APT characterization of irradiation effects on MX phase in reduced-activation ferritic/martensitic steels

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ABSTRACT
Reduced activation ferritic/martensitic steels (RAFMs), such as Eurofer 97 and F82H, are designed to enhance the high-temperature strength by forming the fine dispersive particles of the MX phase. However, the stability of MX phase is still not fully understood. The objective of this study is to determine irradiation effects on the MX phase of Eurofer 97 and F82H. The irradiation experiments were performed at the Swiss Spallation Neutron Source (SINQ) at a temperature of ∼300 °C to a dose of ∼20 dpa. The current work reveals the irradiation effect on the MX phase on an atomic scale by atom probe tomography (APT). The irradiation on the one hand can affect the composition of the MX phase, on the other hand, induces interface segregation. Compared with the nitride in the unirradiated Eurofer 97, the nitride in the irradiated specimen contains less V and Ta, while more Cr, Fe, Mn, and W. The irradiation-induced segregation shows consistency among different interfaces between the MX nanoprecipitate, the matrix and the M23C6 precipitate that the undersized elements, Mn, Si, and Cu are enriched, oversized elements W, V and Ta are depleted, while the spallation transmutants Ca, Sc, and K, being largely oversized elements, enriched at the phase boundary as well. The irradiation-induced changes of the MX phase indicate that in the current irradiation condition the MX phase endures an initial transformation process to Z-phase and in the meanwhile a dissolution process at the edge. Ta in the RAFM steels plays a similar role as Nb in the conventional ferritic/martensitic (FM) steels during the MX phase to the Z-phase transformation process where Nb diffuses out of the MX phase.

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1. Introduction

Reduced-Activation Ferritic/Martensitic (RAFM) steels with around 9% Cr are promising structure materials for the application of future fusion power plants. The operation conditions of fusion reactors require the structure materials to exhibit high thermal stability and simultaneous suppression of low temperature embrittlement under irradiation conditions. The irradiation effects to the matrix materials of Ferritic/Martensitic steels have been widely studied by APT techniques in Eurofer 97 [1–3], F82H [4–7], ODS RAFM steels [2,6,8–11] and many other Fe-9Cr alloys [12–18]. In these materials, irradiation can induced the nano-sized cluster formation [1,2,7,12–18] and grain boundary segregation [3,6,13,14,18].

However, irradiation effects on precipitates, especially MX phase, are barely reported in the APT studies.

The precipitates in FM steels can significantly affect the irradiation resistance and the mechanical properties of materials by introducing hardening and embrittlement at low temperatures, swelling and creep at elevated temperatures [19], and corrosion properties [20]. Irradiation can change the size, density, composition, and structure of the precipitates [21–23], which influences the mechanical properties of materials. Therefore, it is necessary to gain a deep insight into the evolution of precipitates under irradiation. In general, two types of precipitates are formed in FM steels during tempering treatment, chromium-rich carbides and vanadium/niobium-rich fine carbide, nitride or carbonitride [24,25], typically M23C6 (M: Cr, W, Mn, Mo) and MX (M: V, Nb, Ta; X: N, C) [23]. The chromium-rich carbides are mainly formed at the Prior austenite grain boundaries (PAGBs) and martensite lath boundaries, while the MX precipitates are formed both at the boundaries and inside grains. The stability of M23C6 in FM steels has been widely stud-
ied under irradiation in both the conventional FM steels and the RAFM steels [26–36]. M₂₃C₆ endures amorphization at low irradiation temperatures [26,27,29–32] and coarsening at high irradiation temperatures [28]. At low irradiation temperatures (below 300 °C), the MX phase was reported to be stable under high energy neutron irradiation [32,37], while a decrease in size and even disappearing under ion [38] and electron [35] irradiation. At high irradiation temperatures, MX transforms to Z-phase, Cr(V,Nb,N) [39]. The concentration of Cr has a threshold concentration for the phase transformation from MX phase to Z-phase in ~9% [40]. During the transformation, Cr is uptaken to the periphery of MX phase. As a consequence, the high Cr region grows to an appreciable size and forms Z-phase. The size of Z-phase does not seem to have a limiting growth and can be over 500 nm in Fe-12Cr steels [41]. The formation of large Z-phase causes dissolution of MX particles [41]. The finely dispersed nitride precipitates have an important contribution to the creep strength through acting as obstacles for dislocation movement (precipitation strengthening). The large Z-phase does not contribute significantly to precipitation strengthening. Therefore, the MX phase to Z-phase transformation has a detrimental effect on creep strength.

In F82H and Eurofer 97, being categorized as RAFM steels, Mo, Nb and Ni are replaced by W, V and Ta for reducing the generation of long-lived radioactive isotopes under irradiation [42]. RAFM steels are considered as the main candidate structural materials for the application in the fusion DEMO reactor blanket [43]. In a 12Cr RAFM steel, the added V and Ta can promote the precipitation of MX and refine M₂₃C₆ carbides [44]. The average size of MX precipitate in conventional FM steels is in the range of 5–10 nm [45], while in Eurofer 97 it is much bigger, ~ 29 nm [46]. The reason for the bigger size of MX precipitates in Eurofer 97 is still unclear. However, it could be one reason for that RAFM steels show worse thermal creep properties than many present-day 9% Cr steels [47], such as the 9Cr3W3CoVNbBN steel [48], 10%Cr martensitic steels [49], and 9Cr-1Mo martensitic steel [50].

The concentration of Cr in Eurofer 97 and F82H are close to the threshold of phase transformation from MX to Z-phase. In Eurofer 97, by the TEM observation, no fundamental difference in precipitate types and composition was observed after neutron irradiation to 32 dpa at 330–340 °C [46]. The number density of MX remains the same, while the size exhibits a significant growth from statistics [46]. However, the additional information concerning the interface segregation and precise chemical composition, especially the minor solute elements is still unclear and necessary to be revealed by high chemical sensitive technique, atom probe tomography (APT). The APT data can help in understanding not only the evolution of the main composing elements in the MX phase but also the contributions from other elements.

Investigating the MX precipitates in RAFM steels is difficult work, as they are in small sizes with low number density and sometimes adjacent to other precipitates (carbides, intermetallic phase, other nitrides). In literature, the microstructure characterization of the MX phase in RAFM steels is mainly performed by TEM. The advantage of TEM is providing useful information for characterization of the structure changes, such as amorphization, while the chemical accuracy for investigating the interface segregation and composition changes is not as good as APT. In the present study, the effect of spallation irradiation on the MX phase in Eurofer 97 and F82H has been investigated using APT. The composition of vanadium nitride and vanadium carbide have been accurately quantified in Eurofer 97 and F82H, respectively. The phase boundary segregation behaviors at the MX phase to the matrix and MX phase to M₂₃C₆ have been revealed. Through the characterization of irradiation-induced interface segregation and compositional changes of the MX phase, the current results improve the understanding of the evolution of the MX phase under irradiation.

2. Experiments and analysis methods

The F82H steel (IEA Heat 9741) was normalized at 1040°C for 38 min and tempered at 750°C for 1 h in the as-received condition [51]. The composition of F82H in atomic percentage (at%) is 8.3 Cr, 0.59 W, 0.42 C, 0.22 Si, 0.16 Mn, 0.18 V, 0.03 N, and minor Ta, Cu, Ti, P, S, B, Ni, Nb, Al with concentrations less than 0.01 [52,53]. The Eurofer 97 (E83699) received from Karlsruhe Institute of Technology (KIT) was normalized at 979°C for 1 h 51 mins and tempered at 739°C for 3 h 42 min [52]. Air cooling is used after the normalization and tempering treatments. The composition of Eurofer in atomic percentage (at%) is 9.6 Cr, 0.33 W, 0.56 C, 0.14 Si, 0.45 Mn, 0.21 V, 0.07 N, and minor Ta, Cu, Ti, P, S, B, Ni, Nb, Al with concentrations less than 0.05 [51,53].

2.2. Irradiation

The irradiation was carried out in the second experiment of the SINQ Target Irradiation Program (STIP-II) in 2000–2001. In SINQ target, the irradiation particle is a mixed high-energy proton (initial energy 570 MeV) and neutron (energy spectrum from 0 – 570 MeV). During irradiation, the proton beam had beam trips about 50 times per day, and each beam trip lasted a few seconds to minutes. The average irradiation temperature excludes beam trips periods. More detailed information on STIP-II can be found in [54]. An F82H specimen was irradiated to 19.8 dpa at an average temperature 295 °C, with the accumulation of 1740 appm He and 7390 appm H. A Eurofer 97 specimen was irradiated at a similar condition to a dose of 19.8 dpa at 300 °C accumulated 1750 appm He and 7450 appm H.

2.3. APT experiments and data analyses

The general APT sample preparation process by focused ion beam (FIB) is used in this study [55]. The APT experiments are carried out at ETH Zurich in Cameca LEAP 4000X HR. The Laser pulse energy is 100 pJ, with a 200 kHz repetition rate and 0.5% detection rate at 54 K. The APT data reconstruction is based on SEM images and performed using Cameca IVAS™ software versions 3.6.14 & 3.8.4.

The interface segregation behavior of solute elements was analyzed by iso-surface proxigram function in IVAS software. Using the iso-surface proxigram function needs to first generate an isosurface, which corresponds to a particular concentration threshold [56]. The proxigram is a plot of concentration versus distance to the iso-surface [56].

3. Results

3.1. The matrix of RAFM steels

The spallation irradiation effects on the matrix materials of Eurofer 97 and F82H include the generation of transmutants and localized heterogeneous distribution (or nano-sized clusters formation). In the spallation target materials, all possible isotopes (transmutants) with lesser mass than the original one can be generated. The neutronic calculation and APT measurement reveal that the solid transmutants generated in Eurofer 97 and F82H are mainly Ti, Sc, Ca and K with concentrations of 30–300 appm [7,53]. Cr and Mn exhibit a homogeneous distribution in unirradiated F82H and Eurofer 97, while they are heterogeneous distributed in both materials after irradiation, as shown in Fig. 1. The Cr and Mn rich regions are also enriched with solute element Si and transmutant elements Ti, Sc, Ca and K. This phenomenon was also re-
ported in F82H irradiated in the Spallation target at a higher temperature (345 °C) \[7\]. The quantified analyses of these clusters in the present irradiated specimens and many other specimens irradiated at different conditions will be published in a separate paper.

3.2. Mass spectra of vanadium nitrides

Due to the difficulty of APT sample preparation, only three samples with MX nanoprecipitates have been analyzed, i.e., vanadium nitride in the unirradiated and irradiated Eurofer 97 and vanadium carbide in the irradiated F82H. The difficulty is mainly caused by three reasons. First, the volume density of MX phase is pretty low, which can be known from the total concentration of V and Ta, being less than 0.25 at\%. Second, the volume of APT sample is small and normally within several hundred nanometers in length. If the APT sample is prepared blandly from the bulk material, in such a small APT sample volume, it is difficult to get an MX phase. Third, the size of a single MX precipitate is small, normally less than 50 nm \[45,46\]. Therefore, it is difficult to track a certain MX precipitate and make it in the apex of an APT sample.

Mass spectra indexing is a fundamental issue for the analysis of APT data, especially for mass spectra with complicated molecular ions. These molecular ions in the mass spectra are species detected by APT during experiments. Molecular ions are also referred as multiple-ion detection events \[57,58\] and ion pile-ups \[59,60\]. In the modern CAMECA LEAP, the state-of-the-art detector employs the micro-channel plates by which the spatial resolution is highly increased \[61\]. The atoms of molecular ions are therefore assumed to originate from neighboring atoms \[62\], and arrived at the detector as either multiple single ions within the time resolution (less than 5ns) for the time-of-flight \[61\] or evaporated original as molecular ions \[63\]. Here we first give the indexing of the mass spectra from vanadium nitrides. But, indexing the mass spectrum of vanadium carbide is not demonstrated here, as it is relatively easy containing rare molecular ion species of C₂ and C₃.

The mass spectra from the MX nanoprecipitates with V concentration over 25 at\% are listed in Fig. 2 (a-b) and Fig. 2 (c-d) from the unirradiated and irradiated Eurofer 97, respectively. Most of the ions are molecular ions, especially metal nitride ions, in both unirradiated and irradiated MX phase. Spallation transmutant Ti was also detected in molecular ion form (TiN). This is different from the mass spectra in the matrix material of Eurofer 97 that only single Ti ions were detected \[53\]. The formation of TiN molecular ions decreased the concentration of Ti single ions, as compared to the spectra in the matrix \[53\]. Besides, a series of TaₓCᵧNₜHₘ₊ (x, y, z, h, n ≥0) ions were detected, such as C₂N⁺, CN₂⁺, TaH⁺, and TaCNH⁺. Deuterium and tritium, as spallation-generated transmutants, were also generated in the materials \[64\]. The isotope-dilution gas mass spectrometry analyzed results show that the measured deuterium and tritium in steels are 1.5 - 5 at\% and 0.1 - 3 at\% of the total hydrogen, respectively \[64\]. However,
Fig. 2. Mass to charge state ratio spectra of the vanadium nitride in Eurofer 97 of unirradiation (a)-(b) and irradiated (c)-(d) conditions.

At mass to charge ratio peaks of 3 (HD) and 4 (D₂, HT), no obvious peak is observed, as shown in Fig. 2. This phenomenon can be caused by their low concentration in the materials. Due to their minor concentrations, deuterium and tritium are not considered as candidate isotopes in Ta₄C₇N₁₅H₂n⁺ ions. Fig. 2 demonstrates that after irradiation the TaH₄⁺, TaH₃⁺, TaH₂ ³⁺, TaH₂²⁺ and TaH₂³⁺ ions appeared and the content of TaNH₂⁺ and TaH₂²⁺ increased. The concentrations of these ions were calculated with background correction and are listed in Table 1. Regarding the experimental error of 10 appm [53], the data in Table 1 illustrate that no TaH or TaH₂ ions were formed in the unirradiated materials and the counts of TaNH and TaNH₂ ions increased after irradiation.
Table 1
The normalized tantalum hydrides or hydronitrogen concentration by atom probe in the VN phase of unirradiated Eurofer 97 and irradiated Eurofer 97. The total accounts for the two MX precipitates of unirradiated and irradiated materials are 0.2 million and 0.6 million, respectively.

<table>
<thead>
<tr>
<th>Ions (ppm)</th>
<th>TaH⁺⁺</th>
<th>TaH⁺⁺⁺</th>
<th>TaH⁺⁺⁺⁺</th>
<th>TaH⁺⁺⁺⁻</th>
<th>TaH⁺⁻⁻</th>
<th>TaH⁻⁻⁻⁻</th>
<th>TaNH +</th>
<th>TaNH₂ +</th>
<th>TaNH₂⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>47.19</td>
<td>42.53</td>
<td>6.66</td>
<td>2.62</td>
<td>0.26</td>
<td>0.63</td>
<td>0.037</td>
<td>0.017</td>
<td>0.016</td>
</tr>
<tr>
<td>Irradiated</td>
<td>42.42</td>
<td>40.40</td>
<td>10.38</td>
<td>2.04</td>
<td>3.81</td>
<td>0.40</td>
<td>0.144</td>
<td>0.000</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Table 2
The composition of vanadium nitride in both unirradiated and irradiated Eurofer 97, in at%.

<table>
<thead>
<tr>
<th>Element</th>
<th>V</th>
<th>N</th>
<th>Cr</th>
<th>Ta</th>
<th>Fe</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>Si</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>47.19</td>
<td>42.53</td>
<td>6.66</td>
<td>2.62</td>
<td>0.26</td>
<td>0.63</td>
<td>0.037</td>
<td>0.017</td>
<td>0.016</td>
<td>0.014</td>
</tr>
<tr>
<td>Irradiated</td>
<td>42.42</td>
<td>40.40</td>
<td>10.38</td>
<td>2.04</td>
<td>3.81</td>
<td>0.40</td>
<td>0.144</td>
<td>0.000</td>
<td>0.019</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Fig. 3. Vanadium nitride phases in the unirradiated material (left) and irradiated material (right).

3.3. Vanadium nitrides in Eurofer 97

MX phase is usually composed of metal nitride or carbide. Vanadium nitrides were detected in both unirradiated and irradiated Eurofer 97 specimens by APT, as shown in Fig. 3. The distribution of V in the two samples indicates that after irradiation the phase boundary between nitride and matrix is wider.

The composition of the two nitrides is calculated in the region with the localized V concentration of over 40% and listed in Table 2. The ratios of N to V concentration in the two nitrides are similar in the range of 0.90-0.95. The differences between the two nitrides mainly come from the concentration of Fe and Cr. Compared with the nitride in unirradiated Eurofer 97, the nitride in irradiated Eurofer 97 contains less V and more Cr, Fe, Mn, and W. The H stems from the molecular ions of Ta₅C₄N₂H₆ⁿ⁺⁺ (h≠0), which can refer to the mass spectrum Fig. 2. The concentration of these H atoms also increased from 370 ppm to 1480 ppm after irradiation. Fig. 4 shows the concentration profiles of all the detected elements in the two vanadium nitrides, obtained by the proxigram analyses of 25 at% V iso-surface. The APT detected phase boundary range in unirradiated Eurofer 97 is 2-6 nm, which varied with orientation. The range of the interface that parallel to the detection path is around 6 nm, while the vertical one is about 2 nm. In the irradiated sample, a large portion of the phase boundary is parallel to the detection path. The concentration profiles in Fig. 4 (d) indicate that after irradiation the phase boundary range is around 15 nm and much broader than that in the unirradiated specimen. In the unirradiated sample, only Cr and P exhibit extremely low enrichment at the phase boundary. In the irradiated sample, more elements are enriched at the phase boundary, including Mn, Si, Cu, Ca, Sc, and K. Meanwhile, the phase boundary segregation of Cr and P seems to be increased after irradiation. Ti as a transmutant element does not show notable segregation. The only obvious depleted element is W in the irradiated sample. After irradiation, the concentration profile of Ta is significantly different from that in the unirradiated one and varied with the distance from the edge of the MX nanoprecipitates. In the unirradiated materials, the concentration of Ta is relatively homogeneous around 2.5-3 at%. While after irradiation, Ta has a higher concentration on the matrix side and remains similar value at the edge of the MX nanoprecipitate, but decreases in the inner part of the MX phase. The concentration profile of H originally from the Ta₅C₄N₂H₆ⁿ⁺⁺ molecular ions shows the same trend as Ta, see Fig. 4 (e) and (j).

3.4. Three adjacent phases in F82H

In irradiated F82H, an APT sample containing a particle with three phases was analyzed, including the matrix, a chromium carbide, and a vanadium carbide phase. The compositions of the two precipitates are listed in Table 3, where an isosurface of 25 at% V and 30 at% Cr were used to isolate the precipitates. The total atom counts of the M₅₂₅₆ and vanadium carbide phases are 1 million and 7 thousand, respectively. The low amount of vanadium carbide phase results in poor statistics. As a consequence, the minor elements may be neglected. The concentration of C (22.9 at%) in the chromium carbide indicates that it belongs to the M₅₂₅₆ phase. Fig. 5 (a) shows the morphology of the three adjacent phases by a cross-section view of the APT sample. The concentration profiles of log scale in Fig. 5 (b) indicate that W, Ta, and V are depleted at the phase boundary, as highlighted by the red arrows. The corresponding linear scale concentration profile can be found in the data availability.

4. Discussion

4.1. Irradiation effects on MX phase

Although the concentration of N in the nitrides and C in the carbide are around 40% and below 50%, they are still categorized as the MX phase instead of the M₅X phase due to the following reasons: (1) In general, only MX phase are considered to be formed in the FM steels without long-time aging or high temperature irradiation [33,38,65]. The crystal structure of the MX phase was confirmed by the diffraction pattern in TEM in Eurofer 97 [66] and other RAFM steels [67]. (2) As for the high ratio of forming nitride or carbide molecular ions, the detection of N and C can be underestimated [68–70].
Fig. 4. Elemental concentration profiles at the interfaces between VN (right side) and the matrix (left side) in the unirradiated and irradiated Eurofer 97.

Table 3
The composition of the three adjacent phases in irradiated F82H.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>W</th>
<th>Mn</th>
<th>V</th>
<th>Si</th>
<th>N</th>
<th>Ta</th>
<th>Ni</th>
<th>B</th>
<th>P</th>
<th>Ti</th>
<th>Ca</th>
<th>Sc</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>M12C4</td>
<td>29.3</td>
<td>41.3</td>
<td>22.9</td>
<td>4.3</td>
<td>0.29</td>
<td>1.33</td>
<td>0.09</td>
<td>0.02</td>
<td>0.11</td>
<td>0.04</td>
<td>0.18</td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
<td>0.004</td>
</tr>
<tr>
<td>VC</td>
<td>5.1</td>
<td>18.0</td>
<td>37.4</td>
<td>1.8</td>
<td>0.57</td>
<td>30.2</td>
<td>1.14</td>
<td>1.73</td>
<td>3.65</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

The mass spectra of the vanadium nitride phases in Fig. 2 show the detection of complex Ta$_x$C$_y$N$_z$H$_h^{n+}$ ions, which were not detected in the vanadium carbide phase. After irradiation, the concentration of hydrides increased, as shown in Table 1. As H is the most common residual gas in an ultra-high vacuum chamber, the continuous adsorption onto samples and the followed field evaporation is easy to explain, and even the formation of hydride molecular ions is possible. The higher concentration of H detected at the interface can be caused by the lower evaporation field. However, the H is heterogeneously distributed even in the composition stable region of the irradiated MX precipitates, specifically 5 nm – 10 nm region in Fig. 4 (d). The concentration of H from Ta$_x$C$_y$N$_z$H$_h^{n+}$ ion decreases more than half at x=10 nm in comparison with that at distance x=5 nm, as shown in Fig. 4 (e). This phenomenon is
difficult to be explained by the field evaporation mechanism. An interesting finding is the distribution of H in the complex ions \( \text{Ta}_3\text{C}_2\text{N}_2\text{H}_9\text{H}^{n+} \) is the same as Ta, as shown in Fig. 4 (e, j). Tantalum and vanadium are known for their high hydrogen solubility [71,72]. The detection of these hydrogen complexes indicates that the hydrogen absorption mechanism in the VN phase is different from that in the matrix. In this case, N could play an important role in the formation of these ions, as the lack of N in the VC phase of F82H prevents the formation of \( \text{Ta}_3\text{C}_2\text{N}_2\text{H}_9\text{H}^{n+} \) ions. It has also been proven that the addition of nitrogen in pure tantalum changes the prevailing microscopic diffusion mechanism of H [34]. Many researchers found that the additional nitrogen decreases the diffusivity of hydrogen [34] and contributes to hydrogen trapping with a small trapping enthalpy in tantalum [35]. In the nitride, the high concentration of hydrogen with \( \text{Ta}_3\text{C}_2\text{N}_2\text{H}_9\text{H}^{n+} \) forms indicates some special connection among Ta, N, C and H in the MX nanoprecipitate. A similar phenomenon was observed in 304 stainless steel that the Ni riched regions also contain a high concentration of NiH\(^+\) and Kruskus considered H was trapped by Ni [73]. This phenomenon signifies the function of Ta in the vanadium nitride phase for stabilizing the absorbed H. However, in the current work, the contribution of H from the APT chamber cannot be excluded. More accurate experiments can be done by replacing H with D [74] to quantify the function of Ta in the vanadium nitride.

The phase boundary in the irradiated Eurofer 97 is \( \sim 15 \text{ nm} \) and \( \sim 9 \text{ nm} \) broader than that in the unirradiated material. The accuracy of the interface analyses can be influenced by the flight-trajectory abbreviation and variation in the local magnification of different phases [75]. They heavily affect the interface parallel to the detection path and have less effect on the vertical one. The width of the interface accuracy can be estimated by comparing the difference between the horizontal and vertical interfaces of the same sample. The error induced by the flight-trajectory abbreviation and local magnification in the vanadium nitride interface can be estimated by the measured differences of the vertical and parallel ones to the detection path, in \( \sim 4 \text{ nm} \). The 10 nm gap between the unirradiated sample and the irradiated sample is definitely above the APT detection error. The irradiation-induced increasing phase boundary and the decreasing of V and N concentrations at the edge of the nitride indicate the dissolution of this phase, as shown in Fig. 4 and Table 2.

The enrichment of Cr at the interface and in the precipitate suggests the transformation of the VN phase to the Z-phase [40,76]. The physical mechanism of this phase transformation proposed by Mats Hättestrand is that chromium can reduce the misfit between the coherent precipitates and the matrix [77]. The obvious phase transformation was observed in 9 – 12 wt % Cr steels after aging in a temperature range of 600 – 700°C for a long time [76]. In the case of Eurofer 97 irradiated at 300°C, the phase transformation should still be in an incubation period, considering the concentration of Fe (3.8 at%) and Cr (10.4 at%) far below the Z-phase, 40 at% \( \leq \text{[Fe]} - \text{[Cr]} \leq 70 \text{ at%} \) [41,78]. For the RAFM steels, Nb is replaced by Ta, as a function of maintaining a fine grain size and strengthening the materials [79]. As a consequence, Ta replaced Nb in the VN phase. After irradiation, the concentration of Ta decreased, especially in the inner part of the precipitates. This effect has also been observed for Nb in the MX phase during transform to the Z-phase under irradiation [41,76]. Danielsen thinks that such Nb distribution is connected with the nucleation of Z-phase at the periphery of MX precipitates [41]. Therefore, Ta is suspected to play a similar role as Nb in the irradiation-induced evolution of the MX phase transformation. The decreasing concentration of Ta should be associated with the irradiation effect on TaN compounds. In ferritic steels, TaN precipitates show worse stabilities than VN under irradiation [38]. Thus, TaN compounds are suspected to be easier to be decomposed than VN compounds, which is in agreement with the current results. The irradiation-induced evolution of chromium carbides is widely studied in the literature [34,67,80, 33, 81]. It has also been investigated in the framework of SINQ irradiated F82H and Eurofer 97 steels at several different irradiation temperatures and doses. Due to a large amount of results, it will be published in a separate paper.

4.2. Irradiation-induced phase boundary segregation

Despite the segregation behavior of elements being only partially obtained, they show consistency among all the analyzed interfaces. The consistency is shown as: (1) W is depleted at the three types of interfaces: matrix to vanadium nitride, matrix to \( \text{M}_2\text{C}_6 \), and vanadium carbide to \( \text{M}_2\text{C}_6 \); (2) Ta is depleted at two types of interfaces: matrix to \( \text{M}_2\text{C}_6 \) and vanadium carbide to \( \text{M}_2\text{C}_6 \); (3) No confliction segregation behavior has been observed for all the elements; (4) The same segregation behavior for each segregated element have been observed at grain boundaries (unpublished results). The segregation behavior of elements can be summarized as that; the undersized elements enrichment [82], Mn, Si, and Cu are enriched, the oversized elements [82] W, V and Ta are depleted, while the spallation transmutants Ca, Sc, and K, being largely oversized elements [82], enriched at the phase boundary, as well. The undersized elements enrich at boundaries and oversized elements deplete at boundaries is a model used to explain the irradiation-induced segregation and is generally accepted.
when irradiated at low temperatures in various materials [83]. Another important irradiation-induced segregation model is the inverse Kirkendall effect, in which solute elements can diffuse either by solute-interstitial or solute-vacancy mechanism. Wharry [84,85] and Messina [86] simulated the irradiation-induced segregation behaviors of Cu, Mn, and Si in FM steels. Their simulations show that Mn and Si are enriched at grain boundary diffusing either by interstitials, vacancies, or both, while Cu is depleted at grain boundaries through vacancy diffusion at temperatures below 1086 K. Therefore, both irradiation-induced segregation models can be used to explain the segregation behaviors of Mn, Si, Cu, W, V, and Ta. However, the segregation behavior of Ca, Sc, and K is for the first time studied in RAFM steels, as they are spallation-generated elements. Two possible reasons can be attributed to the enrichment of Ca, Sc, and K at phase boundaries: (1) The atomic size of these elements are over 1.5 times of Fe [82], and therefore may no longer be the substitutional elements in FM steels and out of the atomic size-controlled criterion; (2) The concentration of these elements is over their solubility in FM steels and leading to the segregation at various of sinks.

5. Summary and conclusions

After irradiation with high energy mixed spectra of protons and neutrons in a SINQ target, the irradiation affected phase stability of MX phases in Eurofer 97 and F82H was studied by APT. The obtained results are summarized as follows:

1. The complicated mass spectra of vanadium nitride were indexed. A series of Ta₅Ca₃C₈N₄H₉n⁺ (x, y, z, h, n=0) ions were detected, such as C₂N⁴⁺, C₃N₂⁺, TaH⁴⁺, and TaCNH⁴⁺.

2. Compared with the nitride in unirradiated Eurofer 97, the nitride in irradiated Eurofer 97 contains less V and Ta, but more Cr, Fe, Mn, and W. This observation indicates that the vanadium nitride endures a Z-phase transformation process. After irradiation, most of the elements reach a near steady concentration in the inner side of nitride, except for Ta. The concentration of Ta decreases significantly in the inner side of the vanadium nitride from ~3% to ~1.5% than at the edge. H stem from the Ta₅Ca₃C₈N₄H₉n⁺ ions exhibits the same distribution as Ta in the vanadium nitride nanoprecipitate.

3. The interface between vanadium nitride and the matrix is broader in the irradiated Eurofer 97 than that in the unirradiated materials. The broader interface and increasing concentration of V and N in the matrix side indicate the dissolution of vanadium nitride nanoprecipitates.

4. The segregation behavior of solute elements and transmutation elements was detected at the phase boundary between the vanadium nitride and the matrix in Eurofer 97. At this phase boundary, after irradiation, the enrichment of Mn, Si, Cu, Ca, Sc, and K and enhanced segregation of Cr and P was observed, while W depletes and Ti does not show obvious segregation.

5. W, V, and Ta, as over-sized elements are depleted at the phase boundaries of M₂₃Ca / vanadium carbide and M₂₃Ca / matrix.

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

Lijuan Cui: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. Yong Dai: Conceptualization, Methodology, Supervision, Funding acquisition, Writing – review & editing. Stephan S.A. Gerstl: Investigation, Data curation. Manuel A. Pouchon: Supervision.

Data Availability

Data will be made available on request.

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Supplementary materials

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References


