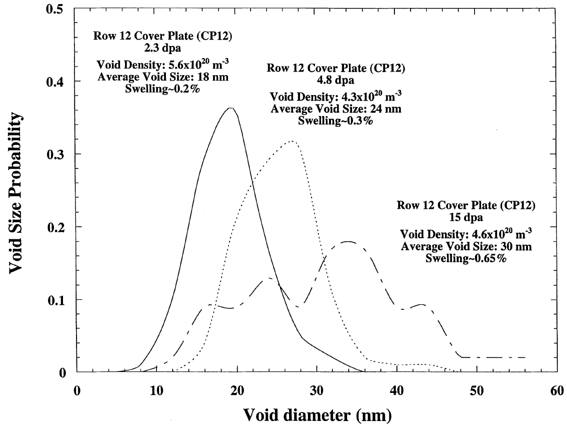

Fig. 13. Void size distributions for cover plate samples irradiated in row 12 to different doses.

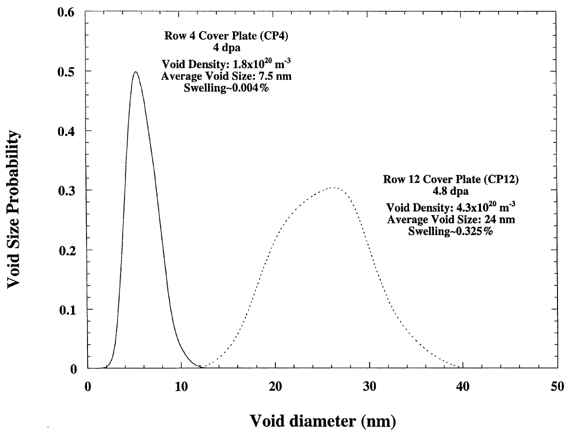

Fig. 14. Comparison of void size distributions for samples irradiated in row 4 (high dose rate) and row 12 (low dose rate).

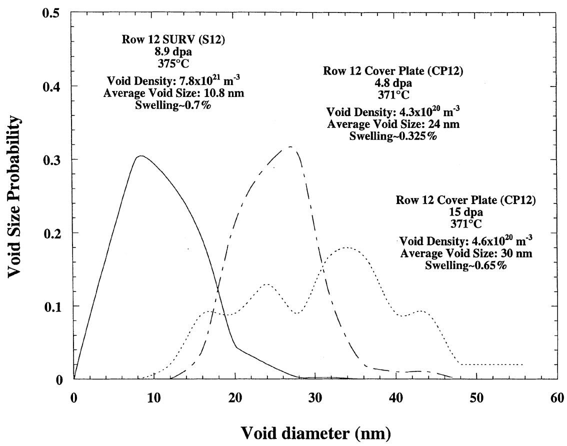

Fig. 15. Comparison of void size distributions for samples irradiated in row 12. Surveillance (SURV) material was milled annealed and cover plate (CP) material was solution annealed.

ent. The annealed cover plate material has a smaller density of much larger voids. This holds true for doses both greater and less than the stress relieved surveillance material.

4. Discussion

The discussion section will focus on three areas: the effect of dose rate, the effect of cold-work, and the differences between thermal aging and irradiation.

4.1. The effect of dose rate on swelling, tensile properties, and fracture mode

Comparison of the properties of cover plate material irradiated in row 4 (CP4) and row 12 (CP12) provides information on the effect of displacement rate on swelling, tensile properties, and fracture mode. For a known void distribution, the void swelling is calculated by

$$\frac{\Delta V}{V} = \frac{4\pi}{3} \int_0^\infty R^3 f(r)\,\mathrm{d}r, \tag{1}$$

where R is the void radius and $f(r)$ is the density function that describes the probability for each possible void diameter. Swelling depends on both the average void size and the distribution of sizes about the average. A large average void size or a wider distribution leads to greater swelling. Fig. 14 indicates that, at temperatures near 400°C, 304 stainless steel irradiated at lower dose rate undergoes more rapid swelling. The average void diameter is larger and the width of the distribution is greater.

The effect of displacement rate on swelling of 304 stainless steel is also examined using Fig. 3. Foster and Flinn [11] devised an empirical stress-free swelling equation for 304 stainless steel. The correlation was based on density measurements taken on samples irradiated in EBR-II covering temperatures from 393–542°C and fluence levels up to 9.3×10^{22} n/cm^2 ($E > 0.1$ MeV) ($\sim$35 dpa). The samples used by Foster and Flinn were irradiated in EBR-II experimental positions. These positions were located in inner rows where the displacement rate is about two orders of magnitude larger than that experienced by the SURV samples in row 12 (typically $\sim 1 \times 10^{-6}$ dpa/s). The predictions of the Foster–Flinn model extrapolated down to the temperature of the SURV specimens (375–400°C) are also plotted on Fig. 3. The Foster–Flinn predictions are consistently smaller than the SURV swelling measurements (the uncertainty in swelling from an immersion density measurement on 304 stainless steel is typically ±0.25%). The comparison indicates that at temperatures near 370°C, lower dose rate irradiation causes greater swelling at a given dose. Greater swelling at lower displacement rate in 304 stainless steel irradiated near 370°C was also found by Porter et al. [12] and Garner [13,14] and predicted theoretically by Mansur [15]. In contrast to the measurements of this study, Brager et al. [16] compared the effect of displacement rate on the microstructure of 304 stainless steel and found the void density and void diameter were larger in the higher dose rate sample. In Brager's study, the high rate specimen was irradiated at 392°C to 3.1 dpa while the low rate specimen was irradiated at 371°C to 2.6 dpa, conditions similar to the conditions in this study.

Even though the swelling of 304 varies with displacement rate, the tensile properties in this study do not significantly vary with dose rate. The contribution to hardening from the void distribution can be calculated using disbursed barrier theory. The change in yield strength due to voids is given by

$$\Delta\sigma = \sqrt{3} G \mathbf{b} \frac{\sqrt{\rho_\mathrm{v} d_\mathrm{v}}}{\beta_\mathrm{v}}, \tag{2}$$

where G is the shear modulus, $\mathbf{b}$ the Burger's vector, ρ_v the void density, and d_v is the void diameter. At 375°C, the shear modulus is 6.7×10^{10} Pa and the Burger's vector is 2.5×10^{-10} m for austenitic stainless steel [16]. Calculating the increases in yield strength in the cover plate material due to voids at 2.3, 4.8, and 15 dpa gives 92, 93, and 108 Mpa. Comparing these to the increases in yield strength of the cover plate material (Fig. 5), the increase due to the voids is only $\sim$25% of the total increase. Since the void contribution to yield strength is small compared to the scatter in yield strength measurements, the variation of void distribution due to displacement rate is not seen in the yield strength.

Even though differing dose rate did not significantly affect tensile properties, the fracture surfaces for annealed samples tested following 4 dpa of irradiation were slightly different. While the sample irradiated at higher dose rate (CP4) exhibited transgranular plastic dimpling as typically seen in unirradiated austenitic stainless steel, the fracture surface in the material irradiated at lower dose rate (CP12) exhibits less dimpling and the appearance of fine-scaled tearing. The higher density of larger voids in CP12 may provide lead to the greater tearing. As pointed out by Garner [9], with increasing swelling, the fracture surface makes a transition from ductile dimpling to channel fracture. The early stages of this transition may be evident in the row 12 sample.

4.2. Effect of cold-work

The effect of cold-work on swelling can be examined by comparing the SURV (S12) material with the annealed cover plate (CP12) material irradiated in row

12 (see Fig. 15). Swelling measurements at 8.9 dpa for the SURV material and 15 dpa for the cover plate material are similar, but the cover plate material has a smaller density of larger voids. Even at 4.8 dpa, the voids in the cover plate material are larger than the SURV material at 8.9 dpa. Interpolating the cover plate data to around 9 dpa and comparing to the SURV material at 8.9 dpa. Interpolating the cover plate data to around 9 dpa and comparing to be SURV material indicates that the cold-worked SURV material has greater swelling. The greater swelling in the cold-worked material differs from that of Busboom et al. [17] who found that increased cold-work reduced the swelling of 304 stainless steel irradiated at 450°C. Since the SURV and cover plate material are not from the same lot of 304 stainless steel, the slight differences in composition between the SURV and cover plate material may have a greater effect than the cold-work.

The change in mechanical properties as a function of dose is typical of irradiated 304 stainless steel. For the annealed cover plate material (CP12), the yield strength increases and uniform elongation decreases with increasing dose. For the stress relieved (S12) material that starts with significant cold-work, there is little change in either yield strength or uniform elongation. As noted in describing Fig. 10, the uniform elongation as a function of irradiation hardening $(1-(\sigma_y/\sigma_u))$ is independent of initial cold-work, damage rate, or composition, i.e., all the data points fall within a similar scatterband.

4.3. Irradiation versus thermal aging

The effect of irradiation versus thermal aging can be analyzed by comparing the irradiated surveillance (S12) material with thermally aged surveillance material. While an increase in radiation dose causes a decrease in density, no change in density occurs due to thermal aging. Neither irradiation nor thermal aging causes a significant increase in room temperature yield strength for initially cold-worked material. Therefore, the void distribution that leads to swelling in the irradiated samples either does not contribute significantly to hardening in this cold-worked material or the hardening due to voids is balanced by recovery of the dislocation structure.

5. Conclusions

The effect of radiation dose rate, cold-work, and thermal aging on 304 stainless steel has been studied. For samples irradiated near 370°C, decreasing the dose rate causes an increase in swelling, has no measurable effect on tensile properties, and changes fracture mode from transgranular dimpled failure to a finer-scaled tearing. For doses to 18 dpa, the void distribution does not significantly affect the tensile properties. Regardless of initial cold-work, composition, or dose rate, 304 retains significant ductility up to doses of 18 dpa. In material with significant initial cold-work, neither irradiation to 13 dpa nor thermal aging for 18 years has a significant effect on tensile strength or uniform elongation.

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