

# Irradiation-induced swelling of pure chromium with 5 MeV Fe ions in the temperature range 450–650 °C

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## ABSTRACT

A surface coating using pure chromium has been proposed to increase the accident tolerance of Zircaloy cladding in pressurized water reactors. However, there is not much irradiation experience with Cr alloys and especially pure Cr. In the present study, pure chromium was irradiated with 5 MeV Fe ions to 50 peak dpa (displacements per atom) at temperatures of 450, 500, 550, 600 and 650 °C. Then irradiation at the peak swelling temperature of 550 °C was conducted to 50, 100, 150 peak dpa. Swelling at 50 dpa was observed over the entire temperature range studied, 450–650 °C, but appeared to be decreasing strongly at the temperature boundaries of the experiment. After an initial transient of rapid swelling, chromium was observed to swell at a rate of ~0.03–0.04%/dpa (up to 120 local dpa), which is much lower than pure Fe at 0.2%/dpa. This low swelling rate was found to be relatively insensitive to dpa rate, which varied by a factor of ~2 over the depth of data collection. Swelling was observed to begin quickly with an incubation period less than 10 dpa. Self-organization in the form of void ordering was observed to be developing at 50 dpa, becoming better defined with increasing dose. The void alignment direction is determined to be the  $\langle 111 \rangle$  axial direction.

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## 1. Introduction

The Fukushima Daiichi reactor accident displayed the weakness of Zircaloy cladding under loss of cooling accidents in rapid hydrogen generation from the steam oxidation reaction leading to explosions [1]. Among various approaches to improve the accident tolerance of the fuel pin, coating of the Zircaloy cladding surface is promising, especially if a thin layer of the chosen coating material can minimize impact on neutron economy, thereby allowing the low neutron absorption benefit of Zircaloy cladding to be retained [2–5].

Chromium is a promising coating candidate material that has a reasonable neutron capture cross-section and good hardness and wear resistance. Most importantly, chromium can form a thin layer of tenacious chromium oxide on the cladding surface for superior corrosion resistance, which makes it ideal as additional protection on Zircaloy cladding for enhanced accident tolerance under normal and accident conditions for a pressurized water reactor (PWR). Initial studies at various laboratories indicate that chromium is a vi-

able choice using various coating techniques [2–6]. For instance, cold spray coating technology of chromium on Zircaloy-4 has been developed, showing good quality control on interface adhesion and porosity [6]. Chromium coatings do not appear to involve significant interface reaction with Zircaloy-4, which is an additional benefit. Many other coating materials such as FeCrAl and MAX phase have been shown to develop reaction interfaces, an issue that is problematic at high damage levels [7,8].

The radiation response of chromium has not been studied in the West, but this metal in both lightly and heavily alloyed forms was considered as a potential fast reactor cladding material in the Soviet Union. Several low-alloyed chromium candidates were irradiated with neutrons in Research Institute of Atomic Reactors in Russia and were also irradiated with Cr ions in the Kharkov Institute of Physics and Technology in Ukraine. The latter laboratory also irradiated pure chromium for comparison. Some data were published in Western journals but most of the data from these studies are available only in older, internal and limited-distribution reports written in Russian. These data are reviewed in this report.

Three low alloying chromium-base alloys were irradiated in Russia, using both the SM-2 mixed spectrum reactor and the BOR-60 fast reactor to doses as high as 45 dpa (displacement per atom),

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with one dilute chromium alloy designated BH-2 K with minor additions of La, V, Ta and C (<1% total) reaching swelling levels of 2.2 to 2.8% at 650–750 °C and doses of 40–45 dpa. One significant surprise at the time was that swelling was observed at all temperatures studied in the 400–829 °C range. This temperature range is above the normal operation range of PWRs, but temperatures lower than 400 °C were not examined since these experiments were directed primarily toward fast reactor application. The alloy compositions and the results of these experiments are provided in the supplementary document.

Very limited Russian neutron data were reported [9,10]. A series of 3 MeV Cr<sup>3+</sup> ion irradiations were conducted on pure chromium in the Ukraine over the same temperature range, showing relatively good agreement with the neutron data, with ion-induced swelling starting immediately without significant incubation delay and reaching 4–7% at ~80 dpa in the range 650–750 °C [11]. The ion-induced swelling rate of pure chromium at 650 °C appears to be on the order of ~0.03%/dpa. It also appears that swelling at very low doses involves a higher swelling-rate transient since the data do not extrapolate back to zero swelling [11]. These data are also provided in the supplementary document.

The data range employed in the earlier ion irradiation studies was expanded by Bryk et al. and presented in an open literature paper as a base for comparison with the ion-induced swelling of three chromium-base alloys, leading to the conclusion that the swelling behavior was not very sensitive to the minor low alloying composition, although the pure Cr data were not covered in any depth in this paper [12]. In Bryk's paper the irradiations were conducted to doses as high as 180 dpa over the range 550–800 °C [12]. Swelling reached ~9% at 180 dpa and 730–750 °C in one of the chromium-base alloys but was observed to develop significant spatial heterogeneity arising from phase decomposition of the alloys. It was noted that voids developed almost immediately at very low doses in both pure chromium and the alloys. One micrograph was presented that showed that one of the alloys exhibited development of void ordering into a superlattice, but the temperature at which ordering occurred was not specified in the paper.

Kuprin et al., also in Ukraine at the same laboratory, more recently studied swelling of pure arc evaporation deposited chromium induced by 1.4 MeV Ar ion irradiation at 400 °C to 5, 15, and 25 dpa [13]. They found swelling of 0.16% at 5 dpa and 0.66% at 25 dpa, again suggesting a swelling rate of ~0.03%/dpa at 400 °C. No mention was made of void ordering in this study. Kuprin's primary conclusion was that swelling in chromium appears to be too small to be a major concern in light water reactor applications where the dose of fuel cladding would never reach 25 dpa [13]. This study suffers somewhat from the use of a rather shallow-penetrating ion, requiring data extraction very close to the surface (~100 nm) in order to avoid the very strong effect of the injected interstitial. If there is a strong effect of temperature on the swelling it was not explored in this single temperature experiment, but the combined results of both the Bryk and Kuprin studies imply that while there is a temperature dependence of the void size and concentration distributions, the post-transient swelling rate is very small at ~0.03%/dpa and not very sensitive to irradiation temperature over the range of 400–700 °C [12,13]. Note that both the Bryk and Kuprin studies were conducted on the same accelerator (ESUV-1) but years apart and with different ions, different energies and different dpa rates.

Another published Russian report addressed the phase stability and void swelling at 600–750 °C in the BOR-60 fast reactor of two highly alloyed candidates, Cr-10Fe-Zr,Y and Cr-35Fe-Zr,Y [14]. For the purposes of the current study it is sufficient to note that swelling was observed in these alloys under most irradiation conditions.

In the current study, the Texas A&M 3 MV NEC tandem accelerator was used to obtain an expanded understanding of the temperature, dose and dose rate dependence of void swelling in pure chromium. It was also desired to explore the depth dependence of swelling over the full ion range. At this point it is not certain whether neutron-induced swelling will occur at PWR-relevant temperatures nor is it certain whether there is a strong temperature dependence of the post-transient swelling rate that would require the use of a temperature shift associated with the much higher-than-neutron dpa rate used in the ion simulation.

However, the strong oxide-forming nature of chromium poses a problem for ion simulation of swelling in our accelerator facility. Ideally, Cr self-ion irradiation is the best choice for high levels of damage introduction into pure chromium, but Cr ion beam production using SNICS (Source of Negative Ions by Cesium Sputtering) is very weak with unstable ion current, largely due to its strong oxygen affinity constantly sealing the surface of the ion source. Therefore, in the present study, 5 MeV Fe ion irradiation was performed to study the swelling dependence on damage level, dpa rate and irradiation temperature, as the first step to identify and evaluate irradiation performance limitations of chromium coating.

In contrast to the previous studies: (1) 5 MeV Fe ions were used to create a much deeper depth profile; (2) the void depth dependence was extracted using FIB-produced lamella to evaluate the influence of the free surface, injected interstitial and depth-dependent changes in dpa rate; (3) the irradiation temperature range was chosen to be 450–650 °C, searching for the swelling peak at 50 dpa; (4) and finally, at the maximum swelling temperature of 550 °C observed at 50 dpa, irradiation was conducted to doses of 100 and 150 peak dpa to obtain a swelling rate over a wide range of displacement dose.

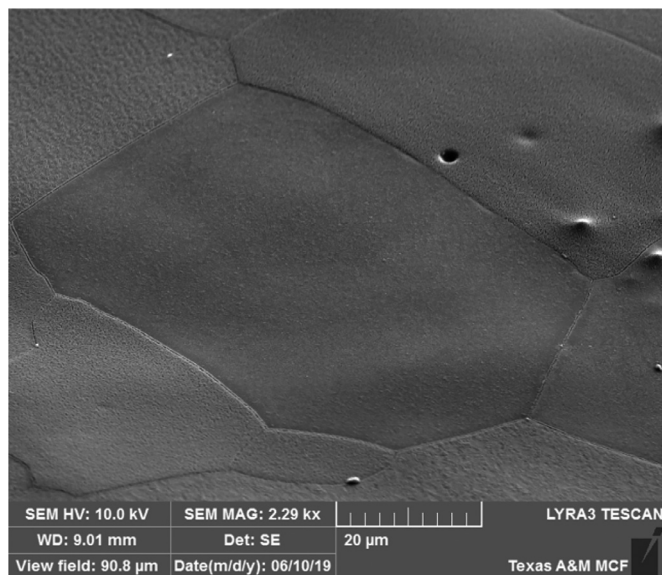
## 2. Experimental procedure

The chromium was obtained from American Elements Inc. Table 1 gives the composition of the Cr sample. The purity of Cr is >99.7%. The largest impurity contribution comes from Fe which is about 0.2%. Each specimen was polished first using SiC paper, followed by further polishing with a Tenupol 5 twin jet electro-polisher. The polishing solution was 5% perchloric acid in methanol. The solution temperature was cooled to be ~20 °C with an external liquid nitrogen bath. The polishing time was ~20 s with a voltage bias of 20 V. After polishing, samples were repeatedly rinsed in methanol. Fig. 1 shows a SEM surface image of a typical polished specimen. Grain boundaries are clearly visible, with no visible scratches within the grains, both indicating that there was no significant residual surface deformation. The typical grain size was found to be ~100 µm.

Each polished specimen had dimensions of 5 mm × 5 mm × 1 mm. The thickness of only 1 mm was chosen to minimize any temperature gradient between the specimen surface and the target hot stage, producing <2 °C temperature rise based on a finite element analysis considering both black body radiation and beam power deposition. The 5 MeV Fe ion irradiation was performed using a static defocused beam to avoid suppression of void nucleation characteristic of rastered beams [15]. Multiple thermocouples were used to monitor the temperature changes on both the target holder and the sample. The target chamber pressure during the irradiation was  $6 \times 10^{-8}$  torr or better. During irradiation, multiple beam deflectors were used to filter out contaminants such as C, N and O [16,17]. Liquid nitrogen trapping in the target chamber was applied to further improve the vacuum. A thermocouple attached to the hot stage was used for automatic temperature control. The temperature fluctuation during the irradiation was <5 °C.

**Table 1**  
Composition of Cr.

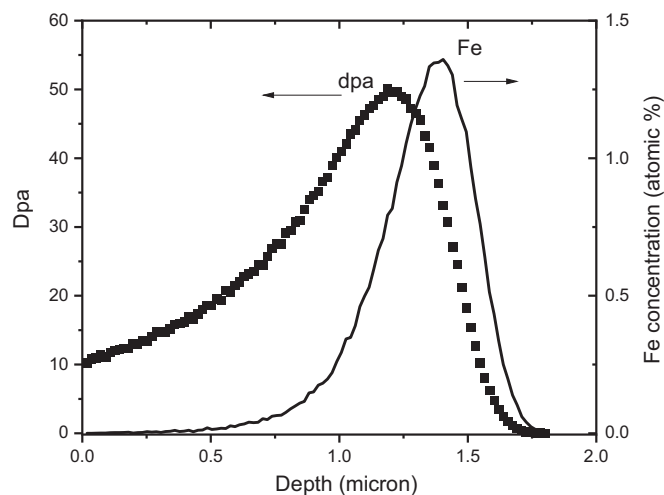
| Element             | Fe   | Al | C  | Ca | Cu | W   | Mo | Na | P | Pb | Si |
|---------------------|------|----|----|----|----|-----|----|----|---|----|----|
| Concentration (ppm) | 2000 | 10 | 40 | 20 | 5  | 100 | 50 | 10 | 5 | 5  | 80 |

**Fig. 1.** SEM image of an electropolished chromium specimen prior to irradiation.

The study included two sets of experiments. First, a temperature dependence study was conducted in which irradiation proceeded to 50 peak dpa at temperatures of 450 °C, 500 °C, 550 °C, 600 °C, and 650 °C where the outer temperature limits were determined by probing for those temperatures where swelling was falling strongly. The second irradiation set was a dose dependence study in which the temperature was fixed at 550 °C (once it was determined to be the maximum swelling temperature in the previous irradiation set) and irradiation then proceeded from 50 to 100 and 150 peak dpa. The Stopping and Range of Ions in Matter (SRIM) code (2013 version) was used for damage calculation [18]. The Kinchin-Pease mode with a Cr displacement energy of 40 eV was used as suggested by Stoller et al. [19]. The peak dpa rate was  $1.7 \times 10^{-3}$  dpa/sec for a beam current of 200 nA over an area of 6 mm × 6 mm.

Bright field transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), with a high angle annular dark field (HAADF) detector on a FEI Tecnai F20 ST with an operating voltage of 200 kV, were used to characterize microstructures. The Focused ion beam (FIB) lift-out technique was used to prepare TEM specimens. The voltage of the Ga beam was 30 kV at the beginning of the lamella preparation. The voltage was reduced to 5 kV for the final thinning. The thickness of each TEM lamellae was measured using standard electron energy loss spectroscopy (EELS) on the FEI Tecnai F20 equipped with a Gatan imaging filter.

**Fig. 2** shows that the maximum predicted range of Fe ions is  $\sim 1.8 \mu\text{m}$  with a peak in the implanted distribution at  $\sim 1.4 \mu\text{m}$  while the dpa damage distribution peaks at  $\sim 1.2 \mu\text{m}$ . Normally one would avoid swelling data collection in the implanted region to avoid complexity from injected interstitial suppression, but in this case we must also avoid the implantation-induced composition change, reaching a peak level of  $\sim 4\%$  Fe at 150 peak dpa. Therefore, the region shallower than 700 nm was used to determine the swelling behavior, but as shown later, there is value in considering the full-range swelling distribution.

**Fig. 2.** SRIM-predicted distributions of dpa damage and Fe concentration, resulting from normal-incidence 5 MeV Fe ions into pure chromium, for a dose corresponding to 50 peak dpa.

### 3. Results

**Fig. 3a** shows a cross-sectional TEM micrograph of pure chromium irradiated at 50 peak dpa and 550 °C. Superimposed are SRIM-predicted dpa and implant profiles. Voids in the ion irradiated specimens are not very visible when imaged in exact focus, and under-focusing is needed to image the voids. **Fig. 3b** shows an enlarged image at the Fe projected range, where voids are present. It has been reported that injected interstitials almost always suppress void formation of most pure metals and alloys in injected region [15,20–26]. As discussed later, the presence of voids at the Fe projected range occurs only at relatively low damage region (50 peak dpa for **Fig. 3a**). When the damage level is further increased, i.e. to 150 peak dpa, void densities drop significantly in this region (to be shown later). **Fig. 3c** shows void depletion along a grain boundary, a feature universally observed in hundreds of previous swelling studies on many metals. **Fig. 3b** and **c** are taken from the regions marked by two boxes in **Fig. 3a**. As for the near-surface region, a high density of voids exist immediately beneath the surface with no denuded zone. Note that some erosion of the TEM lamellae surface during thinning was observed. This may have removed the void denuded zone at the surface, if indeed originally there was one present. But the erosion does not cause noticeable swelling profile shifting. We repeated FIB and TEM characterization on a few samples and found those void swelling distributions were roughly the same within the statistical fluctuations.

One very important finding in the present study is that voids in Cr are becoming progressively aligned with increasing dose. If one looks closely at **Fig. 3a** a developing tendency for void alignment can be seen in the 50 peak dpa specimen. Lines of voids can be seen moving from left to right at an upward angle of  $\sim 15\text{--}20^\circ$ . Since void alignment was not yet evolved into periodic superlattice formation, it is very difficult to collect alignment evidence using diffraction patterns. In order to further understand the alignment, an EBSD scan was performed over the sample surface prior to FIB cutting. Based on grain orientation information, two grains were selected for FIB lift out: one is  $\langle 110 \rangle$  oriented with respect to

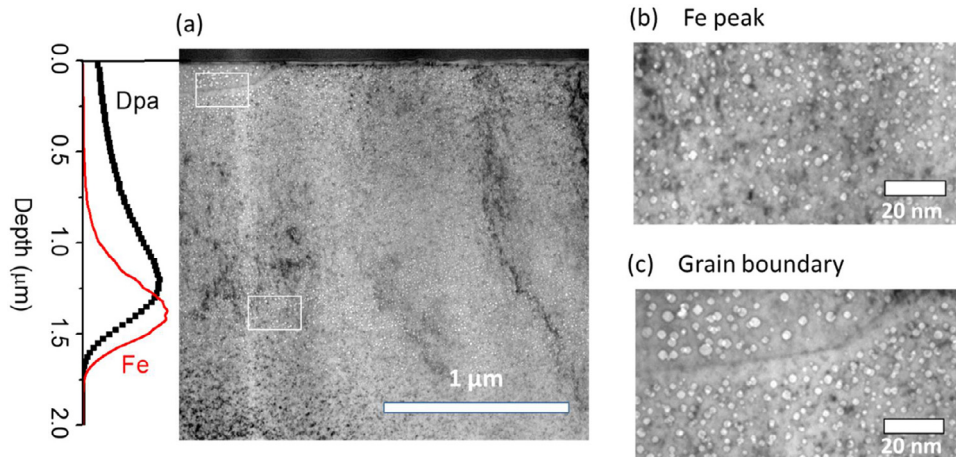


**Fig. 3.** (a) Cross-sectional TEM image (under-focused) of pure chromium irradiated to 50 peak dpa at 550 °C. (b) An image from the region near the projected range of Fe implants, marked by the bottom box in Fig. 3a. (c) An image from a region containing a grain boundary in the peak implanted zone, marked by the top box in Fig. 3a.

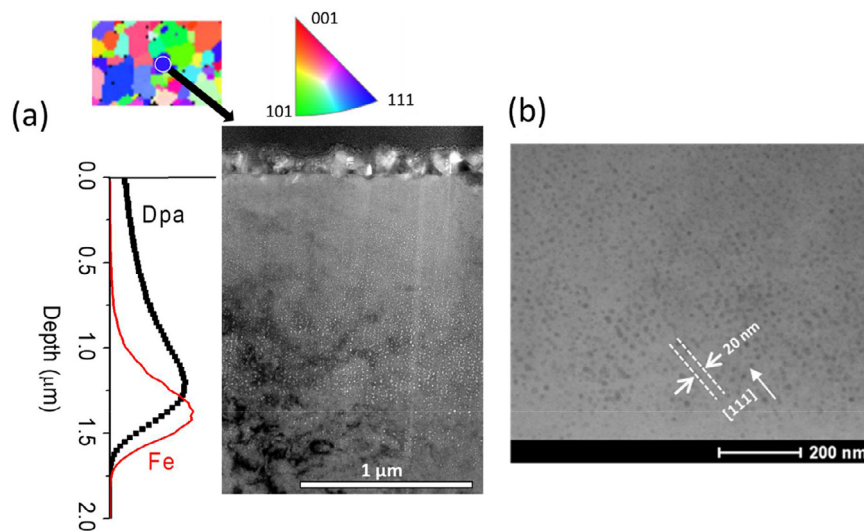


**Fig. 4.** (a) Cross-sectional TEM image of specimen irradiated to 100 peak dpa at 550 °C. The grain is  $\langle 111 \rangle$  oriented. Superimposed are the SRIM predicted dpa and implant profiles. (b) An enlarged STEM image showing development of void alignment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the surface normal and the other is  $\langle 111 \rangle$  oriented. Under slight rotation adjustment about the original sample normal direction, vertical void alignment easily appears (with the alignment direction along the surface normal direction). On the other hand, for the  $\langle 110 \rangle$  oriented grain, void alignment does not appear along the original sample normal direction. These observations indicate that the void alignment direction is along the  $\langle 111 \rangle$  axial direction.

Fig. 4a shows a clearer image of void alignment in the 100 peak dpa specimen at 550 °C. The grain is  $\langle 111 \rangle$  oriented, selected based on EBSD mapping. The voids are aligned along the vertical direction of the image. As additional evidence of easier visualized ordering, Fig. 4b shows an enlarged STEM image under optimized tilting. Voids appear as dark spots with roughly equal spacing, but the regularity is not yet completely established at this dose level. The inter-void distance, judged by two closest parallel void alignment lines, is about 20 nm as shown in Fig. 4b.

The void swelling was calculated by  $V_{\text{void}}/(1 - V_{\text{void}})$ , where  $V_{\text{void}}$  is the volume fraction of voids in the lamella, which is measured by summing individual voids observed from TEM. The uncertainty is largely determined by the thickness variation of the specimen. Electron energy loss spectroscopy (EELS) measurements were repeated at different locations. The statistical error of the

void count was greatly minimized by having a sufficient number of voids.

Fig. 5 shows that the swelling does not vary strongly with depth at 50 peak dpa in the depth range of 200 to 600 nm but does have a quite discernible dependence on temperature. The swelling region is divided into bins with 100 nm width. Each point represents the average value over a depth range  $\pm 50$  nm from that depth point. We selected the range of 200 nm to 600 nm for swelling analysis, to avoid surface effects, injected interstitial effects, and composition changes. A full range void swelling behavior due to these complexities is discussed later. Fig. 6 presents the swelling at 50 peak dpa, averaged over the depth region of 200 to 600 nm, as a function of irradiation temperature. Note that this depth region has no significant composition change due to injected Fe atoms (assuming no Fe diffusion). The maximum swelling is observed at 550 °C, but it cannot be determined from these data alone whether this temperature dependence represents variations in either the transient duration or the post-transient swelling rate or possibly a combination of both.

Fig. 7a and b show the void diameters and void densities of the 50 peak dpa irradiated sample. Void diameters, as shown in Fig. 7a, are largest at 550 °C, although the statistical er-

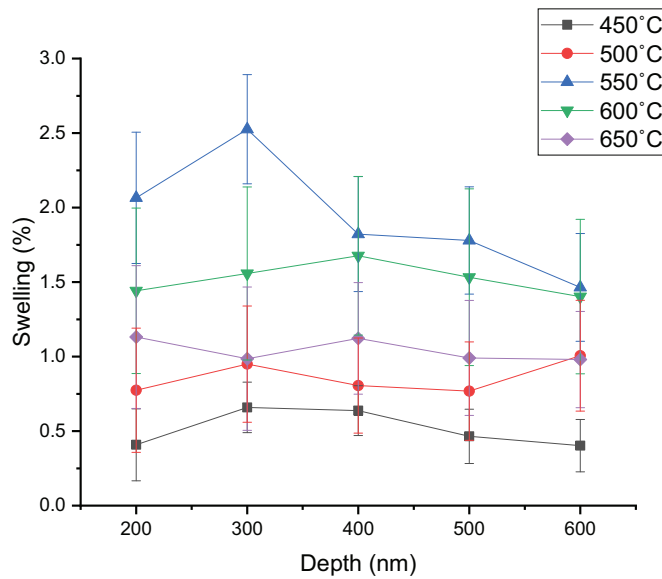


**Fig. 5.** Depth-dependent swelling of pure Cr at 50 peak dpa, measured in the depth region  $\leq 600$  nm to avoid injected interstitial and Fe contamination effects. The error bars represent standard deviation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

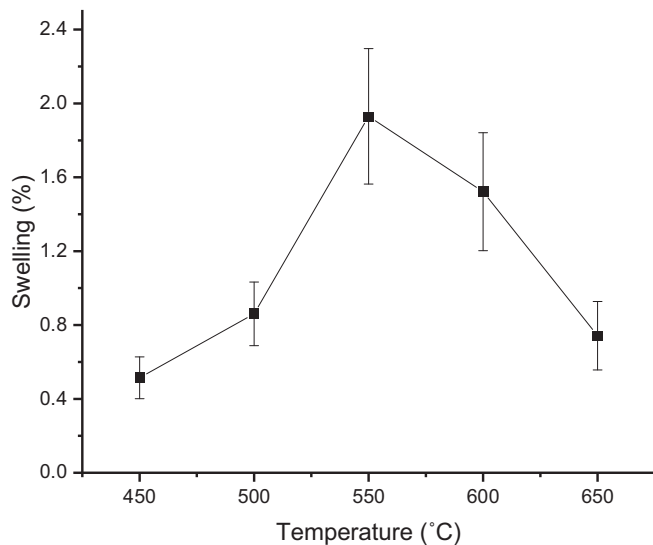


**Fig. 6.** Void swelling of pure Cr irradiated to 50 peak dpa, as a function of irradiation temperature. Swelling values presented here are averaged over the 200 nm to 600 nm depth range to minimize the influence of both the surface and the implanted ions.

ror is relatively large. From 450 to 550 °C, the void diameters increase from  $4.0 \pm 0.9$  nm to  $8.1 \pm 2.1$  nm. From 550 °C to 650 °C, the void diameters decrease from  $8.1 \pm 2.1$  nm to  $6.6 \pm 2.2$  nm. Void densities, on the other hand, reduce from  $1.3 \times 10^{17} \text{ cm}^{-3} \pm 1.7 \times 10^{15} \text{ cm}^{-3}$  at 450 °C to  $5.6 \times 10^{16} \text{ cm}^{-3} \pm 6.3 \times 10^{16} \text{ cm}^{-3}$  at 550 °C. From 550 °C to 650 °C, void densities do not vary much. The void density is  $5.2 \times 10^{16} \text{ cm}^{-3} \pm 9.4 \times 10^{15} \text{ cm}^{-3}$  at 650 °C.

After the maximum swelling temperature (550 °C) was determined, irradiation was performed to study the dpa dependence of swelling at 550 °C. Fig. 8a–c shows TEM images of samples after 50, 100, and 150 peak dpa irradiation at 550 °C, respectively. Again, no obvious surface void depletion zone was observed. Fig. 9a and b summarize the void diameter and density measurements at different peak dpa values.

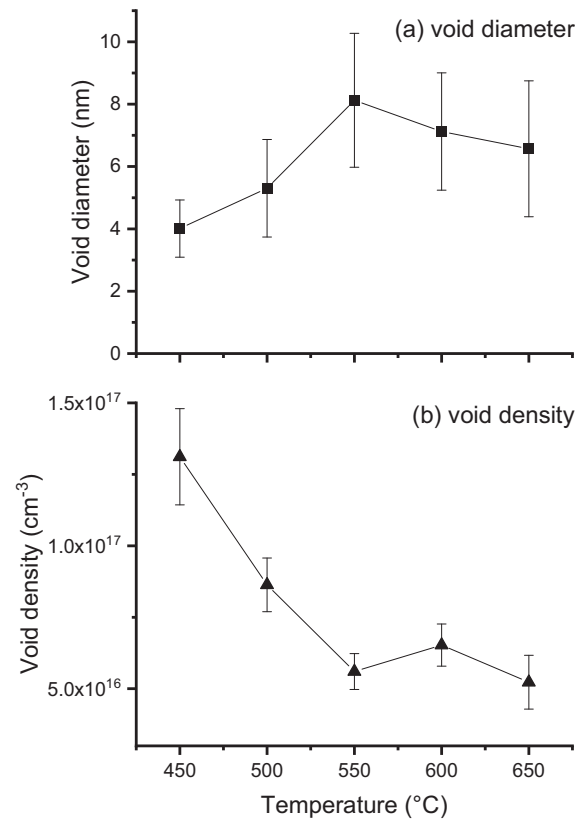


**Fig. 7.** (a) Void diameters and (b) void densities of the 50 peak dpa irradiated specimens, as a function of irradiation temperature. Data presented here are averaged over the depth range of 200 nm to 600 nm.

The TEM cross-sectional images were divided into 100 nm wide bins to probe the depth dependence of swelling as a function not only of dpa but also dpa rate, the latter varying as a function of depth. As shown in Fig. 9a, the void diameters increase with increasing damage levels, both as a general trend at different depths at one peak dose, and for the same depth at different doses. Note that the diameters did not show significant decreases at the peak injected range as one might expect due to injected interstitial suppression.

On the other hand, void concentrations do vary as a function of depth. As shown in Fig. 9b, for depths  $< 1000$  nm with negligible Fe interstitial injection, the void densities increase with increasing dpa. In contrast, at  $\sim 1.4 \mu\text{m}$ , void densities are locally reduced to almost zero when peak dose values are larger than 50 dpa. The void density variations dominate the swelling variation with depth. To further explain the injected interstitial effects, Fig. 10 shows the cross sectional TEM image of 150 peak dpa irradiated sample. Note that the void density is greatly reduced in the Fe projected range. This is very different from the 50 peak dpa irradiated sample in which void densities are not reduced significantly in the Fe projected range (as shown in Fig. 3a and b). A strong suppression of void formation occurs at relatively high damage level.

#### 4. Discussion

Our observed maximum swelling temperature is 550 °C. Note that this peak swelling temperature is higher than that of pure Fe and Fe-based ferritic-martensitic alloys ( $\sim 475$  °C) previously conducted at Texas A&M University on the same accelerator at nominally similar irradiation conditions [26]. Since the melting point of Cr is higher than that of Fe (1907 vs. 1538 °C) this upward shift in

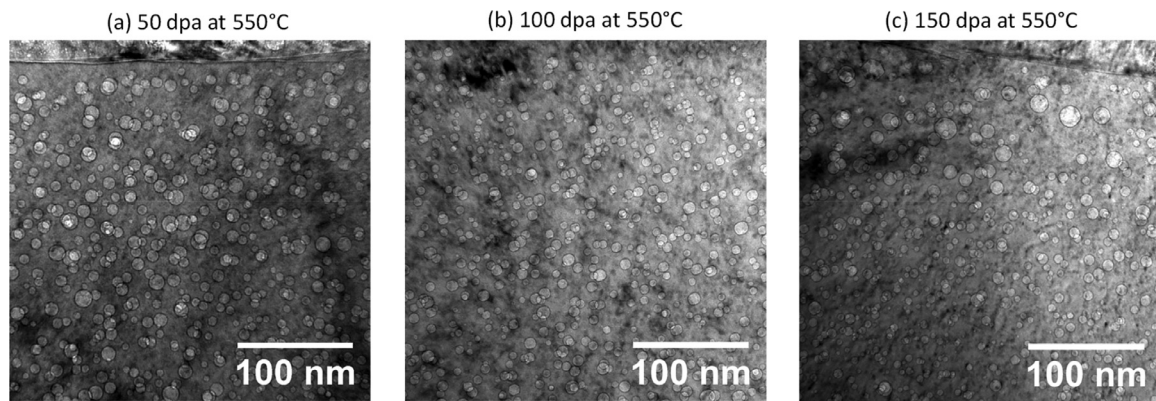


**Fig. 8.** TEM micrographs (under-focused) of specimens irradiated to 50, 100, and 150 peak dpa values at 550 °C. The images were taken immediately beneath the ion-incident surface.

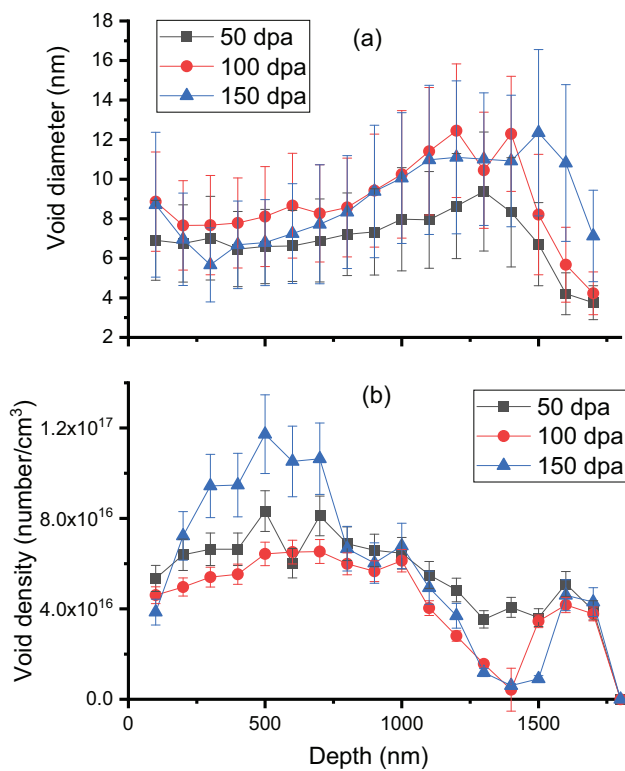


**Fig. 9.** (a) Void diameters and (b) void densities as a function of depth after irradiation at 550 °C to 50, 100, and 150 peak dpa.

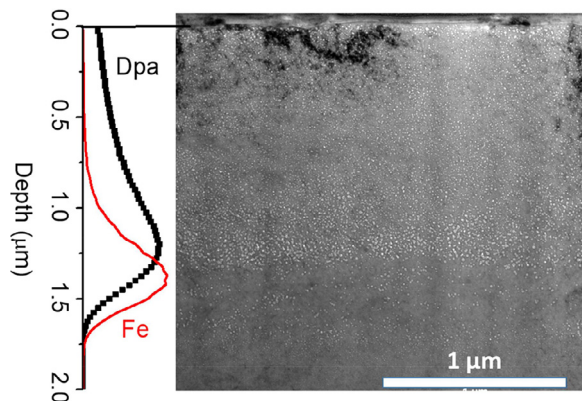


**Fig. 10.** Cross-sectional TEM image (under-focused) of specimen irradiated to 150 peak dpa at 550 °C.

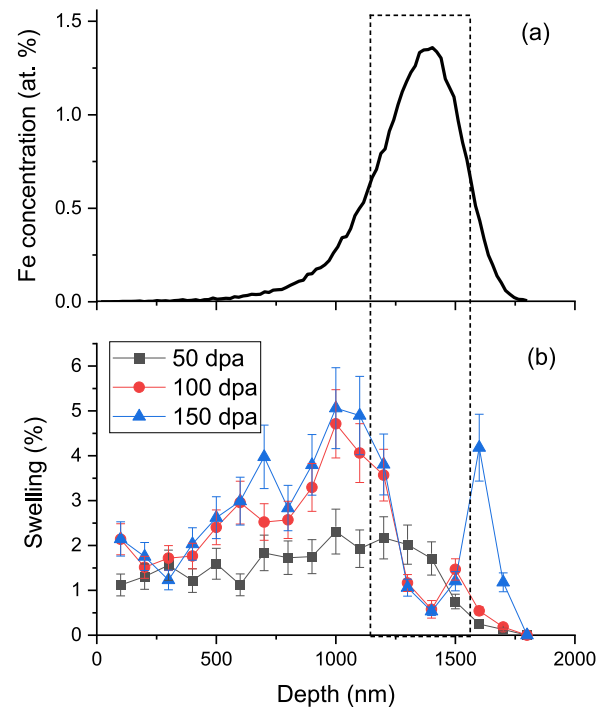


**Fig. 11.** (a) SRIM-predicted Fe implant distribution for 50 peak dpa irradiation, and (b) swelling as a function of depth in pure chromium irradiated at 550 °C to 50, 100, and 150 peak dpa. The box indicates the region of maximum compositional alteration by Fe implantation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

peak swelling temperature is expected since swelling is known to be best described using homologous temperatures.

Void superlattices and gas bubble superlattices have been reported in many metals under conditions of gas ion implantation, heavy ion irradiation, and neutron irradiation as summarized in various review articles [27–30]. Although a bubble superlattice has been previously observed in chromium [30], this is the first time in open literature that chromium has been seen to develop a void superlattice. The inter-void spacing and equilibrium size of bcc metals are known to be dependent on irradiation temperature and dpa rate as illustrated by studies on molybdenum [31].

Fig. 11a shows the SRIM-predicted Fe distributions for comparison with the depth-dependent swelling values shown in Fig. 11b. The shadowed region around  $R_p$  marks the region of significant Fe interstitial injection. Swelling for 50 peak dpa shows small varia-

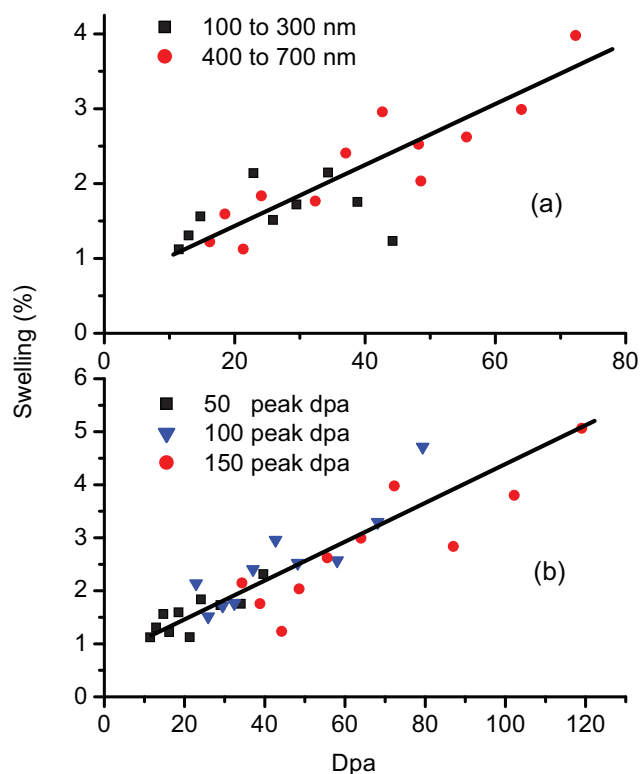


**Fig. 12.** (a) Average swelling at 550 °C as a function of local dpa for two depth regions, showing no strong sensitivity of swelling to the factor of ~2 difference in average dpa rate. (b) Swelling in individual 100 nm bins below 700 nm, ignoring any differences in dpa rate, showing that swelling appears to be increasing with increasing dpa level almost everywhere but is not sensitive to the local dpa rate.

tion as a function of depth, but at 100 and 150 dpa, swelling is greatly suppressed in the box region. For the region shallower than 1000 nm, swelling increases with increasing local dpa. The overall swelling profiles, as shown in Fig. 10b, suggest that the SRIM prediction is reasonably accurate.

Excluding the region affected by injected interstitials and the associated composition change, we analyzed swelling as a function of dpa. Fig. 12a plots the swelling over the depth region of 100 to 300 nm (in black) and also over the region of 400 to 700 nm (in red) at all three doses of 50, 100 and 150 peak dpa. These two choices of depth range were made to see if there was an obvious difference between the two data sets arising solely from their difference in local dpa rate which is roughly a factor of 2. Note that in many previous studies, swelling as a function of dpa for different depth regions often shows different behavior where dpa rate differences primarily affect the duration of the transient regime of swelling [32–34]. Although there is some scatter, all data points in both sets appear to follow a line with slope of ~0.03% per dpa. Based on this result, Fig. 12b was constructed that presents all depth-dependent swelling values for each depth bin for all three irradiation doses, without differentiation of the measurement depth or associated dpa rate. A linear dependence on local dose seems to be a good approximation with a slope of ~0.04% per dpa. In summary, there does not appear to be a discernible dependence of swelling in this limited experiment on dpa rate. Note that the dpa rate variation between the two sets is only about a factor of two and the changes may be simply not large enough to clearly see an effect. Note also that the swelling curve in Fig. 12b has a non-zero intercept at zero dose, implying that there is low dose transient at much higher swelling rate before the post-transient rate is established.

Void formation behavior observed in this study and in the Russian/Ukrainian studies are remarkably similar, showing that chromium exhibited some unusual characteristics compared to other bcc metals. First, the post-transient rate was remarkably low compared to another bcc metal,  $\alpha$ -Fe, which swells at ~0.2%/dpa in both neutron and self-ion irradiation, [15,16,20,35,36]. As a rule bcc metals are known to have lower post-transient swelling rates compared to fcc metals such as  $\gamma$ -Fe at ~1%/dpa [36,37] and copper at ~0.5%/dpa [38], but the rate of ~0.03–0.04%/dpa for bcc chromium is unexpectedly low even for bcc metals.

Second, it appears that there is initially a higher transient swelling rate at very low dpa levels before settling down to the post-transient rate, as was observed in both the Ukrainian and Texas A&M studies. This behavior has been observed before in other pure metals, however and therefore is not so surprising [39,40]. What is surprising, however, is that there appears to be an independence of the post-transient swelling rate, often referred to as the steady state swelling rate, on dpa rate over the factor of ~2 studied in this experiment. Perhaps these two items are linked in that the rate dependence in many studies on other metals and alloys was manifested primarily in the duration of the transient regime [32–34], and in the case of chromium the transient duration is already near zero.

The lack of void suppression in the injected interstitial region at 25 dpa is another feature showing chromium to be different from other metals and alloys. Void suppression in this injected region has been a general phenomenon in almost all ion-irradiated metals, which is attributed to elimination of void nucleation by “excess” interstitials. These excess interstitials arise from two combined effects. One effect is the spatial difference in vacancy and interstitial distributions, with the latter slightly being deeper than that of the former, leading to excess interstitials near the end of range [20]. The other effect is the extra atoms injected into this area due to implantation. However, note that 100 and 150 dpa there exists a local depression of swelling but not its complete absence. Perhaps the increasing local concentration of Fe atoms at these doses is involved, but this possibility requires additional study.

While self-organization has not been observed in commercial structural alloys, it is well known that both pure fcc (Cu, Ni, Al) and bcc (Mo, Nb) metals and some dilute binary alloys can self-organize to develop dislocation loop lattices and walls, as well as void lattices and bubble lattices [27–30], and it appears that chromium is no exception with respect to bubble and void lattice formation. Bryk did not provide any evidence of loop lattices, but he noted that loops persisted to very high dpa levels, behavior not usually observed in structural alloys [11,12]. For bcc metals these superlattices form on  $\langle 111 \rangle$  directions, forming  $\{110\}$  planes and are best visualized by imaging using the  $\langle 111 \rangle$  crystal orientation.

Various models have been developed to explain void superlattice formation including elastic interactions of voids, spatial fluctuations of defects and anisotropic mass transport. The principle concept of the most popular anisotropic mass transport model is that voids aligned along close-packed directions shield each other from one-dimensional migrating crowdion or interstitial dumbbells [41,42]. Under such a shadowing condition, voids located on the same line are protected from being diminished by the voids immediately ahead of them. For those voids that are not completely aligned, the non-shadowed portion of the void will tend to disappear due to its higher likelihood to interact with interstitials. For slightly unaligned voids, they will therefore shift their centers for better alignment against interstitials. It is unclear at this stage which type of interstitial defects are responsible in this void alignment process. They might be crowdions, a chain of displaced interstitial-vacancy cluster, or interstitial dimers, or glissile dislocation loops.

Credibility of ion irradiation to emulate neutron irradiation damage has been a topic of great interest for decades. Several recent studies have noted the significance of radiation-enhanced diffusion from implants out of the injected region [43,44]. Diffusion of implanted Fe or extra interstitials may affect void swelling at shallower depths, leading to low swelling rates or swelling saturation as observed in the present study. Swelling saturation can also be caused by void ordering, as pointed out by various reviews. From 550 °C to 650 °C, void diameters decrease slightly, which might be caused by radiation-enhanced diffusion. We cannot conclude this effect at the present stage due to insufficient data on diffusion kinetics of Fe in Cr and point defect migration in Cr. Such an effect is difficult to evaluate using a depth profiling technique, i.e., energy-dispersive X-ray spectroscopy (EDS) profiling of Fe in Cr, due to the following two reasons: (1) Fe concentrations, even for the highest dpa irradiation, are below the EDS detection limit. We could not get any Gaussian-like Fe profiles using STEM-EDS analysis, and (2) Even if Fe profiles can be measured, their connection to the injected interstitial effect cannot be easily established. Fe atoms in Cr most likely diffuse as interstitial dumbbells. For each diffusion event, the Fe may change from an interstitial defect (as one interstitial in a dumbbell) to a substitutional atom, kicking one Cr lattice atom out of its lattice site. This Cr interstitial will continue the diffusion in a new dumbbell configuration. Therefore, Fe atoms are left behind, but the injected interstitial effect will continue to propagate towards shallow depths. The chance for Fe being switched back to an interstitial is non-zero, but it is very small. Note that the Fe implant concentration is much lower than that of Cr matrix atoms. One Cr interstitial in  $\langle 110 \rangle$  Fe-Cr dumbbell can push any of its eight neighboring Cr atoms to form a new  $\langle 110 \rangle$  Cr-Cr dumbbell. But the chance being switched back to form Fe-Cr dumbbell in the next diffusion step is 1/8.

## 5. Conclusions

The void swelling behavior of Cr has been studied using 5 MeV Fe ion irradiation over the temperature range of 450–650 °C. Void swelling peaks at 550 °C, reaching ~2% swelling after 50 peak dpa irradiation. Compared with pure iron with a post-transient swelling rate of ~0.2%/dpa, pure chromium swells at a much lower rate of ~0.03–0.04%/dpa (up to 120 local dpa). Void alignment along the  $\langle 111 \rangle$  axial direction was observed. Swelling, while possessing a very low post-transient rate in both this and earlier studies, begins to rise quickly with an incubation dose less than 10 dpa, exhibiting a higher transient swelling rate before settling down onto the post-transient value. Over the factor of two in dpa rate explored in this experiment no clear influence of dpa rate on swelling was observed. Note that the dpa rate range was quite limited in the present study. While these results are encouraging with respect to the use of Cr for improving accident tolerance, additional studies need to be conducted at lower PWR-relevant temperatures, preferably using neutrons, and over a wider range of dpa rates to provide confidence in the chromium coating concept.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Ekaterina Ryabikovskaya:** Investigation. **Aaron French:** Investigation. **Adam Gabriel:** Investigation. **Hyosim Kim:** Investigation. **Tianyao Wang:** Investigation. **Korosh Shirvan:** Conceptualization,

Writing - review & editing. **Frank A. Garner:** Methodology, Writing - review & editing. **Lin Shao:** Supervision, Conceptualization, Writing - original draft.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jnucmat.2020.152585.

## References

- [1] The Fukushima Daiichi Accident (PDF), IAEA - International Atomic Energy Agency, Vienna, August 31, 2015, pp. 131–132. ISBN 978-92-0-107015-9.
- [2] A.S. Kuprin, V.A. Belous, V.N. Voyevodin, R.L. Vasilenko, V.D. Ovcharenko, G.D. Tolstolutskaia, I.E. Kopanets, I.V. Kolodiy, Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air, *J. Nucl. Mater.* 465 (2015) 400–406.
- [3] I. Idarraga-Trujillo, M. Le Flem, J.C. Brachet, M. Le Saux, D. Hamon, S. Muller, V. Vandenberghe, M. Tupin, E. Papin, E. Monsifrot, A. Billard, F. Schuster, Assessment at CEA of coated nuclear fuel cladding for LWRs with increased margins in LOCA and beyond LOCA conditions, Conference Paper LWR Fuel Performance Meeting, Top Fuel 2 (2013) 860–867.
- [4] H.-G. Kim, I.-H. Kim, Y.-I. Jung, D.-J. Park, J.-Y. Park, Y.-H. Koo, Adhesion property and high-temperature oxidation behavior of Cr-coated Zircaloy-4 cladding tube prepared by 3D laser coating, *J. Nucl. Mater.* 465 (2015) 531–539.
- [5] S.J. Zinkle, K.A. Terrani, J.C. Gehin, L.J. Ott, L.L. Snead, Accident tolerant fuels for LWRs: a perspective, *J. Nucl. Mater.* 448 (2014) 374–379.
- [6] M. Ševcůček, A. Gurgun, A. Seshadri, Y. Che, M. Wagih, B. Phillips, V. Champagne, K. Shirvan, Development of Cr cold spray-coated fuel cladding with enhanced accident tolerance, *Nuclear Engineering and Technology* 50 (2018) 229–236.
- [7] J.G. Gigax, M. Kennas, H. Kim, T. Wang, B.R. Maier, H. Yeom, G.O. Johnson, K. Sridharan, L. Shao, Radiation response of Ti2AlC MAX phase coated Zircaloy-4 for accident tolerant fuel cladding, *J. Nucl. Mater.* 523 (2019) 26–32.
- [8] J.G. Gigax, M. Kennas, H. Kim, B.R. Maier, H. Yeom, G.O. Johnson, K. Sridharan, L. Shao, Interface reactions and mechanical properties of FeCrAl-coated Zircaloy-4, *J. Nucl. Mater.* 519 (2019) 57–63.
- [9] V.I. Trefilov, V.F. Zelenskiy, I.M. Nekhludov, A.N. Rakitskiy, V.N. Voyevodin, L.S. Ozhigov, V.S. Karasev, A.P. Rudoy, V.N. Minakov, Y.V. Milman, A.S. Davidenko, Minor-alloyed Cr-based alloys, RM-8 (1991)185–194 (in Russian).
- [10] V.P. Chakin, V.A. Kazakov, "Radiation resistance of minor-alloyed Cr alloys", RIAR preprint No. 7 (790), RIAR, Dimitrovgrad, 1990, in Russian.
- [11] V.V. Bryk, V.N. Voyevodin, V.F. Zelenskiy, B.V. Matveenko, I.M. Nekhludov, V.K. Horenko, T.P. Chernyaeva, A.N. Rakitskiy, V.I. Trefilov, Investigation of radiation swelling of the deformed minor-alloyed Cr alloy under its irradiation in the accelerator, VANT (1981) 33–38 in Russian.
- [12] V.V. Bryk, V.N. Voyevodin, I.M. Nekhludov, A.N. Rakitskiy, Microstructure investigation of Cr and Cr alloys irradiated with heavy ions, *J. Nucl. Mater.* 225 (1995) 146–153.
- [13] A.S. Kuprin, V.A. Belous, V.N. Voyevodin, R.L. Vasilenko, V.D. Ovcharenko, G.D. Tolstolutskaia, I.E. Kopanets, I.V. Kolodiy, Irradiation resistance of vacuum arc chromium coatings for zirconium alloy fuel claddings, *J. Nucl. Mater.* 510 (2018) 163–167.
- [14] V. Chakin, V. Kazakov, Yu. Goncharenko, Z. Ostrovsky, Formation of the  $\sigma$ -phase in Cr-Fe alloys under irradiation, *J. Nucl. Mater.* 233–237 (1996) 573–576.
- [15] J.G. Gigax, E. Aydogan, T. Chen, D. Chen, L. Shao, Y. Wu, W.Y. Lo, Y. Yang, F.A. Garner, The influence of ion beam rastering on the swelling of self-ion irradiated pure iron at 450°C, *J. Nucl. Mater.* 465 (2015) 343–348.
- [16] L. Shao, J.G. Gigax, D. Chen, H. Kim, F.A. Garner, J. Wang, M.B. Toloczko, Standardization of accelerator irradiation procedures for simulation of neutron induced damage in reactor structural materials, *J. Nucl. Mater.* 409 (2017) 251–254.
- [17] J.G. Gigax, H. Kim, E. Aydogan, F.A. Garner, S. Maloy, L. Shao, Beam-contamination-induced compositional alteration and its neutron-atypical consequences in ion simulation of neutron-induced void swelling, *Mat. Res. Lett.* 5 (2017) 478–485.
- [18] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, SRIM – the stopping and range of ions in matter, *Nucl. Instr. Meth. Phys. Res. B* 268 (2010) 1818–1823.
- [19] R.E. Stoller, M.B. Toloczko, G.S. Was, A.G. Certain, S. Dwaraknath, F.A. Garner, On the use of SRIM for computing radiation damage exposure, *Nucl. Instr. Meth. Phys. Res. B* 310 (2013) 75–80.
- [20] L. Shao, C.-C. Wei, J. Gigax, A. Aitkaliyeva, D. Chen, B.H. Sencer, F.A. Garner, Effect of defect imbalance on void swelling distributions produced in pure iron irradiated with 3.5 MeV self-ions, *J. Nucl. Mater.* 453 (2014) 176–181.

- [21] F.A. Garner, Impact of the injected interstitial on the correlation of charged particle and neutron-induced radiation damage, *J. Nucl. Mater.* 117 (1983) 177–197.
- [22] C. Sun, F.A. Garner, L. Shao, X. Zhang, S.A. Maloy, Influence of injected interstitials on the void swelling in two structural variants of 304L stainless steel induced by self-ion irradiation at 500°C, *Nucl. Instr. Meth. Res. B* 409 (2017) 323–327.
- [23] C. Sun, L. Malerba, M.J. Konstantinovic, F.A. Garner, S.A. Maloy, Emulating neutron-induced void swelling in stainless steels using ion irradiation, in: *Proceedings of the 18th International Conference on Environmental Degradation of Materials in Nuclear Power Systems–Water Reactors, The Minerals, Metals & Materials Series*, 2017, pp. 669–680.
- [24] J.G. Gigax, T. Chen, Hyosim Kim, J. Wang, L.M. Price, E. Aydogan, S.A. Maloy, D.K. Schreiber, M.B. Toloczko, F.A. Garner, L. Shao, Radiation response of alloy T91 at damage levels up to 1000 peak dpa, *J. Nucl. Mater.* 482 (2016) 257–265.
- [25] E. Getto, G. Vancoervering, G.S. Was, The co-evolution of microstructure features in self-ion irradiated HT9 at very high damage levels, *J. Nucl. Mater.* 484 (2017) 193–208.
- [26] E. Aydogan, T. Chen, J.G. Gigax, D. Chen, X. Wang, P.S. Dzumaev, O.V. Emelyanova, M.G. Ganchenkova, B.A. Kalin, M. Leontiva-Smirnova, R.Z. Valiev, N.A. Enikeev, M.M. Abramova, Y. Wu, W.Y. Lo, Y. Yang, M. Short, S.A. Maloy, F.A. Garner, L. Shao, Effect of self-ion irradiation on the microstructural changes of alloy EK-181 in annealed and severely deformed conditions, *J. Nucl. Mater.* 487 (2017) 96–104.
- [27] K. Krishan, Invited review article ordering of voids and gas bubbles in radiation environments, *Radiat. Eff.* 66 (1982) 121–155.
- [28] W. Jäger, H. Trinkaus, Defect ordering in metals under irradiation, *J. Nucl. Mater.* 205 (1993) 394–410.
- [29] N.M. Ghoniem, D. Walgraft, S.J. Zinkle, Theory and experiment of nanostructure self-organization in irradiated materials, *Journal of Computer-Aided Materials Design* 8 (2002) 1–38.
- [30] D.J. Johnson, P.B. Mazey, Gas-bubble superlattice formation in bcc metals, *J. Nucl. Mater.* 218 (1995) 273–288.
- [31] F.A. Garner, J.F. Stubbins, Saturation of Swelling in Neutron Irradiated Molybdenum and its Dependence on Irradiation Temperature and Starting Microstructural State, *J. Nucl. Mater.* 212–215 (1994) 1298–1302.
- [32] F.A. Garner, Chapter 6: Irradiation performance of cladding and structural steels in liquid metal reactors, in: *Vol. 10A of Materials Science and Technology: A Comprehensive Treatment*, VCH Publishers, 1994, pp. 419–543.
- [33] T. Okita, N. Sekimura, F.A. Garner, L.R. Greenwood, W.G. Wolfer, Y. Isobe, Neutron-induced microstructural evolution of Fe-15Cr-16Ni alloys at ~ 400°C during neutron irradiation in the FFTF fast reactor, in: *10th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors*, 2001 issued on CD format, no page numbers.
- [34] T. Okita, N. Sekimura, T. Iwai, F.A. Garner, Investigation of the synergistic influence of irradiation temperature and atomic displacement rate on the microstructural evolution of ion-irradiated model austenitic alloy Fe-15Cr-16Ni, in: *10th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors*, 2001 issued on CD format, no page numbers.
- [35] B.H. Sencer, F.A. Garner, Compositional and temperature dependence of void swelling in model Fe-Cr base alloys irradiated in EBR-II, *J. Nucl. Mater.* 283–287 (2000) 164–168.
- [36] F.A. Garner, M.B. Toloczko, B.H. Sencer, Comparison of swelling and irradiation creep behavior of fcc-austenitic and bcc-ferritic/martensitic alloys at high neutron exposure, *J. Nucl. Mater.* 276 (2000) 123–142.
- [37] F.A. Garner, Recent insights on the swelling and creep of irradiated austenitic alloys, *J. Nucl. Mater.* 122–123 (1984) 459–471.
- [38] F.A. Garner, H.R. Brager, K.R. Anderson, Neutron-induced changes in density and electrical conductivity of copper alloys at 16 to 98 dpa and 430°C, *J. Nucl. Mater.* 179–181 (1991) 250–253.
- [39] B.N. Singh, S.J. Zinkle, Defect accumulation in pure fcc metals in the transient regime; a review, *J. Nucl. Mater.* 206 (1993) 212–229.
- [40] B.N. Singh, A. Horsewell, P. Toft, D.J. Edwards, Temperature and dose dependencies of microstructure and hardness of neutron irradiated OFHC copper, *J. Nucl. Mater.* 224 (1995) 131–140.
- [41] H.L. Heinisch, B.N. Singh, Kinetic Monte Carlo simulations of void lattice formation during irradiation, *Phil. Mag.* 83 (2003) 3661–3676.
- [42] S.Y. Hu, D.E. Burkes, C.A. Lavender, D.J. Senor, W. Setyawan, Z. Xu, Formation mechanism of gas bubble superlattice in UMo metal fuels: Phase-field modeling investigation, *J. Nucl. Mat.* 479 (2016) 202–215.
- [43] P.J. Doyle, K.M. Benensky, S.J. Zinkle, Modeling the impact of radiation-enhanced diffusion on implanted ion profiles, *J. Nucl. Mater.* 509 (2018) 168–180.
- [44] S.J. Zinkle, L.L. Snead, Opportunities and limitations for ion beams in radiation effects studies: Bridging critical gaps between charged particle and neutron irradiations, *Scri. Mater.* 143 (2018) 154–160.