

The time dependence of proton irradiation effect on the intergranular oxidation of 316 L stainless steel in high-temperature hydrogenated water

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ABSTRACT

The time dependence of proton irradiation effect on the intergranular oxidation of 316 L stainless steel in simulated PWR primary water was clarified for the first time by ruling out the interference from grain boundary structure dependence. Interestingly, proton irradiation has an acceleration effect on the intergranular oxidation of 316 L stainless steel after shorter-term oxidation (less than 500 h) but a mitigation effect at later stage (more than 500 h). It was found that Cr depletion at the pristine grain boundary due to radiation-induced segregation (RIS) plays a dominant role at the early stage of oxidation, resulting in a deeper intergranular oxidation than in the non-irradiated region. Nevertheless, the Cr content at the intergranular oxide tip in the irradiated region builds up faster than in the non-irradiated region with time due to the enhanced solute (especially Cr) diffusivity in the irradiated region. The positive effect of enhanced Cr diffusivity on resistance to intergranular oxidation gradually dominates after longer-term immersion and eventually leads to a shallower intergranular oxide penetration in the irradiated region. The faster intergranular oxidation in irradiated region due to RIS at the early stage partly explains the accelerated crack propagation of irradiated material as the oxidation condition at the crack tip is similar to that at the early stage.

1. Introduction

Irradiation-assisted stress corrosion cracking (IASCC) describes an enhancement of inherent susceptibility to stress corrosion cracking (SCC) for alloy which is simultaneously subjected to irradiation, mechanical stress, and an aggressive environment [1–4]. This degradation mode has been recognized as a major cause of failure for the core components in nuclear power plants, especially the baffle/former bolts in light water reactors [3,5]. An understanding of the mechanism of IASCC is needed to provide a scientific basis for designing mitigation strategies. Up to now, although a lot of research has been done [3,4], there is still no consensus on the IASCC mechanism. The IASCC process should be closely related to the irradiation effects, including complex microstructure changes in material (e.g., dislocation loops, voids, radiation-induced segregation (RIS)) and water radiolysis. To elucidate the IASCC mechanism, it is critical yet challenging to separate and clarify the roles of those contributing factors.

Localized deformation has been widely accepted as critical precursor for IASCC occurrence [3,6]. The localized heterogeneous deformation in

form of dislocation channels is related to the defect clusters induced by irradiation [7]. When the dislocation channels terminate at grain boundaries and pileups occur, the local stress concentrates at the grain boundaries and cracks initiate [8,6,9]. Numerous studies have been conducted to reveal the correlation between localized deformation and IASCC susceptibility [6,8–12]. However, it is not enough to elucidate the IASCC mechanism only from the perspective of mechanics. Indeed, increasing results suggest that intergranular oxidation is a critical precursor for SCC initiation and propagation of austenitic stainless steels [13–16] and nickel base alloys [17–19] in high-temperature water. Nevertheless, experimental studies are still limited regarding the role of intergranular oxidation in IASCC. The process of intergranular oxidation of irradiated stainless steels should be directly affected by grain boundary composition, especially RIS at grain boundary [20,21]. Therefore, it is critical to evaluate the role of RIS in intergranular oxidation behavior to better understand the mechanism of IASCC.

Currently, most studies on the influence of RIS on the intergranular oxidation of irradiated stainless steel support that radiation-induced Cr depletion at grain boundary enhances intergranular oxidation. For

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Table 1
Details about the RHABs.

ED	GB	GB Plane indices		Euler angles: $\langle \varphi_1, \Phi, \varphi_2 \rangle$ in ($^\circ$)		MA in ($^\circ$)
		Grain 1	Grain 2	Grain 1	Grain 2	
2 h	GB _{A1}	(−3 −5 −2) _{−0.62°}	(−4 6 −7) _{−2.11°}	(265.5;35.3;55.1)	(26.4;21.0;87.4)	57.3
	GB _{A2}	(−3 −5 −2) _{−1.76°}	(−4 6 −7) _{−1.01°}			
72 h	GB _{B1}	(1 7 −10) _{−1.54°}	(1 −1 −2) _{−2.64°}	(96.6;33.5;52)	(156.3;26.8;88.3)	29.5
	GB _{B2}	(1 7 −10) _{−2.35°}	(1 −1 −2) _{−3.25°}			
200 h	GB _{C1}	(2 −1 −1) _{−2.47°}	(4 0 −3) _{−1.58°}	(189.2;24.9;10.6)	(161.8;19.2;2.2)	36.0
	GB _{C2}	(2 −1 −1) _{−1.59°}	(4 0 −3) _{−3.58°}			
500 h	GB _{D1}	(1 0 −1) _{−2.51°}	(−3 1 9) _{−1.41°}	(121.1;34.6;88.4)	(12.5;42.6;38.8)	54.7
	GB _{D2}	(1 0 −1) _{−0.62°}	(−3 1 9) _{−2.54°}			
750 h	GB _{E1}	(−5 −1 −7) _{−3.32°}	(−3 −1 −5) _{−1.23°}	(223.1;19.4;77.4)	(53.9;43.8;23.2)	46.8
	GB _{E2}	(−5 −1 −7) _{−2.15°}	(−3 −1 −5) _{−3.45°}			
1000 h	GB _{F1}	(−1 −3 1) _{−3.21°}	(0 4 −3) _{−1.05°}	(278.8;34.8;11.0)	(45.9;24.4;53.2)	49.9
	GB _{F2}	(−1 −3 1) _{−2.94°}	(0 4 −3) _{−1.22°}			

ED represents the exposure durations.

GB represents the grain boundary.

MA represents the misorientation angle.

example, Boisson et al. [22] studied the early-stage oxidation (after 24 h) of proton-irradiated stainless steel (1.5 dpa) in simulated pressurized water reactor (PWR) primary water and found that the intergranular oxide penetration is deeper in the irradiated area (141 ± 2 nm) than in the non-irradiated area (42 ± 2 nm). Moreover, Fukumura [23] et al. also reported the degree of grain boundary oxidation of neutron-irradiated stainless steels increases with increasing radiation dose (3 dpa, 19 dpa, and 73 dpa) after exposure to a PWR water environment for 1149 h. Deng et al. [24] studied the oxidation behavior of high-angle grain boundaries from the solution annealed and proton-irradiated samples (0.5 and 3 dpa) after testing in simulated PWR primary water for 500 h and achieved a similar conclusion. These authors suggested that irradiation promotes intergranular oxidation due to the radiation-induced Cr depletion at grain boundary.

Although these previous works seem to consistently support the accelerating effect of irradiation on intergranular oxidation, there are some common limitations. It has been reported that the difference in grain boundary structure would result in different resistances to RIS [25, 26] and intergranular oxidation [27–29]. Unfortunately, the studies mentioned above did not control the structure of the studied grain boundary, thus the robustness of the achieved conclusions was compromised. Recently, Wang et al. [30] clarified the irradiation effect on intergranular oxidation of 316 L stainless steel in simulated PWR primary water after 1000 h exposure by ruling out the interference from the difference in grain boundary structure. Surprisingly, the results show that proton irradiation has a mitigation effect on intergranular oxidation. According to this work, the higher resistance to intergranular oxidation in irradiated regions results from the faster transportation of active elements (especially Cr) along grain boundary. Nevertheless, the current researches are mostly based on results from single-duration exposure test. A comprehensive study on the time dependence is required to establish a complete understanding of irradiation effect on intergranular oxidation.

In this paper, the time dependence of the proton irradiation effect on the intergranular oxidation of 316 L stainless steel in simulated PWR primary water was investigated after multiple exposure durations (2 h, 72 h, 200 h, 500 h, 750 h, and 1000 h). The microstructure and microchemistry of intergranular oxide were compared between the irradiated and non-irradiated regions from the same grain boundaries after each exposure duration. The results are discussed in relation to the irradiation effect on intergranular oxidation and IASCC process.

2. Experimental

2.1. Material and sample preparation

The chemical composition of solution-annealed (SA) 316 L austenitic

stainless steel is 16.2 wt.% Cr, 10.11% Ni, 2.06% Mo, 1.58% Mn, 0.35% Si, 0.17% Co, 0.017% Ta, 0.001% S, 0.036% P, 0.37% Cu, 0.017% C, and Fe in balance. The bulk material was machined into square bars (20 mm $\times$ 2 mm $\times$ 2 mm) by electrical discharge machining (EDM). The obtained sample was mechanically ground with silicon carbide papers from 400 to 2000 grit and then electropolished in an alcohol solution consisting of 10% perchloric acid for 20 s at -40°C .

The proton irradiation experiment (2 MeV protons, $360 \pm 10^\circ\text{C}$) was performed in a 3 MeV Pelletron accelerator at the Michigan Ion Beam Laboratory (MIBL) at University of Michigan. The irradiation damage was estimated to be 2.5 displacements per atom (dpa), and the damage rate was around 1×10^{-5} dpa/s. The depth damage profile was calculated by SRIM 2013 [31] with quick Kinchin-Pease option using a displacement energy of 40 eV. Only the central 10 mm of the square bar was directly irradiated. The depth of irradiation damaged layer is around 20 μm and a nearly 15 μm thick uniformly-damaged region (UDR) was created. The procedure of proton irradiation experiment was described in more detail in our previous work [32].

After proton irradiation, the cross-section of 316 L stainless steel bar was polished. Another stainless steel square bar was mounted next to the proton-irradiated sample to minimize chamfering the edge of cross-section during sample preparation. Then, the cross-section was wet ground using silicon carbide papers from 400 to 3000 grit, followed by mechanical polishing with 1.5 μm , 0.5 μm diamond polishing pastes, and finally vibration-polished with 60 nm colloidal silica suspension for at least 3 h. Thereafter, the grain boundary network across the irradiated and non-irradiated regions on the cross-section was characterized using an FEI Helios Nanolab 600 system equipped with a Nordlys electron back scattering diffraction (EBSD) detector. An accelerating voltage of 25 kV and a probe current of 5.5 nA were used to obtain the EBSD mapping at a step size of 2 μm .

2.2. Exposure test

The exposure test was performed using a refreshed 3.6-L stainless steel autoclave in the laboratory of Xi'an Jiaotong University. The specimen was exposed to simulated PWR primary water (320 $^\circ\text{C}$, 150 bar, 30 cc $\text{H}_2/\text{kg H}_2\text{O}$) at a flow rate of 12 L/h for 2 h, 72 h, 200 h, 500 h, 750 h and 1000 h. It should be noted that the exposure durations were calculated cumulatively, i.e., only a single specimen was used for all the oxidation times. During the test, the dissolved oxygen (DO) and conductivity of both the inlet and outlet water were continuously monitored with Mettler Toledo sensors.

2.3. Microstructure characterization

After each exposure duration, the sample was removed from the

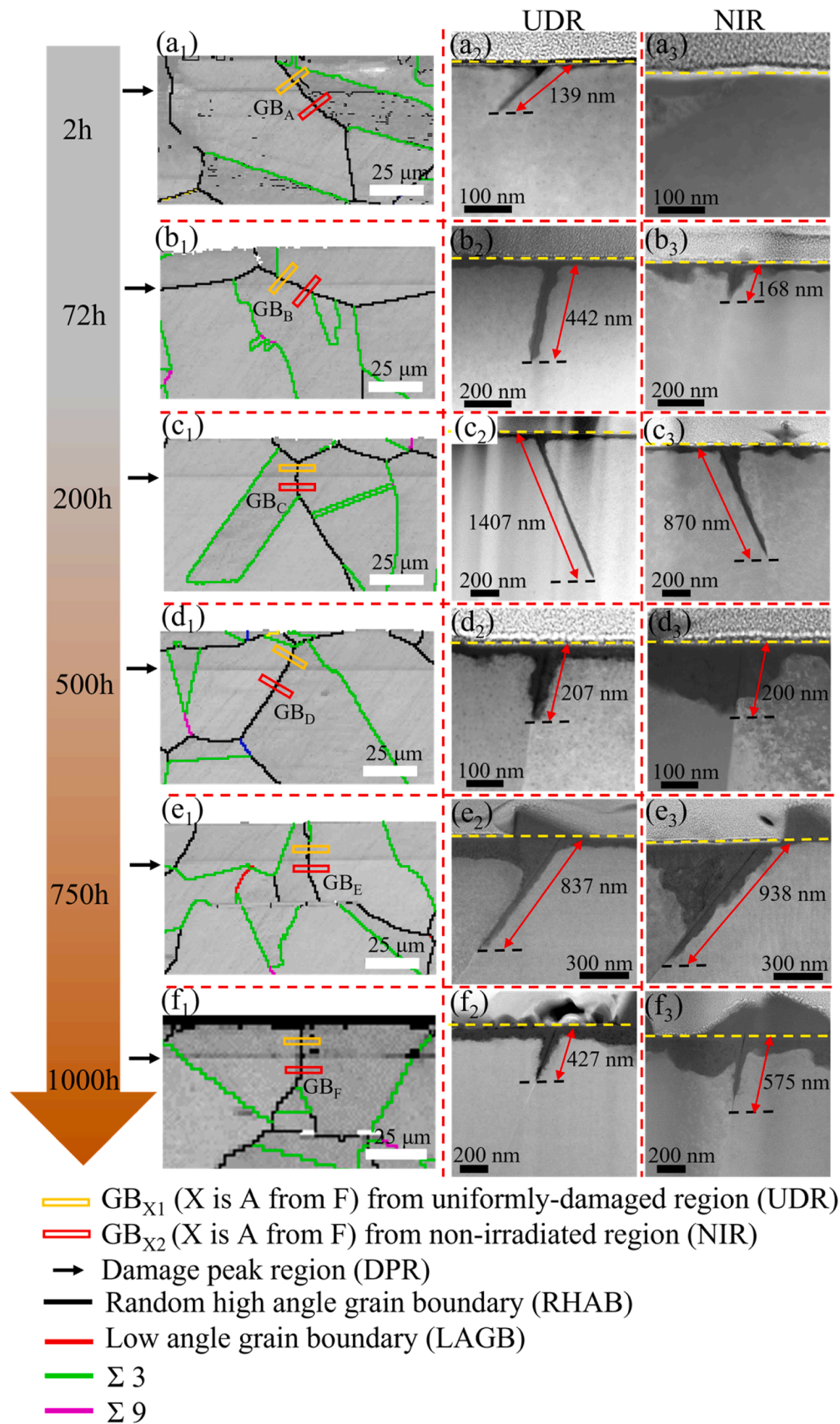


Fig. 1. Intergranular oxide penetrations after six exposure durations. (a₁-f₁) EBSD band contrast maps showing the TEM lamellae extraction on the cross-section of irradiated surface, (a₂-f₂) STEM-HAADF images of grain boundaries extracted from UDR and (a₃-f₃) STEM-HAADF images of grain boundaries extracted from NIR after different immersion times.

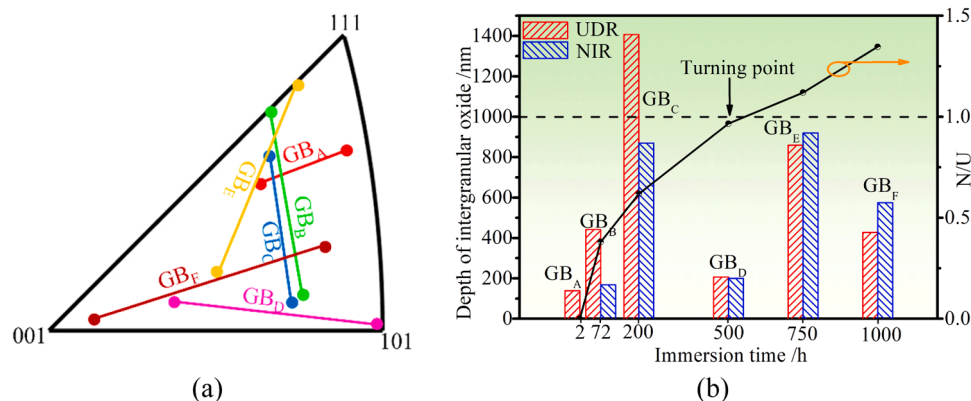


Fig. 2. (a) Plane indices of sampled grain boundaries marked in the inverse pole figure (IPF), (b) intergranular oxide depths from the irradiated and unirradiated regions after different exposure durations. (N/U represents the ratio of intergranular oxidation depths of the un-irradiated grain boundary to its irradiated counterpart).

autoclave for further characterization. From the EBSD mapping, straight random high angle grain boundaries (RHABs) spanning both the irradiated and non-irradiated regions were selected from the cross section of irradiated surface. Two transmission electron microscopy (TEM) lamellae were extracted from UDR and non-irradiated region (NIR) of the selected RHAB. The TEM lamellae were extracted using an FEI Helios Nanolab 600 Dual Beam focused ion beam (FIB) and finally polished with 5 kV Ga⁺ ion to a thickness of ~90 nm as previously described [30]. A pair of TEM lamellae were extracted for each exposure duration and designated as GB_{X1} (from UDR) and GB_{X2} (X is from A to F), respectively. A total of twelve TEM lamellae were obtained. The sampled grain boundaries were apart far enough from each other and the subsequent exposure of target grain boundaries was not affected by ion beam bombardment during FIB machining. It should be noted that the data from GB_F (exposure duration of 1000 h) has been reported in our previous study [30]. The grain boundary plane index was calculated using the Euler angles $\langle \phi_1, \Phi, \phi_2 \rangle$ and grain boundary trace angles [33]. The structure information of these RHABs is summarized in Table 1. A JEOL 2100F TEM microscope was used for microstructure analyses in bright and dark field imaging modes along with selected area electron diffraction (SAED) at 200 kV. A JEOL JEM-F200(HR) microscope was used to obtain high-angle annular dark-field (HAADF) images in scanning TEM (STEM) mode. With the aid of Image J software, the intergranular oxide penetration was measured from the STEM-HAADF images, as shown in Fig. 1. Moreover, two 100 mm² energy dispersive spectroscopy (EDS) detectors equipped in the JEOL JEM-F200(HR) were used for microchemical analyses. The grain boundary was tilted to an edge-on position before the STEM-EDS measurement. EDS mappings were obtained at 512 × 512 pixels with a dwell time of 2 milliseconds. EDS line scans were performed at a step size of 0.5 or 1 nm, depending on the line length. The probe size was set to 5. It should be noted that the counts of identified elements were used for EDS mapping.

3. Results

Six pairs of oxidized RHABs from the irradiated and non-irradiated regions after different exposure durations (2 h, 72 h, 200 h, 500 h, 750 h, and 1000 h) have been sampled and characterized in this work. After 1000 h immersion test, a preliminary check on the variation in the oxidation depth along a single grain boundary was conducted on an irradiated grain boundary (shown in supporting information). These two sampled regions were several microns apart and the depths of intergranular oxide are almost identical (608 nm vs. 612 nm) (Fig. S1). Thus, the inherent fluctuation in oxidation depth along a single grain boundary is quite small when the sampled regions are only several microns apart. Fig. 1 shows traces of sampled grain boundaries on the cross-

section of the irradiated surface and the STEM-HAADF images of the cross-sections. From Fig. 1, the traces of these six RHABs are quite straight and span across the damage peak which were denoted by black arrows. The interface between the outer and inner oxide layers corresponds to the original sample surface and was marked on the STEM-HAADF images with yellow dashed lines. The intergranular oxide penetrations of GB_{X1} (extracted from UDR, Fig. 1a₂-f₂) and GB_{X2} (extracted from NIR, Fig. 1a₃-f₃) were marked on the STEM-HAADF images. It should be noted that the intergranular oxide depth was measured as the length from the original surface (i.e., the outer/inner oxide interface) to the intergranular oxide tip along the grain boundary as the preferential intergranular oxidation (PIO) started from the original surface. The plane indices of sampled grain boundaries were marked in the inverse pole figure (IPF) (Fig. 2a). Fig. 2b summarizes the measured intergranular oxide depths from the irradiated and non-irradiated regions over the exposure duration. The intergranular oxidation depths are mostly less than 1 μm in this work but the location of the sampled grain boundaries in UDR is several microns beneath the proton-irradiated surface. Therefore, the edge effect on the oxidation kinetics in UDR does not need to be considered. From Fig. 2b, after an exposure duration of 2 h, the intergranular oxide depth of GB_{A1} is 139 nm while intergranular oxidation in NIR did not start yet. The intergranular oxide depth increases continuously from 2 to 200 h and the oxidation depth of UDR is consistently larger than that of NIR. When the exposure duration was extended to 500 h, the intergranular oxide depths of GB_D (500 h) in UDR and NIR are similar, i.e., 207 nm and 200 nm, respectively. As the exposure duration was further increased, the intergranular oxide depth in UDR gets smaller than that in NIR. The depth of intergranular oxidation did not increase monotonically with immersion time because the sampled grain boundaries have different structures. Nevertheless, the ratio of intergranular oxidation depth (NIR/UDR) increases monotonously from 0 to 1.35 as the exposure duration increases from 2 h to 1000 h. Thus, intergranular oxidation was promoted by proton irradiation when the exposure time is less than 500 h, while it was inhibited after longer exposure time. Five pairs of grain boundaries were selected to show the evolutions of microstructural and microchemical features over the exposure duration. The selected grain boundaries are GB_A (2 h), GB_B (72 h), GB_D (500 h), GB_E (750 h) and GB_F (1000 h).

3.1. GB_A (2 h)

Fig. 3a shows the STEM-HAADF image and STEM-EDS mappings of GB_{A1} (2 h) from UDR. From Fig. 3a, a continuous oxide layer was formed on the surface. From the EDS mappings, the intensity of Cr is significantly higher than that in the matrix. There is no apparent variation in chemical composition between the region just beyond the intergranular

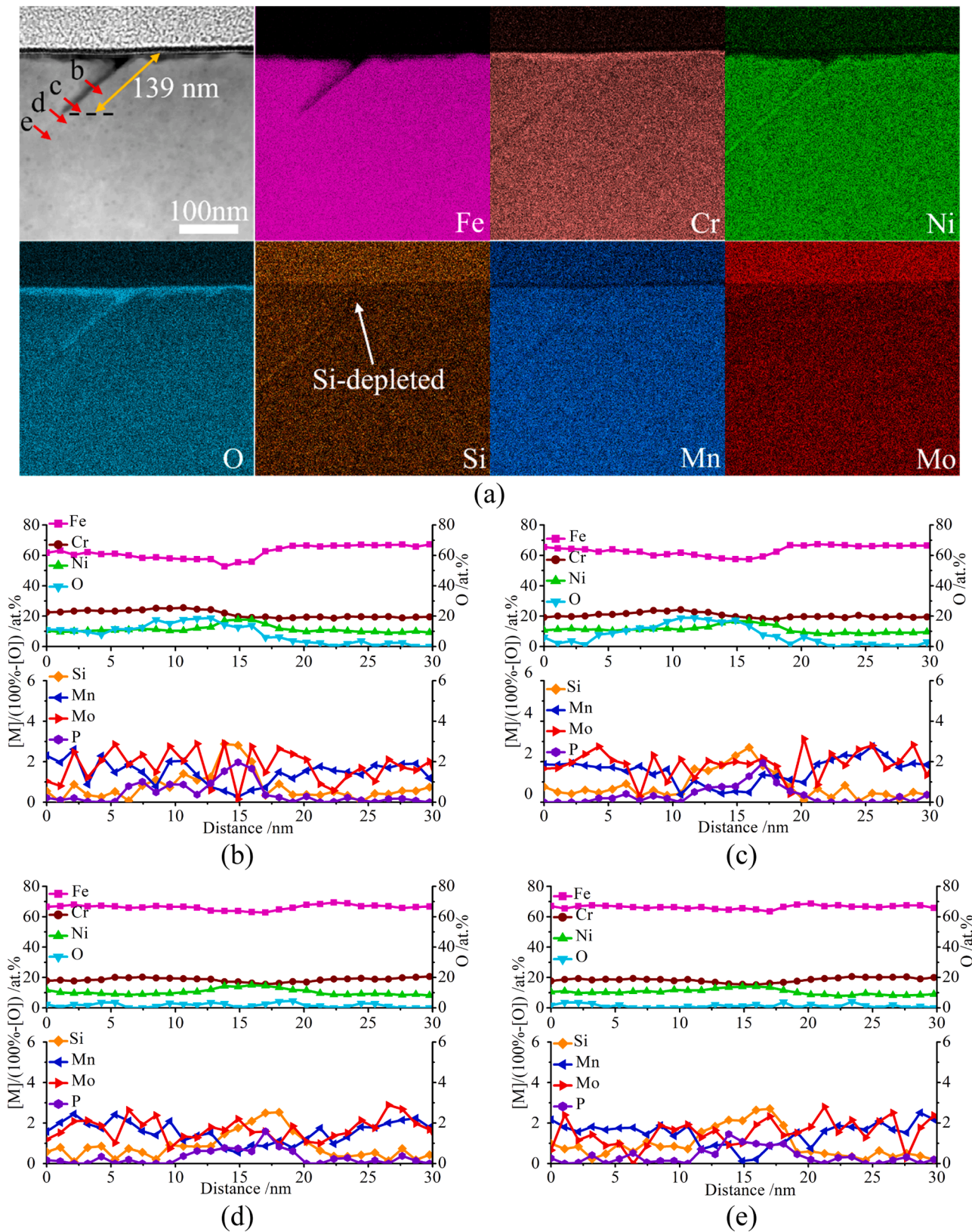


Fig. 3. (a) STEM-HAADF image with EDS mappings of GB_{A1} (2 h) from UDR and (b-e) EDS line profiles along the lines in (a). (M represents base elements).

oxide and the pristine grain boundary. The depth of intergranular oxide along GB_{A1} (2 h) is around 139 nm. The degree of element enrichment or depletion at the intergranular oxide (grain boundary) is defined as the difference in element content between the intergranular oxide (grain

boundary) and alloy matrix near the intergranular oxide (grain boundary). The intergranular oxide and pristine grain boundary (refer to the grain boundaries that have not been affected by oxidation) are depleted in Cr and Mn while enriched in Ni. It should be noted that most of the

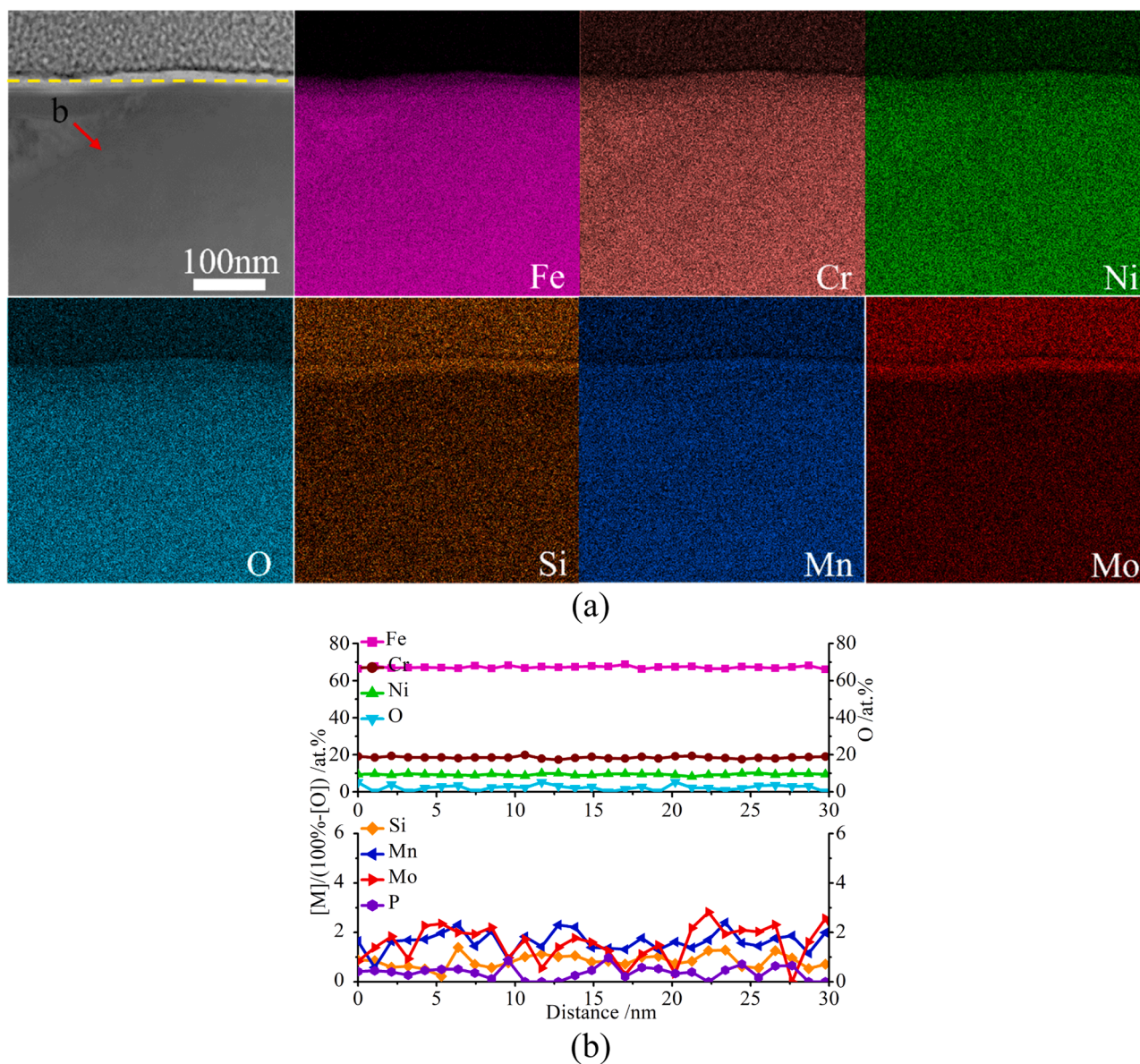


Fig. 4. (a) STEM-HAADF image with EDS mappings of GB_{A2} (2 h) from NIR and (b) EDS line profiles along the line in (a). (M represents base elements).

intergranular oxide and pristine grain boundary are enriched in Ni and Si except for a segment of intergranular oxide near the sample surface, indicating that Ni and Si in intergranular oxide tend to dissolve into high-temperature water near the sample surface.

Some EDS line profiles were taken as indicated in Fig. 3a. Fig. 3b and c show the EDS line profiles across the intergranular oxide. It should be noted that the atomic percentage of metal elements in oxides was obtained without counting oxygen. From Fig. 3b and c, there is nearly no change in Cr, Si and Ni contents along the intergranular oxide. Overall, the intergranular oxide is depleted in Cr and Mn while enriched in Ni, Si and P. Right beyond the intergranular oxide tip (Fig. 3d), the Si, Cr, Ni, Mn and P contents are about 2.5 at.%, 15.6 at.%, 14.5 at.%, 0.9 at.% and 1.6 at.%, respectively, which are similar to those at the pristine grain boundary (Fig. 3e) (Si: 2.7 at.%, Cr: 15.2 at.%, Ni: 14.1 at.%, Mn: 0.8 at.%, P: 1.5 at.%). It should be noted that the active elements (especially Cr and Si) levels just beyond the intergranular oxide tip are comparable to those at the pristine grain boundary, suggesting that no evident element diffusion occurred during 2 h oxidation. The magnitudes of Cr depletion and Si enrichment at the pristine grain boundary are 4.7 at.% and 2.3 at.%, respectively. It should be noted that the Mo content in the

intergranular oxide and pristine grain boundaries has not changed. As the signal peak of S overlaps with that of Mo and its content is low, S is not counted here.

Fig. 4 shows the STEM-HAADF image and STEM-EDS of GB_{A2} (2 h) from NIR. From Fig. 4a, no oxide layer was formed on the sample surface. Moreover, intergranular oxidation did not occur yet after an exposure duration of 2 h. Fig. 4b shows the EDS line profiles across the GB_{A2} (2 h). As expected, no element segregation was observed. Moreover, another pair of grain boundaries from the irradiated (GB_{A1-1}) and non-irradiated (GB_{A2-1}) regions after 2 h immersion test were sampled in this work (shown in supporting information). From Fig. S2, the intergranular oxide depth from UDR is 184 nm while intergranular oxidation in NIR has not started yet. The ratio of intergranular oxidation depth (NIR/UDR) is 0, which is consistent with that from GB_{A1} and GB_{A2} (Figs. 3 and 4).

3.2. GB_B (72 h)

Fig. 5 shows the STEM-HAADF image and EDS mappings of GB_{B1} (72 h) in UDR. From Fig. 5, a continuous oxide layer was formed on the

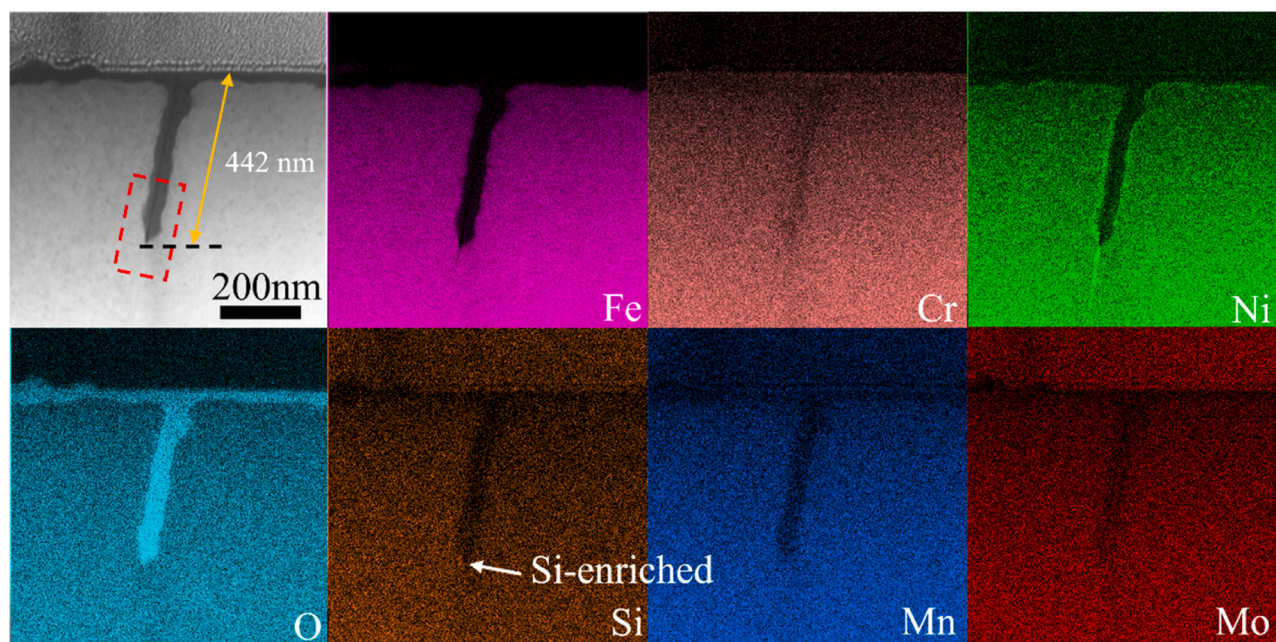


Fig. 5. STEM-HAADF image with EDS mappings of GB_{B1} (72 h) from UDR.

sample surface and penetrative intergranular oxidation occurred. The intergranular oxide is enriched in Cr and the oxide tip is enriched in Si. The penetration depth is around 442 nm. Beyond the intergranular oxide, there is a grain boundary segment enriched in Ni. The intergranular oxide tip was analyzed with STEM-EDS at higher magnification, as shown in Fig. 6a, a segment about 50 nm long is enriched in Si in the intergranular oxide tip. Interestingly, a section of grain boundary is depleted in Si (about 100 nm long) beyond the intergranular oxide compared to the pristine irradiated grain boundary where Si was initially enriched due to RIS. Meanwhile, Ni is further enriched on top of RIS while Cr and Fe are depleted. Such additional chemical segregation results from oxidation and this region is termed as “oxidation-affected zone” (OAZ) hereafter [30]. RIS can be clearly observed beyond the OAZ. The pristine segment of GB_{B1} (72 h) is enriched in Ni, Si and P while depleted in Fe, Cr and Mn from the EDS mapping (Fig. 6a). The EDS line profiles across the intergranular oxide along GB_{B1} (72 h) are shown in Fig. 6b–d. From Fig. 6b and c, Si content in the intergranular oxide decreases gradually from 6.9 ± 0.5 at.% (Fig. 6c) to 1.9 ± 0.6 at.% (Fig. 6b) when moving away from the oxidation front to the surface, indicating that Si tends to dissolve away after being oxidized. Moreover, Si depletion (relative to the pristine irradiated grain boundary) was observed beyond the intergranular oxide (Fig. 6a and e). As reported in our previous work [30], Si enriched at the grain boundary due to RIS can diffuse rapidly to the oxidation front and get oxidized. Unlike in GB_{A1} (2 h), Cr is enriched in the intergranular oxide of GB_{B1} (72 h) (Fig. 6b–d). As mentioned before, intergranular oxidation results in further depletion of Fe, Cr and enrichment of Ni just beyond the oxidation tip (Fig. 6e and f) on top of RIS (Fig. 6g). A 100 nm long and 8 nm wide OAZ was developed beyond the oxide tip (Fig. 6a and e). The magnitude of Cr depletion in the OAZ is as high as 9.0 at.% (Fig. 6e). The RIS at the pristine segment grain boundary is presented in Fig. 6g. The magnitudes of Si enrichment and Cr depletion at GB_{B1} (72 h) are 4.6 at.% and 5.3 at.%, respectively. The magnitude of P enrichment at GB_{B1} (72 h) is 3.0 at.% (Fig. 6g) and the P level decreases dramatically from the pristine grain boundary to the intergranular oxidation front (Fig. 6e). Moreover, there was no P enrichment in the intergranular oxide of GB_{B1} (72 h) near the sample surface (Fig. 6b), indicating that P has completely dissolved into water. The Mo content is higher at the intergranular oxide (Fig. 6b and c) than that at the pristine GB_{B1} (72 h) which was probably induced by the

depletion of other metallic elements as the Mo profiles in the OAZ (Fig. 6e and f) and pristine grain boundary (Fig. 6g) were similar.

Fig. 7 shows the STEM-HAADF image and STEM-EDS results of GB_{B2} (72 h) from NIR. As shown in Fig. 7a, the intergranular oxide and oxide layer are enriched in Cr and there is no apparent change in chemical composition from the region just beyond the intergranular oxide to the pristine grain boundary. The depth of intergranular oxide in NIR is around 168 nm. Some EDS line profiles were taken as indicated in Fig. 7a. Fig. 7b and c show the EDS line profiles across the intergranular oxide. From Fig. 7b, the magnitude of Cr enrichment in the intergranular oxide tip of GB_{B2} (72 h) is about 26.2 ± 1.5 at.% which is lower than that in GB_{B1} (72 h) (31.8 ± 2.4 at.%). No Si enrichment was observed in the intergranular oxide tip of GB_{B2} (72 h). Furthermore, there was no elemental segregation or OAZ beyond the intergranular oxide of GB_{B2} (72 h) (Fig. 7a and d).

Fig. 8a and b show the over-focus and under-focus TEM bright field images of GB_{B1}. Some voids in the intergranular oxide and matrix were denoted. Fig. 8c shows the under-focus TEM bright field image of the enlarged intergranular oxide tip of GB_{B1} (72 h). From Fig. 8c, a region adjacent to the grain boundary is free of voids. Sekio et al. [34] have also reported the formation of void-denuded zone near grain boundaries in neutron and electron-irradiated samples. Another irradiation induced-defect (i.e., dislocation loops) was observed near the grain boundary (shown in Fig. 8d). The dark field image (from the circled spot in the insert of Fig. 8e and f) of the oxide and the SAED patterns (the inserts of Fig. 8e and f) show that both the intergranular oxides and the oxide layers on the sample surface are mainly composed of spinel which is epitaxial with the matrix. Fig. 9a shows the TEM bright field image of GB_{B2} (72 h) from NIR. Fig. 9b and c show the dark field images of the intergranular oxide and oxide layer on the sample surface. From the SAED patterns (inserts in Fig. 9b and c), the intergranular oxide and oxide layer also have a spinel structure which is epitaxial with the matrix, suggesting that proton irradiation did not change the structure of the oxide. As previously reported in our study [30], the intergranular oxide has a spinel structure after exposure to simulated PWR primary water for 1000 h, suggesting that the structure of the oxide would not change with immersion time.

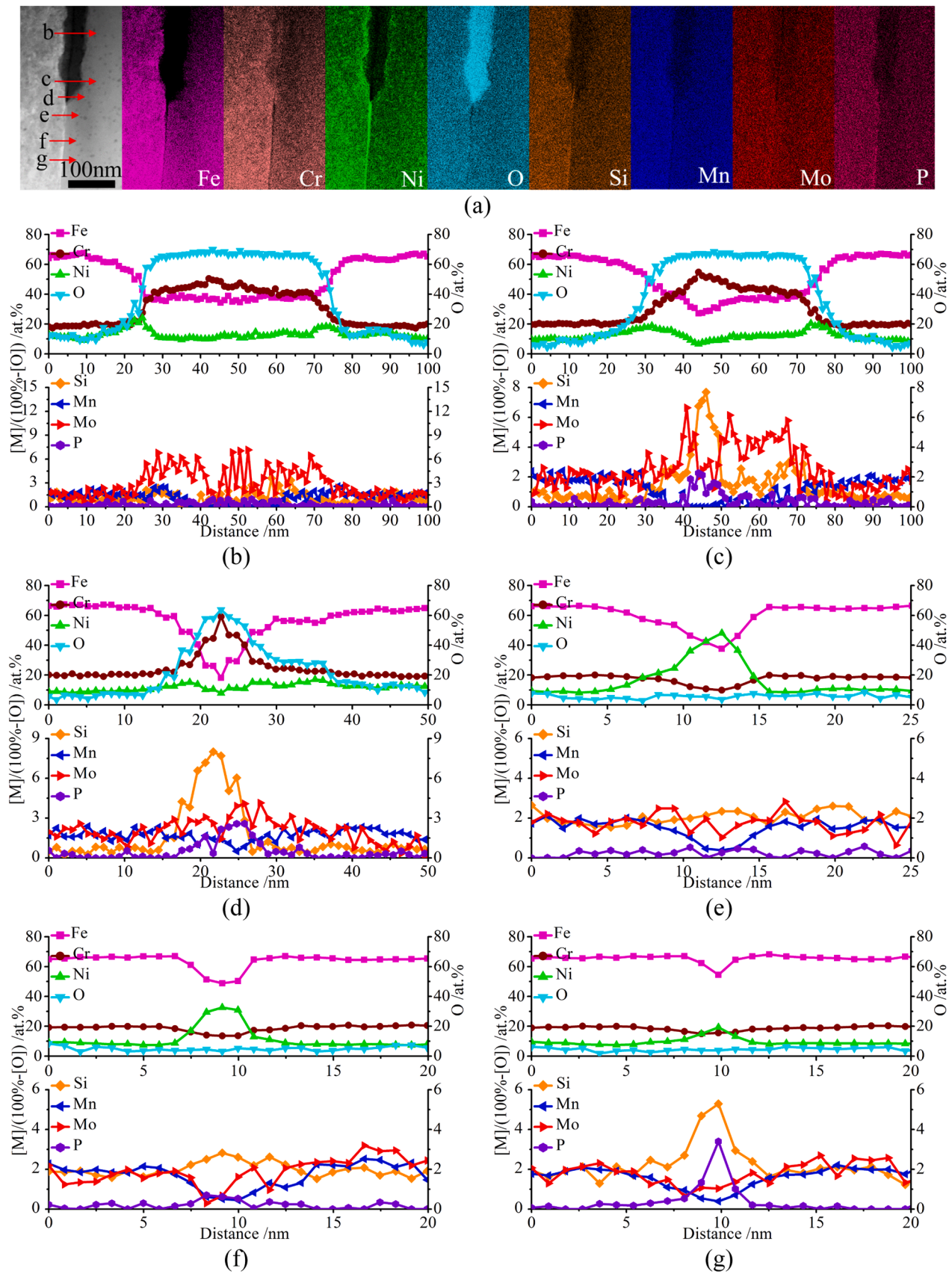


Fig. 6. (a) STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{B1} (72 h) (shown in Fig. 5 with red dotted line) in UDR and (b–g) EDS line profiles along the lines in (a). (M represents base elements).

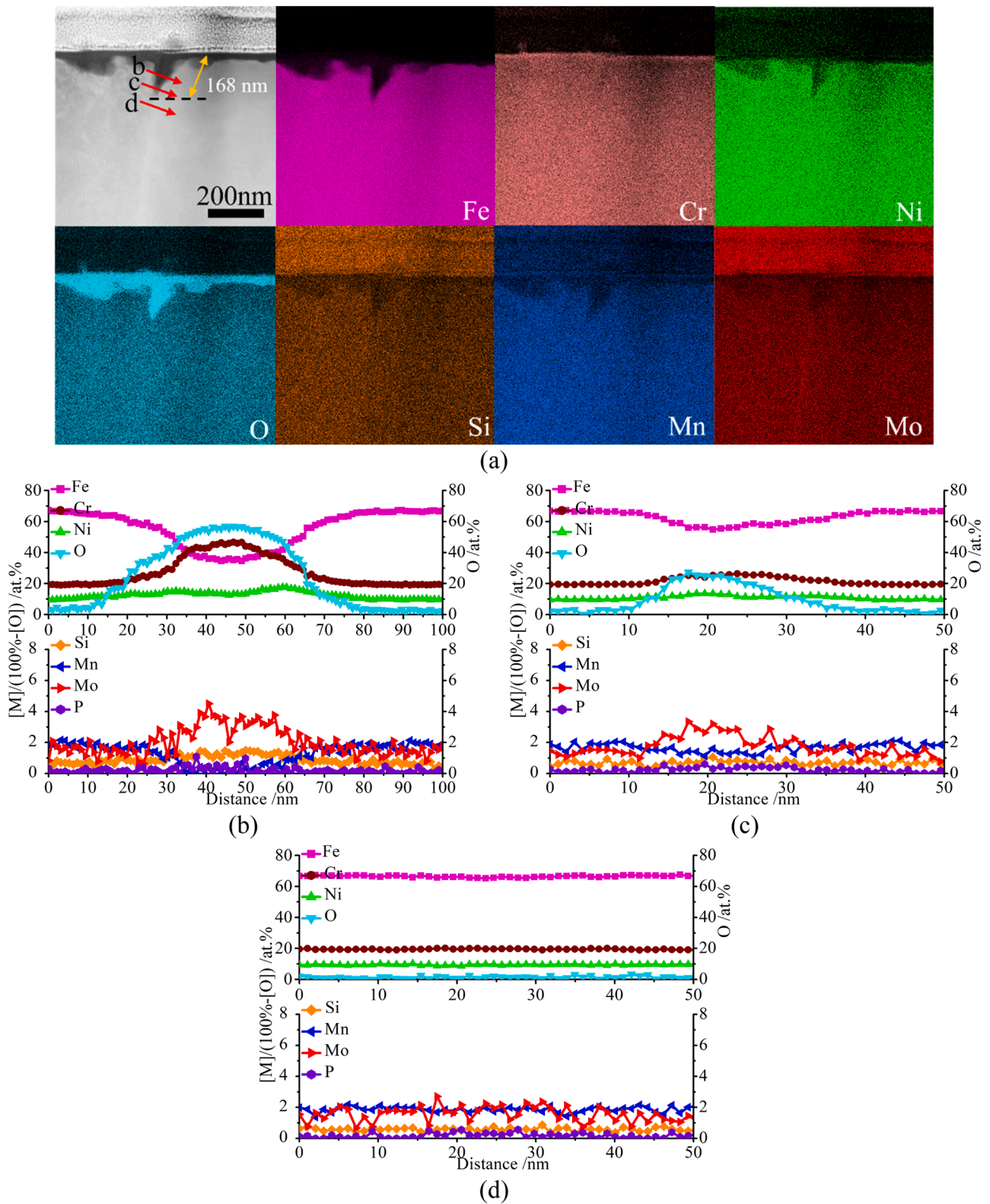


Fig. 7. (a) STEM-HAADF image with EDS mappings of GB_{B2} (72 h) from NIR and (b-d) EDS line profiles along the lines in (a). (M represents base elements).

3.3. GB_D (500 h)

Fig. 10a and b show the STEM-HAADF images with EDS mappings of GB_{D1} (500 h) and GB_{D2} (500 h). As shown in Fig. 10, continuous oxide layers were formed on the sample surfaces for both UDR and NIR. A continuous Ni-enriched transition zone lies beneath the surface oxide

layer on UDR while Ni is slightly enriched at the oxide layer/matrix interface in NIR. More interestingly, the inner oxide on UDR is more uniform and thinner compared to that on NIR. This phenomenon has been reported in our previous work [35]. The depths of intergranular oxide in UDR and NIR are nearly the same (207 nm vs. 200 nm). These two samples show distinct differences in the chemical composition of

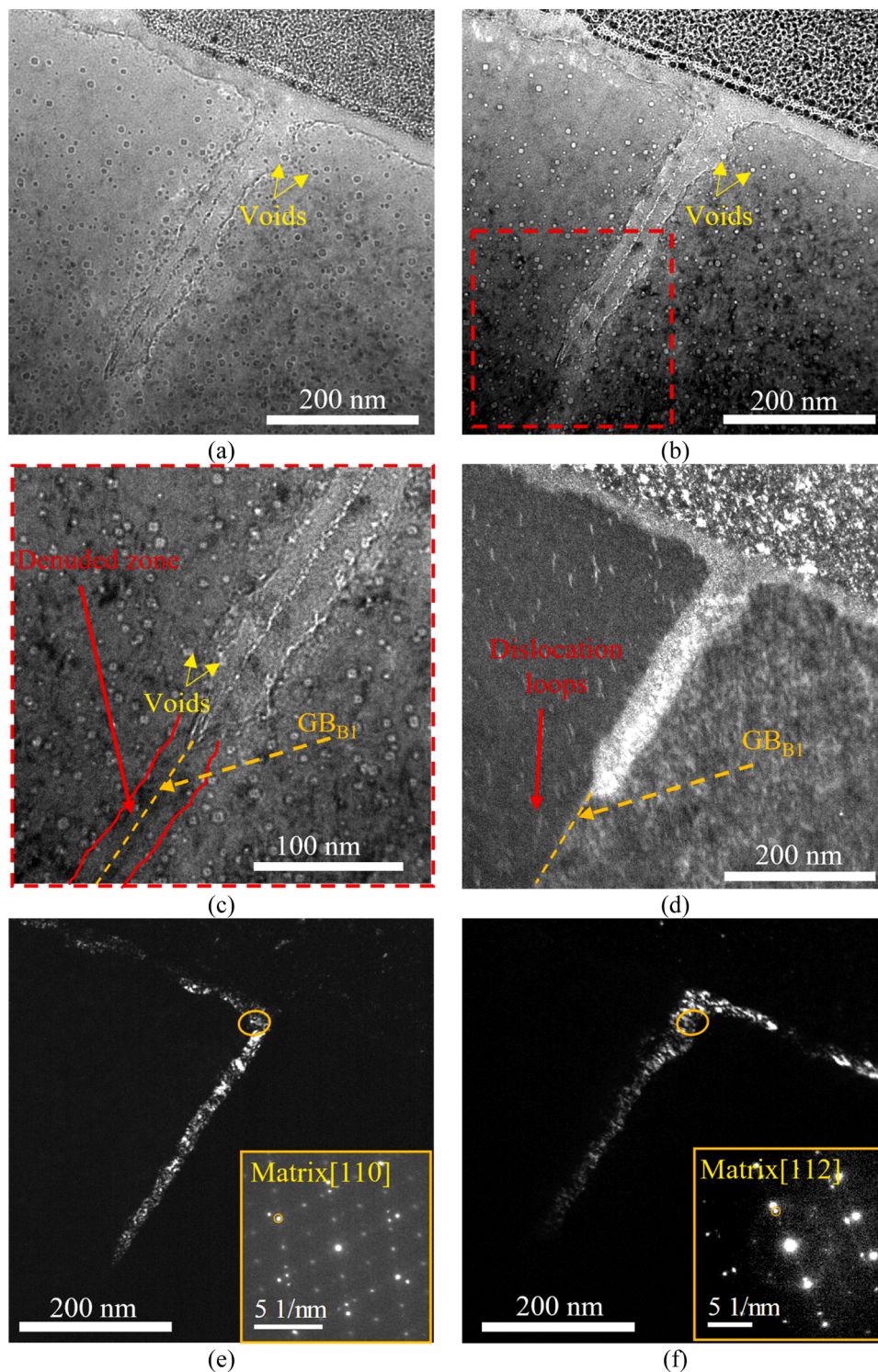


Fig. 8. (a) TEM bright field over-focus image of the GB_{B1} (72 h) from UDR, (b) TEM bright field under-focus image of the GB_{B1} (72 h), (c) TEM bright field under-focus image of the enlarged intergranular oxide tip of GB_{B1} (72 h), (d) TEM dark field image of the dislocation loops near the grain boundary, (e-f) TEM dark field images of the spinel oxide.

intergranular oxide. Despite radiation-induced Cr depletion at the pristine irradiated grain boundary, the intergranular oxide along GB_{D1} (500 h) is richer in Cr. The feature of Si distribution along GB_{D1} (500 h) is similar to those along GB_{B1} (72 h) and GB_{C1} , i.e., Si is enriched at the intergranular oxide tip and depleted along a grain boundary segment just beyond the oxide (relative to the pristine irradiated grain boundary). The size of OAZ beyond the intergranular oxide (quantified by

length and width) in UDR is much larger than that in NIR. Beyond the OAZ segment, RIS is clearly visible along the pristine grain boundary of GB_{D1} (500 h), which is not observed at GB_{D2} (500 h).

Fig. 11a shows the STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{D1} (500 h). The scanned area covers a segment of intergranular oxide, OAZ and the pristine grain boundary. Some EDS line profiles across the intergranular oxide

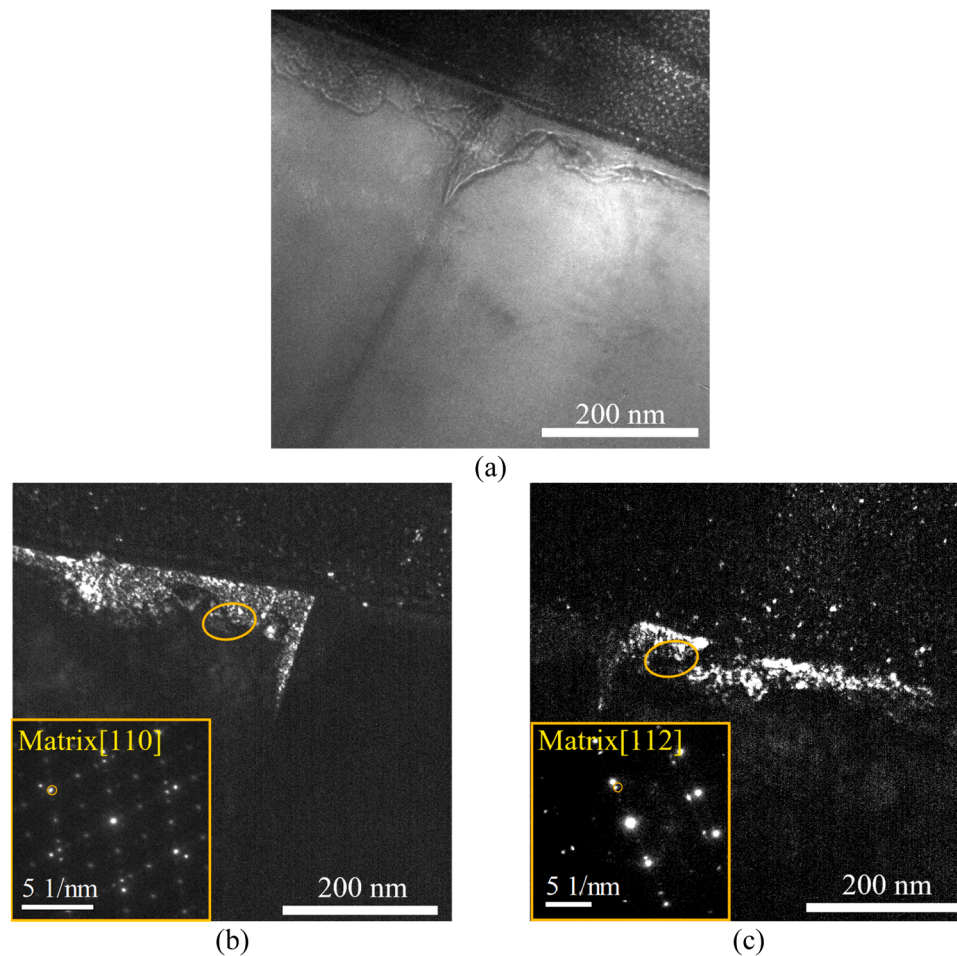


Fig. 9. (a) TEM bright field image of the GB_{B2} (72 h) from NIR, (b-c) TEM dark field image of the spinel oxide.

(Fig. 11b and c), OAZ (Fig. 11d and e) and pristine grain boundary (Fig. 11f) were taken. From Fig. 11b and c, the magnitude of Si enrichment at the intergranular oxide tip is 8.9 ± 0.9 at.% (Fig. 11c) and then drops quickly when approaching the sample surface (Fig. 11b). The magnitude of Cr enrichment in the intergranular oxide tip is as high as 47.5 ± 2.0 at.% (Fig. 11c). As mentioned above, intergranular oxidation induces additional element segregation at the grain boundary just beyond the intergranular oxide tip. This was again confirmed in GB_{D1} (500 h) (Fig. 11d and e). The length and width of OAZ are around 280 nm and 17 nm, respectively. The magnitudes of Cr depletion and Ni enrichment in the OAZ are 11.5 at.% and 48.6 at.% (Fig. 11d). Beyond the OAZ segment, element segregation due to RIS was observed at the pristine grain boundary. (Fig. 11f).

Fig. 12a shows the STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{D2} (500 h). From Fig. 12a, Cr is slightly enriched in the intergranular oxide and Ni is significantly enriched beyond the intergranular oxide tip. Moreover, Mo enrichment was observed along the oxidized and pristine grain boundary. As previously reported in our study [30], Mo enrichment was only observed at some of the grain boundaries and does not change the intergranular oxidation behavior. Fig. 12b and c show the EDS line profiles across the intergranular oxide of GB_{D2} (500 h). The chemical composition of intergranular oxide in NIR significantly differs from that in UDR. As shown in Fig. 12c, the magnitude of Cr enrichment in the intergranular oxide tip of GB_{D2} (500 h) is remarkably lower than that in GB_{D1} (500 h) (34.0 ± 2.9 at.% vs. 47.5 ± 2.0 at.%). Beyond the intergranular oxide, an OAZ approximately 40 nm long and 8 nm wide was observed (Fig. 12a and d). The magnitudes of Cr depletion and Ni enrichment in the OAZ are 1.4 at.% and 9.1 at.%, respectively. It should be noted that

the degree of element segregation in the OAZ in NIR is much lower than that in UDR. Beyond the OAZ segment, element segregation was not detected.

3.4. GB_E (750 h)

Fig. 13a and b show the STEM-HAADF images with EDS mappings of GB_{E1} (750 h) and GB_{E2} (750 h) from UDR and NIR, respectively. The features of inner oxide layer and Ni-enriched transition zone that lie beneath the oxide layer on UDR and NIR were similar to those after 1000 h-exposure [35]. The depth of intergranular oxide in UDR is larger than that in NIR (938 nm vs. 837 nm). The chemical composition of intergranular oxide in UDR and NIR shows distinct differences, especially in the Cr content. The intergranular oxide in UDR is much richer in Cr than that in NIR. Moreover, the size of OAZ beyond the intergranular oxide (quantified by length and width) of GB_{E1} (750 h) is much larger than that of GB_{E2} (750 h).

Fig. 14a shows the STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{E1} (750 h). Some EDS line profiles across the intergranular oxide (Fig. 14b and c), OAZ (Fig. 14d and e) and pristine grain boundary (Fig. 14f) were taken. As shown in Fig. 14b, the magnitudes of Si and Cr enrichment at the intergranular oxide tip are 13.3 ± 1.5 at.% and 49.5 ± 3.0 at.%, respectively. The intergranular oxide tip appears to penetrate into the OAZ (Fig. 14a and c). As mentioned above, intergranular oxidation induced additional element segregation at the grain boundary just beyond the intergranular oxide tip. This was again confirmed in GB_{E1} (750 h) (Fig. 14d and e). The length and width of OAZ are around 215 nm and 26 nm, respectively. The magnitudes of Cr depletion and Ni enrichment in the OAZ are 13.2

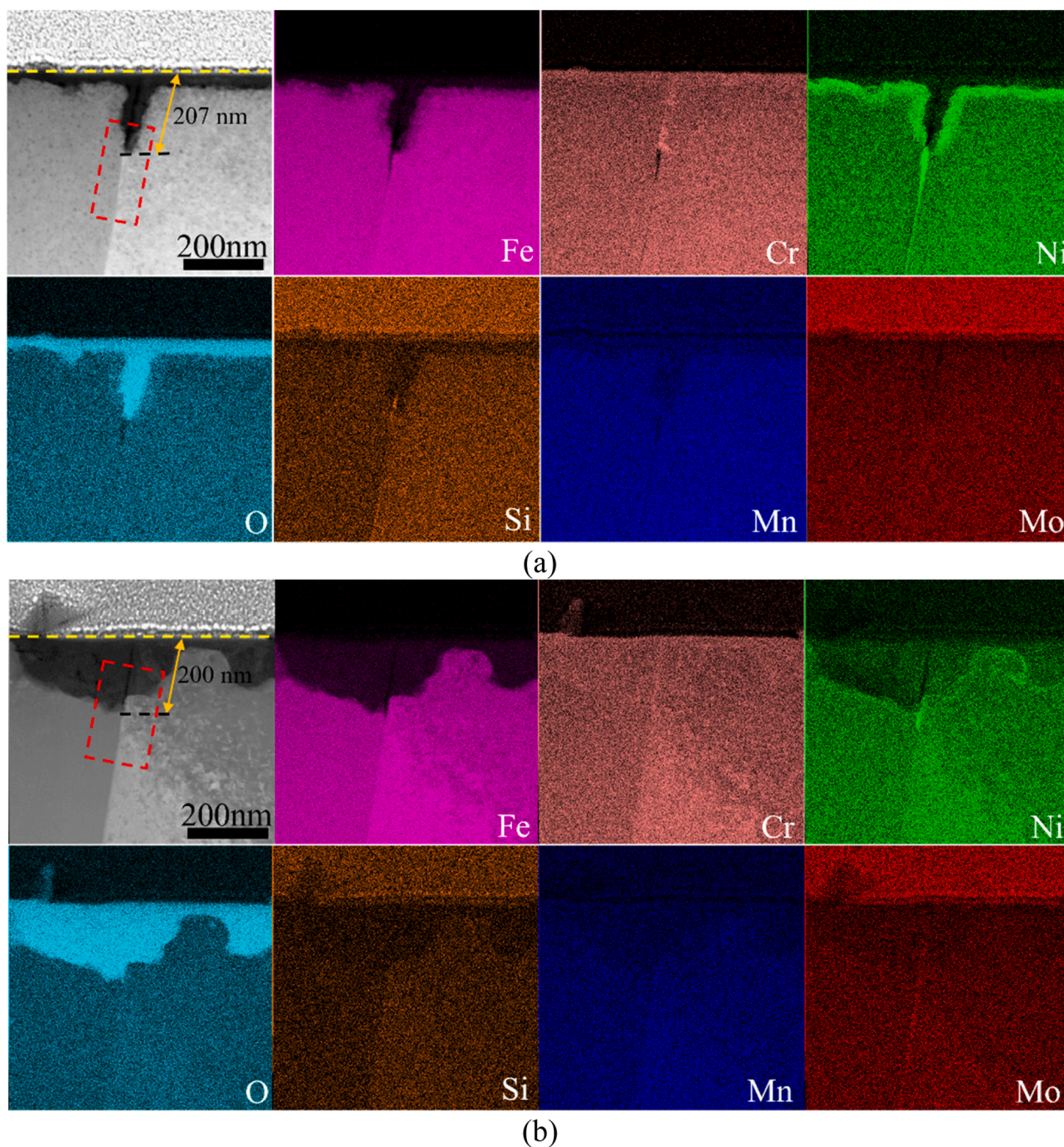


Fig. 10. STEM-HAADF images with EDS mappings of (a) GB_{D1} (500 h) and (b) GB_{D2} (500 h) from UDR and NIR, respectively.

at.% and 55.6 at.% (Fig. 14d). Beyond the OAZ segment, element segregation due to RIS was observed at the pristine grain boundary. (Fig. 14f).

Fig. 15a shows the STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{E2} (750 h). From Fig. 15b and c, the magnitude of Cr enrichment in the intergranular oxide tip in NIR is much smaller than that in UDR (Fig. 14b) (33.4 ± 4.0 at.% vs. 49.5 ± 3.0 at.%). Moreover, there was no apparent OAZ beyond the intergranular oxide (Fig. 12a and d). Beyond the intergranular oxide tip, element segregation was not detected except for Mo enrichment (Fig. 15e). Table 2 lists the details of OAZ in UDR and NIR after different immersion times. From Table 2, the size of OAZ and the magnitude of Cr depletion in OAZ in UDR are always larger than those in the corresponding NIR regardless of the immersion time.

Fig. 16a shows the changes in Cr content at the intergranular oxide tip in UDR and NIR as a function of immersion time. From Fig. 16a, as the oxidation time increases from 2 h to 72 h, the intergranular oxide tip in UDR changes from Cr-depleted to Cr-enriched. The difference in the Cr content at the intergranular oxide tip between UDR and NIR increases monotonically with increasing immersion time. Meanwhile, the ratio of intergranular oxidation depth (NIR/UDR) also increases monotonously from 0 to 1.35, suggesting that the resistance to intergranular oxidation is closely related to the degree of Cr enrichment. The Cr content at the pristine grain boundary varies slightly among those six grain boundaries in UDR and NIR. Fig. 16b shows the changes in Si content at the intergranular oxide tip and pristine grain boundary in UDR. From Fig. 16b, there is noticeable variation in Si segregation among the sampled grain boundaries. The Si content at the intergranular oxide tip in UDR is

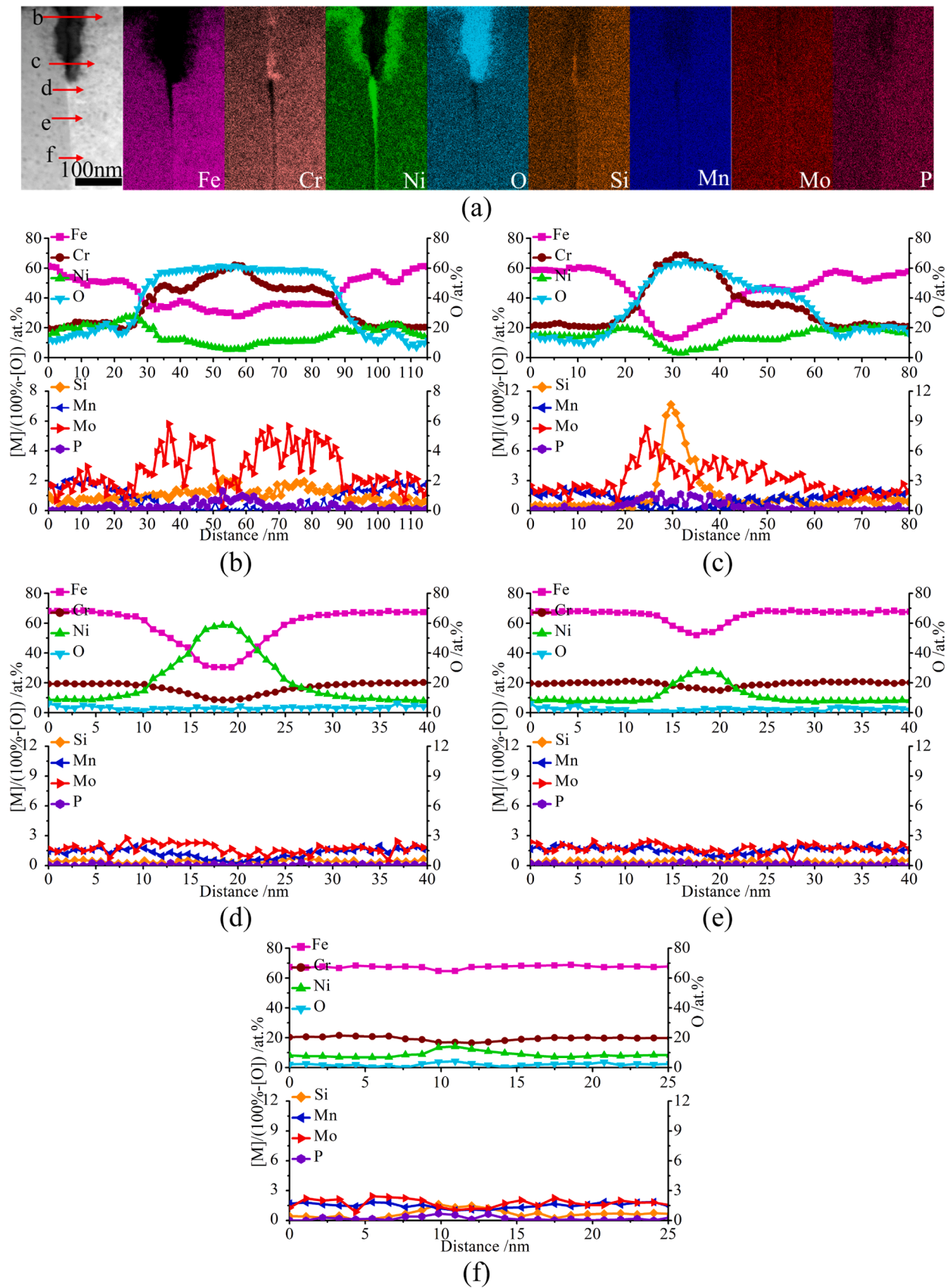


Fig. 11. (a) STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{D1} (500 h) (shown in Fig. 10a with red dotted line) in UDR and (b–f) EDS line profiles along the lines in (a). (M represents base elements).

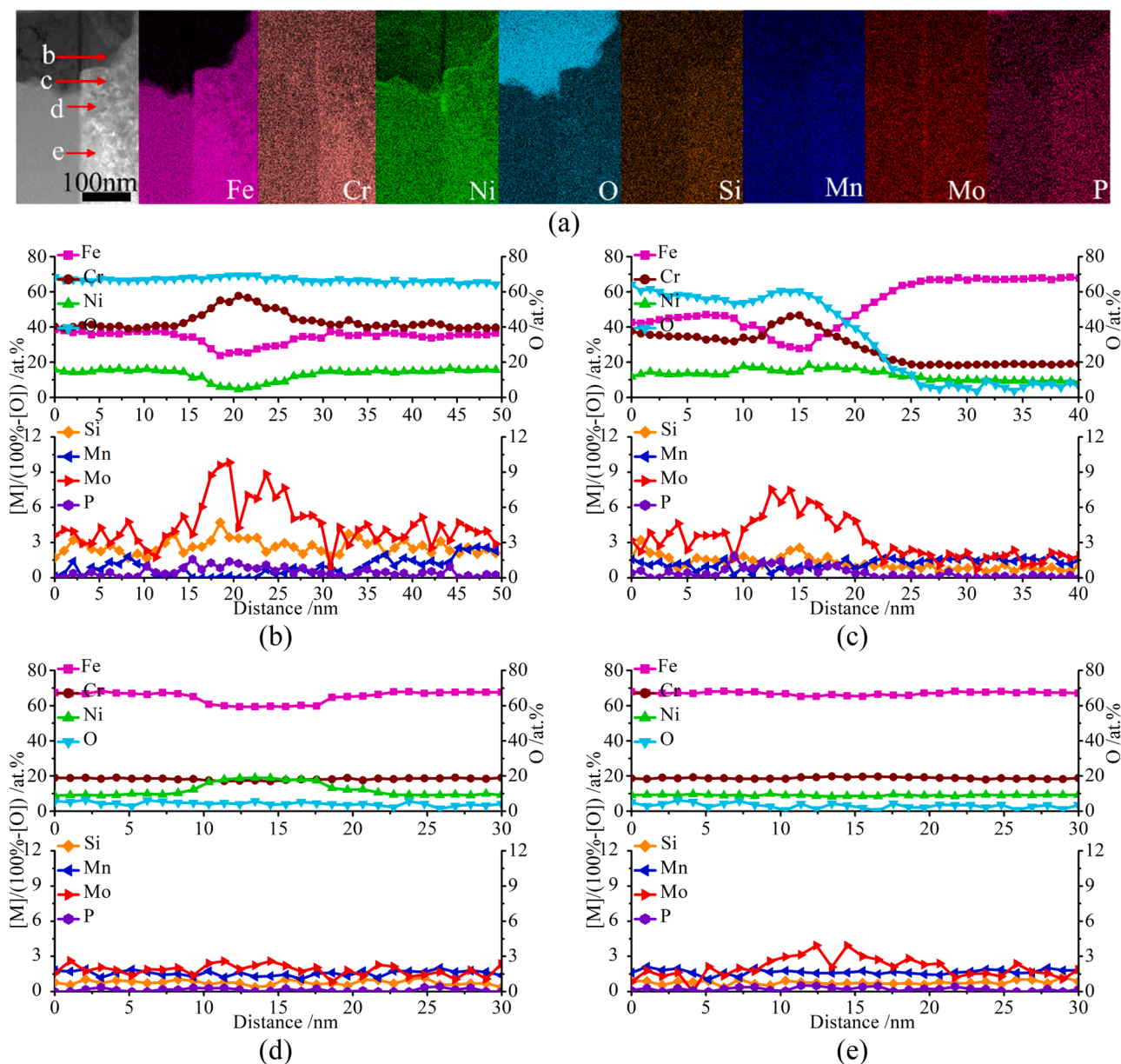


Fig. 12. (a) STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{D2} (500 h) (shown in Fig. 10b with red dotted line) in NIR and (b–e) EDS line profiles along the lines in (a). (M represents base elements).

comparable with that at the pristine grain boundary after an exposure duration of 2 h. Thereafter, the Si content at the intergranular oxide tip gets much larger than that at the pristine grain boundary when the immersion time increases from 72 h to 1000 h. It should be noted that the Cr and Si contents at the intergranular oxide tip were calculated from EDS line scan results (within a range of 2.5 nm on both sides of the grain boundary where the oxygen signal is almost constant). The error bars are the standard deviations of the measured results.

4. Discussion

In this section, the microstructural and microchemical features of intergranular oxide from the irradiated region will be firstly compared with those of its non-irradiated counterpart after different immersion times. Then the role of proton irradiation in the intergranular oxidation of 316 L stainless steel in simulated PWR primary water will be summarized. Afterwards, the mechanism of irradiation effect on intergranular oxidation will be discussed and the implication on IASCC

mechanism will be given.

4.1. Time dependence of irradiation effect on the intergranular oxidation

As the immersion time increases, the ratio of intergranular oxidation depth between NIR and UDR rises monotonously (Fig. 2b). The intergranular oxide depths in NIR are smaller than those in UDR when the immersion time is less than 500 h. Thereafter, intergranular oxidation depths in NIR exceed those in UDR. It should be noted that the depth of intergranular oxidation in UDR or NIR does not increase monotonically with immersion time. That should be due to the difference in grain boundary structure, as indicated by the different grain boundary plane indices (Fig. 2a). Indeed, there are clear evidences showing that the intergranular oxidation behavior is highly dependent on grain boundary structure [28,29,36]. Thus, in order to reveal the effect of irradiation on intergranular oxidation behavior, it is imperative to maintain the structure of grain boundary the same. From this work, proton irradiation has an acceleration effect on the intergranular oxidation of 316 L

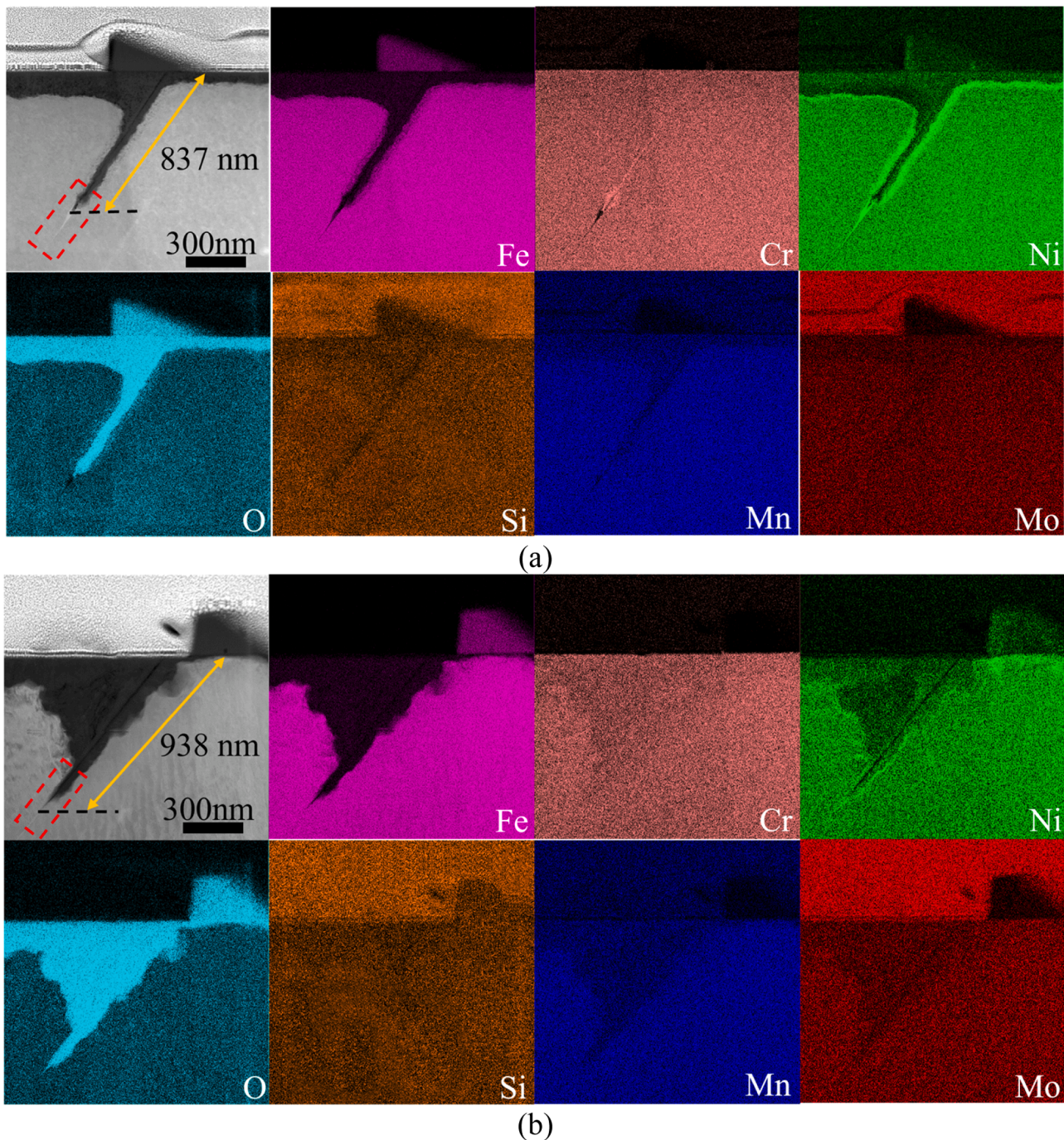


Fig. 13. STEM-HAADF images with EDS mappings of (a) GB_{E1} (750 h) and (b) GB_{E2} (750 h) from UDR and NIR, respectively.

stainless steel in simulated PWR primary water after shorter-term immersion (less than 500 h) but a mitigation effect after longer-term oxidation. Interestingly, our findings differ from some earlier results. For example, previous works [23,24] suggest that irradiated stainless steel shows an enhanced propensity to intergranular oxidation due to RIS after immersion in PWR primary water for longer-term durations (more than 500 h). Such inconsistency probably results from the interference of differences in the structure of sampled grain boundaries as the grain boundary structure was not controlled in those works. Boisson et al. [22] found that proton irradiation promotes intergranular oxidation in a simulated PWR water environment after 24 h immersion, which is consistent with our results, although the interference from difference in grain boundary structure was not ruled out in their study. By

controlling the grain boundary structure as well as acquiring oxidation depth from large sample area, we confirmed that proton irradiation could decelerate intergranular oxidation of 316 L stainless steel in simulated PWR primary water after 1000 h [30]. In this work, it is found for the first time that proton irradiation has different effects on the intergranular oxidation of 316 L stainless steel which are dependent on the immersion time: it accelerates oxidation at the beginning but mitigates oxidation after longer-term exposure.

4.2. Mechanism of time dependence

The mechanism of time dependence of irradiation effect on the intergranular oxidation can be understood from its different roles at

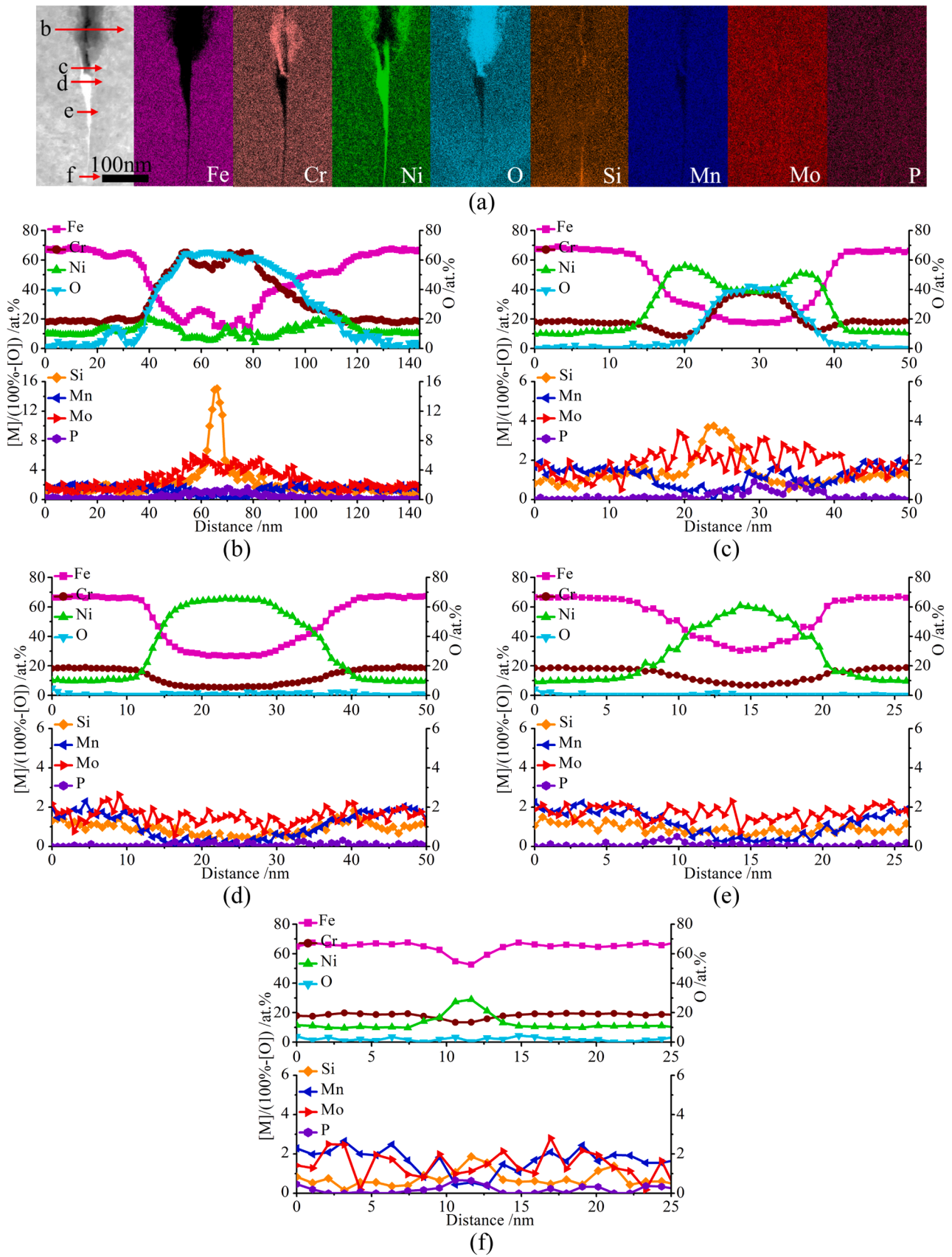


Fig. 14. (a) STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{E1} (750 h) (shown in Fig. 13a with red dotted line) in UDR and (b–f) EDS line profiles along the lines in (a). (M represents base elements).

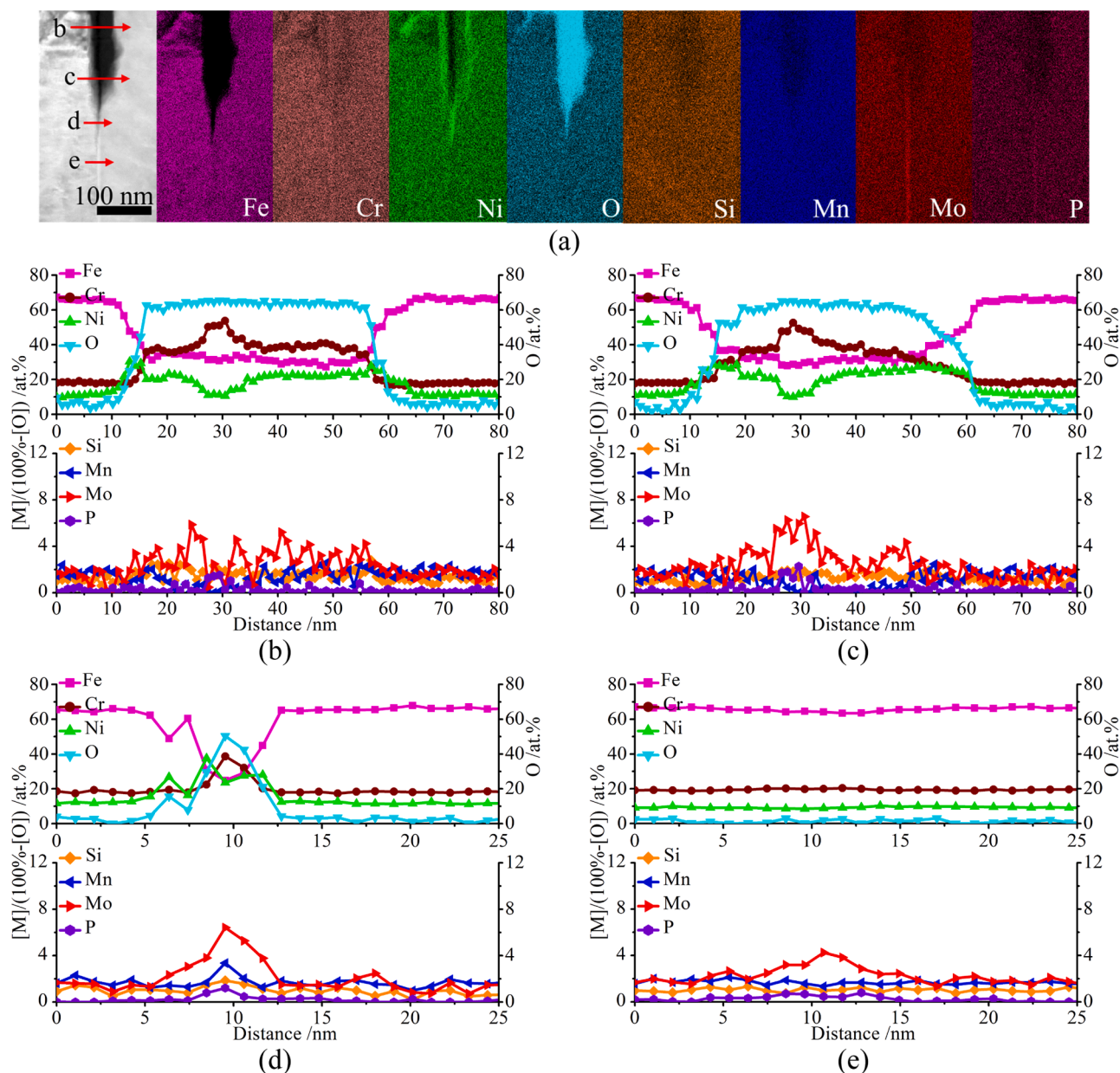


Fig. 15. (a) STEM-HAADF image and EDS mappings of the enlarged intergranular oxide tip of GB_{E2} (750 h) (shown in Fig. 13b with red dotted line) in NIR and (b–e) EDS line profiles along the lines in (a). (M represents base elements).

different stages of oxidation. The pristine grain boundary is depleted in Cr due to RIS, which is detrimental to the oxidation resistance. However, according to our earlier research [30], the resistance to intergranular oxidation of irradiated 316 L stainless steel is enhanced after an exposure duration of 1000 h due to Cr enrichment at the intergranular oxide tip which is ascribed to the promoted element diffusion (especially Cr) by irradiation. Therefore, the difference in oxidation kinetics between an irradiated grain boundary and its non-irradiated counterpart after different immersion times should be dictated by the competition between these two opposite effects. As mentioned above, the intergranular oxide in UDR is depleted in Cr (Fig. 3a–c) and no preferential solute diffusion has occurred yet after an exposure duration of 2 h. In addition, preferential dissolutions of Fe, Si and Ni along the grain boundary can be observed near the surface. The preferential dissolutions of Fe and Ni at the initial stage of aqueous oxidation of stainless steel have also been reported before [37,38]. In this case, Cr depletion from RIS and the fast ingress of oxygen along the defective intergranular oxide are mainly

responsible for the higher intergranular oxidation kinetics in UDR at the initial stage. Up to 72 h, although the solute diffusion along grain boundary is enhanced in UDR, RIS at the pristine grain boundary still plays a dominant role in the intergranular oxidation, resulting in a deeper oxidation in UDR. Such a situation probably continues up to an exposure duration of 500 h but starts to reverse thereafter. The negative effect of RIS on intergranular oxidation resistance is balanced by the positive effect due to the promoted solute diffusion after an exposure duration of 500 h. As the exposure time was further extended, the intergranular oxidation depth in NIR gradually exceeded that in UDR (Fig. 2b). As reported in our previous work [30], after an exposure duration of 1000 h, the average depth of intergranular oxidation in UDR is significantly smaller than that in NIR (428 ± 17 nm vs. 537 ± 19 nm), suggesting that the positive effect of enhanced diffusion on intergranular oxidation resistance overtakes the negative effect of RIS in UDR.

The rivalry between RIS and enhanced solute diffusivity in UDR can be directly reflected from the difference in Cr content at the

Table 2

Sizes of oxidation affected zone (OAZ), magnitude of Cr depletion in OAZ, RIS (Cr) at the pristine grain boundary, and intergranular oxide penetrations of GB_X (X is from A to F).

GB		OAZ* (nm)		Magnitude of Cr depletion in OAZ (at.%)	RIS(Cr) at the pristine grain boundary (at.%)	Intergranular oxide penetrations (nm)
		Length	Width			
2h	GB _{A1}	0	0	–	4.7	139
	GB _{A2}	–	–	–	–	–
72h	GB _{B1}	100	8	9.0	5.3	442
	GB _{B2}	0	0	–	–	168
200h	GB _{C1}	150	10	7.8	4.8	1407
	GB _{C2}	0	0	–	–	870
500h	GB _{D1}	280	17	11.5	3.5	200
	GB _{D2}	40	8	1.4	–	207
750h	GB _{E1}	215	26	13.2	5.5	837
	GB _{E2}	0	0	–	–	938
1000h	GB _{F1}	250	15	8.8	5.7	427
	GB _{F2}	94	5	8.6	–	575

* Oxidation affected zone (OAZ) beyond the intergranular oxide.

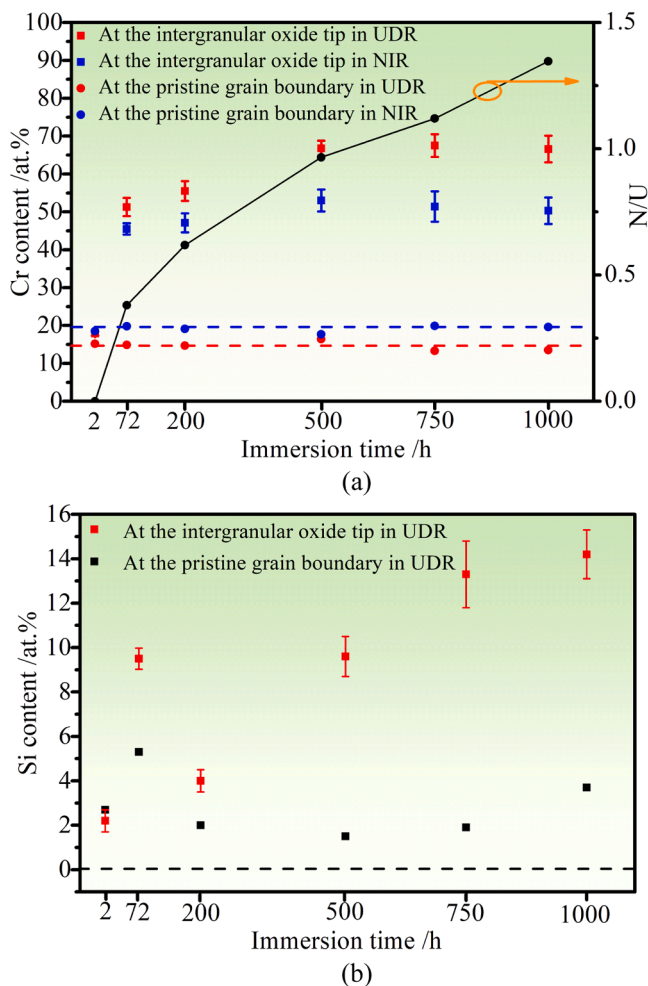


Fig. 16. (a) Changes in Cr content (with the exclusion of oxygen) at the intergranular oxide tip in UDR and NIR as a function of immersion time, (b) Changes in Si content (with the exclusion of oxygen) at the intergranular oxide tip and pristine grain boundary in UDR as a function of immersion time. (N/U represents the ratio of intergranular oxidation depths of the non-irradiated grain boundary to its irradiated counterpart).

intergranular oxide tip between UDR and NIR (Fig. 16a). Such difference in Cr content gradually increases with time and almost saturates after 750 h, suggesting that the enhancement in Cr diffusivity probably levels off after longer time. The Cr content in oxide is closely related to the protectiveness of oxide and the oxidation rate. For instance, Alloy 600 [27,39,40] exhibits much lower intergranular oxidation resistance in the PWR primary water than Alloy 690 [18,28,41] due to the significant difference in Cr content between them (~15% vs. ~30%). Terachi et al. [42] and Kanzaki et al. [43] have also reported that the oxidation kinetics in simulated PWR primary water decreased with increasing Cr content in alloy. Thus, the gradually suppressed intergranular oxidation in UDR should be directly linked to the increasing Cr content at the oxide tip. Apart from Cr, Si is also enriched in the intergranular oxide tip. Fig. 16b shows the Si content in UDR with increasing immersion time. The Si content at the intergranular oxide tip is comparable with that at the pristine grain boundary (2.5 at.% vs. 2.7 at.%) after an exposure duration of 2 h. Thereafter, the Si content in the oxide tip gets much higher than that induced by RIS. The enrichment of Si in the intergranular oxide tip results from its higher oxygen affinity [44,45] and fast diffusivity in austenitic steel [46,47]. As mentioned in our earlier work [30], the efficiency of Cr transport along grain boundary is promoted in UDR mainly due to vacancies created by the preferential diffusion of Si. Although Si-enriched oxide tends to dissolve into high-temperature water, it can serve as a temporary barrier for oxidant ingress in the intergranular oxide tip.

The intergranular oxidation processes of the irradiated grain boundary and its non-irradiated counterpart are summarized in Fig. 17. When the immersion time is less than 2 h, the grain boundary in UDR is oxidized preferentially due to RIS at the pristine grain boundary, while intergranular oxidation has not occurred in NIR. When the immersion time extends to 72 h, intergranular oxidation occurs in both UDR and NIR. The intergranular oxide penetration in UDR is much deeper than that in NIR. For the irradiated grain boundary (Fig. 17a), Si enriched at the pristine grain boundary can diffuse outwards preferentially and get oxidized at the intergranular oxide tip due to its high diffusivity and affinity to oxygen. The fast diffusion of Si creates vacancies that enhance the Cr diffusion to the oxidation front, as indicated by a larger OAZ beyond the oxide tip. Thus, despite Cr depletion induced by RIS at the pristine grain boundary, the Cr content at the intergranular oxide tip in UDR gets increasingly higher than that in NIR after 72 h. The gradually enhanced Cr enrichment at the intergranular oxide tip in UDR helps to mitigate the intergranular oxidation eventually. Hence, when the immersion time reaches 500 h, the intergranular oxidation penetration in UDR is almost identical to that in NIR, indicating that the beneficial effect of enhanced Cr diffusivity on resistance to intergranular oxidation counterbalances the detrimental effect of RIS. Thereafter, the mitigation effect becomes dominant and the intergranular oxide penetration in UDR gets shallower than that in NIR. In summary, RIS at the pristine grain boundary promotes intergranular oxidation after shorter-term immersion (less than 500 h). Nevertheless, the promoted solute diffusion along irradiated grain boundary results in higher Cr content in intergranular oxide which can mitigate the subsequent oxidation. Such an effect gradually builds up with time and finally dominates when the exposure duration is longer than 500 h. Moreover, it is believed that the “equilibrium time” may be dependent on other factors (e.g., damage dose, dissolved hydrogen content, and water temperature) which have been shown to strongly affect the intergranular oxidation kinetics [24, 48,49]. The influence of damage dose deserves consideration. However, a higher damage dose induces more severe RIS and higher solute diffusivity along grain boundary which would produce conflicting effects on the intergranular oxidation kinetics. Thus, further detailed studies should be conducted to clarify the overall effect.

4.3. Implication on IASCC mechanism

Now increasing results suggest that the grain boundary strength

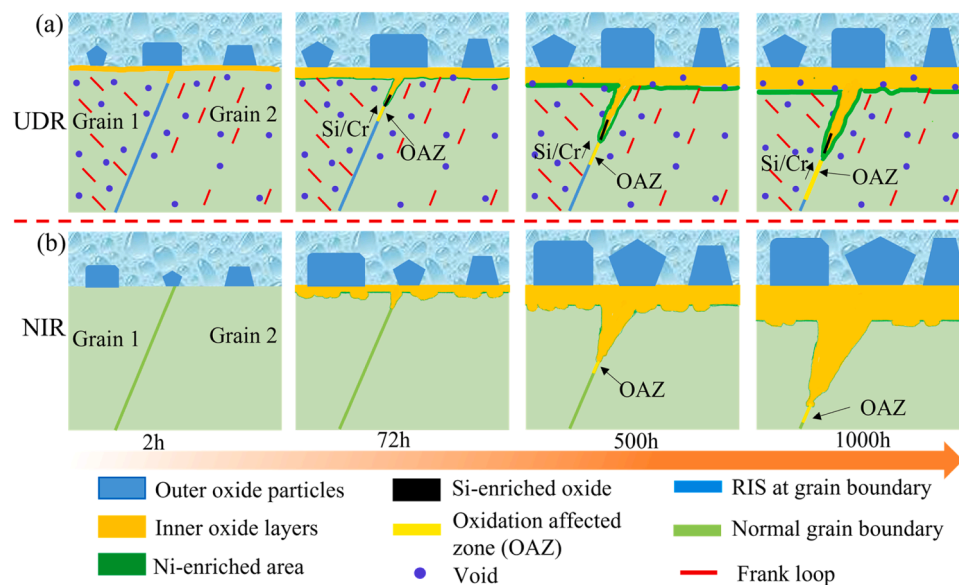


Fig. 17. Schematic of intergranular oxidation behavior for the (a) irradiated grain boundary and its (b) unirradiated counterpart as a function of immersion time.

decreases after intergranular oxidation has occurred and the oxidized grain boundary eventually fractures when its strength drops below the applied stress [40,50–52]. Moreover, many studies [17,53–56] have revealed that intergranular oxidation can always be found ahead of SCC crack tips. Thus, intergranular oxidation degrades the grain boundary strength and appears to be an inevitable precursor of SCC for austenitic stainless steel in high-temperature water. In our previous work, it is confirmed that the intergranular oxide depth in UDR is smaller than in NIR after longer-term immersion in simulated PWR primary water [30]. It has also been pointed out that the Si-enriched oxide formed at the intergranular oxide tip in UDR would be easily breached under stress given the brittle nature of Si-containing oxide [57–59]. Here it is found that at the early stage of oxidation, RIS at the irradiated grain boundary can remarkably promote intergranular oxidation. The promoted intergranular oxidation in UDR at the early stage may lead to accelerated crack initiation if the crack initiates before the transition occurs. More importantly, the acceleration in intergranular oxidation due to RIS at the early stage can be closely linked to faster crack propagation rate in irradiated materials [60]. That is because once the crack initiates, the Si-enriched oxide would quickly dissolve in high-temperature water and the intergranular oxide would become defective in UDR. The outer environment can reach the oxide tip and the oxidation condition gets similar to that at the initial stage of intergranular oxidation. In this case, the negative effect of RIS on intergranular oxidation resistance would be dominant again. Thus, a faster intergranular oxidation rate at the crack tip in UDR would lead to accelerated crack propagation.

5. Conclusions

This study revealed the effect of proton irradiation on the intergranular oxidation of 316 L stainless steel in simulated PWR primary water after different immersion times (2 h, 72 h, 200 h, 500 h, 750 h, and 1000 h) by ruling out the interference from the difference in grain boundary structure. The following conclusions can be drawn:

- (1) The intergranular oxidation in uniformly-damaged region (UDR) is deeper than that in non-irradiated region (NIR) when the immersion time is less than 500 h. Thereafter, the trend reverses, i. e., intergranular oxidation depth in NIR exceeds that in UDR. Thus, the effect of proton irradiation on the intergranular oxidation of 316 L stainless steel varies with the duration of exposure test.

- (2) Radiation-induced segregation (RIS) at the pristine grain boundary plays a dominant role in the intergranular oxidation at the early stage, resulting in a deeper oxidation in UDR. With increasing exposure time, the positive effect of enhanced Cr diffusivity gradually builds up in UDR and finally overtakes the negative effect of RIS after longer-term immersion (more than 500 h), leading to shallower oxide penetration and higher Cr content at the oxide tip in UDR than in NIR.
- (3) The faster intergranular oxidation in UDR at the early stage can partly rationalize the accelerated crack propagation of irradiated material as the oxidation condition at the crack tip is similar to that at the early stage which is dominated by RIS.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2023.119340.

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