

Atomic Origins of Radiation-induced Defects and Interfacial Strengthening in Additively Manufactured Titanium Aluminide Alloy Irradiated with Kr-ions at Elevated Temperature

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ABSTRACT

The irradiation microstructure of the additively manufactured titanium aluminide (TiAl) alloy subjected to in situ transmission electron microscope (TEM) irradiation with 1 MeV Kr ions at the elevated temperature of 873K was investigated. Triangle and large hexagon shaped volume defects were observed within the γ -TiAl phase in the TEM images of the irradiated microstructure. High resolution TEM images and composition analyses revealed the volume defects were vacancy-type stacking fault tetrahedrals (SFTs). Molecular dynamic simulations showed that the increased diffusion coefficient at the elevated temperature promoted the movement and aggregation of vacancies, leading to the formation and growth of SFTs in the irradiated FCC γ phase. The lamellar interfaces in the irradiation microstructure were more effective for acting as strong sinks to absorb the primary point defects and defect clusters at the elevated temperature. The initial defects at the interfaces of

1 the additively manufactured TiAl alloy enhanced the sink strength of the material and greatly
2 refined SFTs near the lamellar interfaces.
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7 **Keywords:** TiAl, additive manufacturing, high temperature irradiation, radiation-induced
8 defects, TEM, TEM image simulation, molecular dynamic simulation.
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1. Introduction

Irradiation temperature is a very important parameter to influence the microstructural changes in metals and alloys used in extreme environments of advanced nuclear systems [1,2]. During irradiation on metallic materials, primary point defects including self-interstitials (SIAs) and vacancies are generated due to the impact of the incident species. With increasing irradiation temperature, five recovery regimes have been found using electrical resistivity measurements for Cu after fast neutron irradiation: immobile SIAs, SIAs migration and immobile vacancies, vacancy migration, migration of vacancy clusters and vacancy-solute complexes, and thermal dissociation of vacancy clusters [1-3]. The developing radiation-induced microstructure with increasing irradiation temperature is therefore largely determined by thermal mobilities or thermal stabilities of the associated defects [2]. A wide variety of defect clusters can be produced during high temperature irradiation such as dislocation loops, stacking fault tetrahedra (SFTs), cavities (voids and gas-filled bubbles), segregation and precipitates etc. [1,4]. The radiation-induced microstructural evolutions can lead to changes in the dimension and mechanical properties of the structural components served at high temperatures such as void swelling and grain boundary embrittlement, limiting the operation life and safety of nuclear reactors. However, the different radiation-induced defects formed at high temperatures may exhibit similar morphologies with a nanoscale size, making it challenging to correctly identify these. It is crucial to reveal the origins of these defects and fully understand their formation and growth mechanisms for developing advanced high-temperature nuclear structural materials.

TiAl alloys exhibit excellent radiation damage tolerance at high temperatures in comparison with other nuclear structural materials [5]. It is reported that no voids were observed in a Ti-47 at.% Al (Ti47Al) alloy after electron irradiation at 773 K to 30 dpa, whereas a large number of voids were formed in 316 stainless steel exposed to similar

1 irradiation conditions [6]. Irradiation hardening i.e. strength increases and ductility decreases
2 with irradiation occurs in most nuclear structural materials. However, for the TiAl alloy
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4 irradiated with neutrons at 873 K, the strength is slightly increased with a dramatic increase
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6 in ductility [7]. The irradiation creep resistance of the TiAl alloy at high temperatures was
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8 comparable with ODS steel and therefore better than for austenitic materials [8].
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11 In order to investigate the high-temperature irradiation behaviour of TiAl alloys, the
12 materials have been irradiated at elevated temperatures or annealed at elevated temperatures
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14 after low-temperature irradiation using various incident species including ion beams,
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16 electrons, protons and neutrons [6,9-18]. It is found that the irradiation temperature has a
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18 great influence on the formation of defect clusters in the Ti47Al alloy under electron
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20 irradiation. A large number of defect clusters were formed below 700 K whereas the number
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22 density decreased sharply at higher temperatures above 700 K and no defect clusters
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24 presented at irradiation temperatures above 773 K [6]. However, it is also reported that
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26 bubbles formed after He-ion irradiation in the temperature range of 873 to 1273 K on a Ti-47
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28 at.% Al-2 at.% W-0.5 at.% Si (Ti47Al2W0.5Si) alloy, and the size of the bubbles increased
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30 with increasing irradiation temperature [12]. The annealing behaviour of radiation-induced
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32 defects in the TiAl alloys has also been investigated [14-16]. The migration of vacancies in a
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34 TiAl alloy under electron irradiation was found to even occur at a low temperature of ~ 450
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36 K, which is lower than the temperature for self-diffusion and thermal vacancy formation [16].
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38 All radiation damage produced in TiAl alloys irradiated with electrons or protons was
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40 annealed out below 800 K regardless of irradiation fluence [14]. However, it was also found
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42 that the large vacancy-type defects introduced to TiAl alloys after fast neutron irradiation in a
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44 heavy water reactor at low temperature can be congregated and were difficult to eliminate
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46 even by annealing at temperatures above 1000 K [11]. The different behaviours of radiation-
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48 induced defects in TiAl alloys at elevated temperatures were not clearly explained and may
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1 relate to their type and nature of the defects and defect clusters formed in different irradiation
2 experiments. However, the atomic origins of the radiation-induced defects and their
3 formation at elevated temperatures in TiAl alloys have not yet been explored.
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7 The irradiation behaviour of TiAl alloys at elevated temperatures is also strongly
8 dependent on the microstructure. The interfaces in the lamellar microstructure have a great
9 influence on the radiation damage tolerance of TiAl alloys at high temperatures. It was
10 reported that cavities were preferentially nucleated on lamellar interfaces during He-ion
11 irradiation on a TiAl alloy at 773 K [17]. Moreover, rod-shaped cavities formed at the α_2/γ
12 lamellar interface of a 45XD TiAl alloy irradiated with He ions at 573 K have a longer shape
13 and a higher density than those at the γ/γ interfaces [9,13]. Also, bubbles formed in the He-
14 ion irradiated Ti47Al2W05Si alloy in the temperature range of 873 to 1273 K were found
15 mainly in the α_2 phase and occasionally in the γ phase [12]. Large bubbles were observed at
16 the interfaces inside the α_2 phase or at the α_2/γ interfaces, but no bubbles in the γ phase at the
17 irradiation temperatures of 1073 K and 1273 K. Nevertheless, there is currently limited
18 experimental work to investigate the origin and mechanism of interfacial strengthening in
19 TiAl alloys irradiated at elevated temperatures.
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22 In the present study, the sample of TiAl alloy fabricated using the gas tungsten arc
23 welding-based additive layer manufacturing (GTAW-ALM) technology was subjected to in-
24 situ Kr-ion irradiation at the elevated temperature of 873 K using the IVEM-TANDEM
25 facility at the Argonne National Laboratory, USA. The irradiated sample was investigated
26 using advanced analytical TEM in combination with TEM image simulation and molecular
27 dynamic (MD) simulation. The atomic origins and formation mechanisms of radiation-
28 induced defects and the strengthening mechanisms of microstructural interfaces in the TiAl
29 alloys at high temperatures are investigated and discussed.
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2. Material and Methods

In order to investigate the irradiation behavior of the GTAW-ALM additively manufactured TiAl alloy at the elevated temperature, the TEM specimen was in-situ irradiated at 873 K using the IVEM-TANDEM facility at Argonne National Laboratory, with 1 MeV Kr²⁺ ions to a maximum dose of approximately 1.25×10^{19} ions/m². The irradiated specimen was then examined ex-situ using advanced analytical TEM via a JEOL 2200FS operated at 200 kV. Detailed procedures and parameters used for manufacturing the material, in-situ TEM irradiation and ex-situ TEM examination are described in detail in the first part of this study [5].

Molecular dynamics (MD) simulations were carried out using the LAMMPS code [19], and the EAM potential developed by Zope and Mishin in 2003 was used for α_2 -Ti₃Al and γ -TiAl phases [20]. In order to investigate the formation and growth mechanisms of defect clusters at the elevated temperature, MD annealing simulation was performed on a supercell of FCC γ -TiAl with $20 \times 20 \times 20$ unit cells consisting of 32,000 atoms. A random distribution of vacancies with various numbers (100, 152, 456 and 912) was generated into the initial supercells which were then annealed at 873 K with the NPT ensemble at zero external pressure. Periodic boundary conditions were applied in all three directions, and a time step of 2 fs were used to ensure good energy conservation and convergence. MD irradiation simulations at 873 K were carried out using the same FCC γ -TiAl supercell, crystal structures with α_2/γ lamellar interfaces or γ/γ true twin boundaries with and without initial defects in the starting microstructure. The defects were identified using Ovito software [21], and the TEM image simulation on the MD simulated microstructure was carried out using JEMS software [22]. The procedures relating to MD irradiation simulation and TEM image simulation have also been explained in detail in [5].

3. Results

3.1 Kr-ion irradiation behaviour at 873 K

The TEM micrographs of a series of irradiated microstructure with increasing irradiation dose during the in-situ Kr-ion irradiation at 873 K are shown in Figure 1. When the irradiation dose reaches 1.56×10^{18} ions/m², the contrast of the component phases in the TEM image becomes complex and new phases seem to form as the TEM contrast is much brighter in some locations than others. These new features in the irradiation microstructure are referred to as volume defects in this study due to their large size and complex morphologies. With increasing irradiation dose, the volume defects continue to grow to become large and more evident in the TEM images. At dark-field (DF) TEM condition, the irradiation microstructure exhibits more complex contrast than the bright-field (BF) TEM condition. The planar defects formed in the room-temperature irradiated microstructure [5] are absent from the high-temperature irradiated sample (Fig.1). This is attributed to the stress concentration generated during Kr-ion irradiation at room temperature for the formation of the planar defects is lowered due to the stress relaxation at the elevated temperature of 873 K.

3.2 The origin of volume defects formed at 873 K

Figure 2 presents the morphologies of the volume defects in the post-irradiation microstructure under the zone axis of $\langle 110 \rangle$. The change in the contrast of the γ phase in the BF TEM image is much severer than that of the α_2 phase (Fig.2a), and the bright features are the volume defects of Fig.1. In the high magnification TEM image (Fig.2b), the bright volume defects exhibit a triangle shape or a large hexagon shape under the beam direction of $\langle 110 \rangle$. In order to identify the new features, nano-beam diffraction patterns (NBD) have been taken in the bright and dark phases as shown in Fig.2b. It is very clear that the two features have the same NBD patterns and in the same orientation, and they are consistent with

1 the SAD pattern of the γ phase under the $\langle 110 \rangle$ zone axis. Hence, the volume defects are not
2 new precipitates formed during high temperature Kr-ion irradiation and are the same γ phase
3 with the matrix. The shape and contrast of the volume defects are much clearer in the STEM
4 images (Fig.2c and 2d). The new volume defects still exhibit white contrast in the BF STEM
5 image (Fig.2c), but dark contrast in the HAADF-STEM image (Fig.2d). The sides of the
6 hexagon-shaped defects form four approximately 125° and two approximately 110° angles
7 with the other sides as shown in Fig.2d. Since for HAADF, contrast increases with atomic
8 number (Z) and can also be influenced by the sample thickness more light elements or less
9 material at the location of the new features may contribute to their dark contrast in the
10 HAADF image [23,24].
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24 In order to measure the difference in the chemical composition between the volume
25 defects and surrounding matrix, point composition analyses and elemental line scans across
26 the defects were carried out to identify the composition and physical change around the
27 defects. Figure 3 presents point compositions, STEM line scan counts (line curves) and
28 chemical element contents (line curves with scatter data) of Ti and Al across the volume
29 defects and their surrounding matrix. Since the TEM specimen was not tilted to a $\langle 110 \rangle$ zone
30 axis for the composition analyses, the volume defects exhibit irregular shape in Fig.3b. It is
31 evident that the volume defects and their surrounding matrix mainly contain Ti and Al
32 elements (Fig.3a). However, the average compositions are 47.6 at.% Ti and 52.4 at.% Al for
33 the matrix, while 60.0 at.% Ti and 40.0 at.% Al for the volume defects, i.e. there are more Ti
34 and less Al in the defects than the matrix. The changes of the contents of Ti and Al across the
35 volume defect are shown in Fig.3c. The content of Ti at the locations of the volume defects
36 are higher than those at the matrix, while the difference in Al between the two regions is
37 opposite to that of Ti (Fig.3c). If the contrast of the defects in the HAADF image was caused
38 by the difference in the chemical composition between the defects and the matrix, the atomic
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number of Ti, 22, is higher than that of Al, 13, and the volume defect should exhibit white contrast instead of the dark one in the HAADF images (Fig.2d and 3b). These results indicate that the composition is not the main factor to influence the contrast of the volume defects, and hence, the defects should have less material than the matrix for their darker contrast in the HAADF images. This is confirmed by the line scan counts of Ti and Al across the volume defects. The line scan counts for a particular element increase with the thickness of the sample and also increase for a higher concentration of the examined element [23]. The scan counts of Ti at the volume defect should be higher and those of Al should be lower than those within the matrix for the two elements if the thickness of the two areas is the same. However, as shown by the line curves (Fig.3c), both Ti and Al are lower at the defects than those within the matrix. These results clearly reveal that the defect areas have much less material than the matrix i.e. the volume defects are clusters of vacancies.

Figure 4 presents HREM morphologies of a volume defect. The defect is seen as an open triangle (Fig.4a) consisting of (-11-1) and (1-1-1) planes under the zone axis of [110]. Prominent bright dots can be observed along these planes, and the cluster of vacancies can result in white contrast of atoms in the HREM image [5]. In order to clearly see the atom arrangement around the volume defect, a high magnification HREM image on the area near one vertex of the triangle is shown in Fig.4b. A line along (-11-1) plane of the matrix, i.e. along the base of the open triangle, was drawn in Fig.4b, and it can be found that the rows of the (-11-1) plane atoms under a lateral shift away from the top of the triangle. This shift is independent of the TEM focus, and there is no extra half plane presented. These TEM image characteristics can be explained by assuming that the defect is a stacking fault tetrahedral consisting of stacking faults on the four {111} planes and with stair-rod dislocations having Burgers vector of $b=a/6\langle 011 \rangle$ along the six $\langle 011 \rangle$ edges [25]. Moreover, on the basis of the facts that the defects exhibit a triangle shape and present in the FCC γ -TiAl, but not in the

HCP α_2 -Ti₃Al of the irradiation microstructure, it is speculated that these volume defects are vacancy-type stacking fault tetrahedral (SFT) formed during the in-situ Kr-ion irradiation at the elevated temperature of 873 K.

In order to further confirm the origin of the volume defects and investigate their formation and growth mechanisms, MD annealing simulations were carried out in γ -TiAl crystal system with $20 \times 20 \times 20$ unit cells consisting of 32000 atoms. A random distribution of vacancies with different numbers was generated in the perfect γ supercells. Figure 4c presents one snapshot of the MD annealing simulation on the crystal structure with 152 random vacancies at the start of the simulation. Triangle shaped defects are observed in projection of the cell in the $\langle 110 \rangle$ direction. The system has 9 defects and the size of the defects changes from 4 to 6 atom planes. One piece with a defect of 5 planes was cut from the system as shown in Fig.4d, and the HREM image simulation on the defect piece was carried out and the result is shown in Fig.4e. The distribution of the vacancies in the defect area is also inserted in Fig.4d, and confirms that the defect is vacancy-type SFT. However, a perfect SFT with 5 planes should contain 35 vacancies, but there are only 18 vacancies in this SFT, and hence not all the substrate positions were taken by vacancies i.e. this SFT is imperfect. As shown in the simulated HREM image, the $(-11-1)$ plane atoms in the triangle are a little away from their normal positions, and the atoms in the defects are indistinct in comparison with the other atoms. These results are similar with the experimental HREM image of Fig.4b and hence further confirm that the volume defects in the irradiation microstructure are SFTs.

The formation and growth of SFTs and the effect of the initial defects on the number and size of SFTs are investigated using MD annealing simulation to TiAl systems with initial vacancy defect in the start microstructure annealed at 873 K as shown in Figure 5. Figure 5a-5e shows the formation and growth of SFTs in the TiAl system with 152 vacancies at 873 K after different simulation durations, and the detail process is shown in the supplementary

movie S1. The initial vacancies distribute uniformly in the start microstructure (Fig.5a). During the MD annealing simulation, vacancies are observed to be mobile (supplementary movie S1). After 20 ns simulation, some vacancies gather together to form small clusters (Fig.5b). The small vacancy clusters move faster than mono-vacancies (movie S1). With increasing the simulation time to 100 ns, the small clusters have transformed into large SFTs (Fig.5c). After 400 ns simulation, only six individual vacancies are left behind, and all other vacancies gather into large SFTs (Fig.5d). During simulation duration up to 400 ns, only 1/6 $\langle 110 \rangle$ stair-rods around the SFTs and 4 interstitials sites with 8 dumbbell interstitials are formed (Fig.5e). The simulation results indicate that the formation and growth of SFT does not necessary need to first form dislocation loops and interstitials, but rather is carried out by aggregation of individual vacancies. This is consistent with the formation of SFTs in the FCC Ni alloy [26]. Hence, the number of initial vacancies in the start microstructure has a great influence on the number and size of SFTs formed during the irradiation at 873 K as shown in Fig.5f-5i. The SFT defects are observed in all the structures after 200 ns MD annealing simulation. For the structures with a low amount of vacancies in the system (100 and 150 vacancies), triangle shaped SFTs are formed, and there are more and larger SFTs in the TiAl system with 152 vacancies (Fig.5g) than that with 100 vacancies (Fig.5f). With further increasing the number of initial vacancies, the aggregation of small SFTs results in the formation of large ones which has a hexagon shape. As shown in Fig.5h for the system with 456 initial vacancies, the $(-11-1)$ plane forms approximately 110° with the $(1-11)$ plane, and approximately 125° with the (002) plane, and hence the defect has four 125° and two 110° angles which are exactly the same with the angles in the hexagon shaped defects in the experimental STEM image of Fig.2d. These results indicate that the hexagon shaped defects are the result of the aggregation of multiple triangle-shaped SFTs. Almost all the SFTs connect together to form large defect clusters for the system with 912 initial vacancies.

In order to further confirm the origin, formation and growth of the SFT defects during irradiation, MD irradiation simulation on the γ -TiAl system was carried out. Figure 6 presents the selected snapshots of the irradiated microstructure after 100 ns MD irradiation simulation. SFTs are observed in the irradiated microstructure, and it seems there are large defect clusters that exhibit irregular shapes (Fig.6a). The distribution of vacancies and interstitials in the irradiated microstructure are shown in Fig.6b and 6c after removing the substrate atoms from the supercell. It is clear that besides vacancy-type SFTs, there are also many individual vacancies dispersed within the irradiation unit (Fig.6b), while interstitials gather together to form the large defect clusters (Fig.6c). Moreover, it can be found that $1/6 \langle 110 \rangle$ stair-rods surround the SFTs whereas $1/6 \langle 112 \rangle$ Shockley dislocations and a small amount of $1/2 \langle 110 \rangle$ perfect dislocations encompass the large interstitial clusters. The interstitial clusters show dot-like defects in the TEM images as revealed in [5]. In addition, the recombination of vacancies and interstitials during MD irradiation simulation greatly reduced the formation and accumulation of the vacancy-type SFTs in comparison with the MD annealing simulations.

3.3 Interfacial strengthening at 873 K

The lamellar interfaces not only act as sinks to absorb primary point defects and defect clusters in the radiation damage process of TiAl alloys at room temperature, but also more effectively at high temperatures [5,9]. Figures 7 and 8 show TEM and STEM images of the radiation-induced defects near the α_2/γ and γ/γ lamellar interfaces. SFTs are not found in the HCP α_2 -Ti₃Al phase, instead, large dot-like defects are observed in the α_2 phase (Fig.7). In the HREM image (Fig. 7c), the contrast of the atoms is not uniform with the white contrast of some atoms being stronger than that for other atoms in both the α_2 and γ phases. The dot-like defects exhibit black and blur atom patterns, indicating that they are interstitial clusters [5].

Moreover, the SFTs are much smaller in the regions near the α_2/γ lamellar interface than those in the region far from the lamellar interface (Fig.7). The width of the region with finer SFTs is approximately 70 nm at the higher-magnification TEM image (Fig.7b) and STEM images (Fig.7d and 7e). The SAD patterns in Fig.8b shows that the two lamellae have the same patterns but under different $\langle 110 \rangle$ orientations, forming a γ/γ twin boundary. The SFTs in the regions near the γ/γ lamellar interface seems slightly finer than those in the regions far from the interface (Fig.8a). However, the difference in the size of SFTs and the width of the refined region for the γ/γ lamellar interface (Fig.8) are much smaller than those for the α_2/γ lamellar interface (Fig.7). These results indicate that the α_2/γ lamellar boundaries are much stronger than the γ/γ boundaries to act as sinks during in-situ Kr-ion irradiation.

In order to investigate the effect of interfaces on the formation and growth of SFTs, MD irradiation simulations on the defect behaviour in the TiAl microstructure with the α_2/γ and γ/γ lamellar interfaces were conducted. Figures 9 and 10 present the selected snapshots of the MD irradiation simulations on the lamellar microstructure with one perfect interface i.e. only atomic mismatches presented on the interfaces or on the lamellar microstructure with initial defects presented in the interface area, respectively. The three pictures from left to right for each condition are simulated microstructure, corresponding vacancies and interstitials. There are both vacancy and interstitial clusters in the microstructure with the perfect and defect interfaces for the α_2/γ and γ/γ lamellar interfaces. However, the interstitial clusters are bigger than the vacancy clusters. Also, there are more interstitials and vacancies in the clusters at the α_2/γ lamellar interface than those at the γ/γ lamellar interfaces. Moreover, there are more and larger defect clusters at the defect interfaces (Fig.10) than those at the perfect interfaces (Fig.9). The SFTs are more evident in the irradiated γ microstructure with the defect interface (Fig.10). These results are consistent with the irradiation results at room temperature for the two structures [5], and hence the initial defects at the interfaces also play an important role in

absorbing defects and defect clusters during irradiation at the elevated temperature. Again, more initial defects at the interfaces of the additively manufactured TiAl alloys should improve their radiation tolerance at the elevated temperatures. Due to the accumulation and recombination of interstitials and vacancies and the annihilation of the two defects in the interface areas, the defect clusters are refined and the number is reduced in the areas near the interfaces, forming defect-refinement zones.

4. Discussion

4.1 The formation and growth of volume defects at elevated temperatures

During irradiation at high temperatures, the movement of atoms in the irradiated microstructure is accelerated and the thermal diffusion coefficients of the defects are also increased. The diffusion coefficients at 873 K for interstitials and vacancies with the defect concentration of 2.5×10^{-3} in the single γ -TiAl phase were estimated using the MD diffusion simulation [5] to be approximately $2.3 \times 10^{-14} \text{ m}^2/\text{s}$ and $1.1 \times 10^{-14} \text{ m}^2/\text{s}$, respectively, which are much higher than those at 300 K, approximately $6 \times 10^{-16} \text{ m}^2/\text{s}$ for interstitials and $5 \times 10^{-26} \text{ m}^2/\text{s}$ for vacancies [5]. The diffusion coefficient for vacancies has a much bigger increase than that for interstitials. Hence, interstitials can form larger clusters at 873 K than those at room temperature (Figs.1 and 6), and vacancies can also form clusters i.e. SFTs at 873 K (Figs.2 and 6). Nevertheless, the diffusion coefficient for interstitials is still twice that for vacancies at 873 K, and hence the interstitials still move faster than the vacancies. More and more interstitials form very large clusters or become lost to sinks than vacancies during irradiation at the elevated temperature, and the interstitial concentration will decay and the vacancy concentration will rise in the matrix. The introduction of vacancies due to irradiation and the movement and aggregation of individual vacancies at the elevated temperatures result in the formation of small vacancy clusters in the irradiation microstructure.

During the MD annealing simulation, small vacancy clusters move faster than mono-vacancies (Movie S1). The reason is that clustering of vacancies significantly decreases migration energy barriers of small vacancy clusters whereas the individual vacancies have high migration barriers [26]. For example, the migration energy barriers for vacancies in the TiAl alloy decrease from the range between 1.15 and 1.35 eV for all the principal mono-vacancy motions to the range between 0.48 and 0.69 eV for di-vacancy diffusion [27]. Hence, the diffusion of small vacancy clusters is much faster than that by mono-vacancies. Mobile vacancy clusters can interact with other clusters, when two small clusters meet, they can join together to form a big one. The most stable configurations of a vacancy cluster are the SFTs [4]. The MD annealing simulation confirms that the origin of the volume defects in the experimental TEM images of the irradiated TiAl sample are SFTs. With increasing the number of vacancies in the SFTs, the movement of the clusters first increase, and then decrease, and become stable once the vacancies at clusters reach a critical number about 15 vacancies (S1). According to the energy principle, a defect is more stable when it has lower formation energy and high binding energy [21,27], and the binding energy for a vacancy cluster increase with increasing the cluster size [4,27]. The SFTs continue to grow large through joining more individual vacancies and small vacancy clusters. It has been reported that dislocation loops were created first for the formation of SFTs [28], and new interstitials self-created by the system act as a part of the building block of the SFT during vacancy clustering in MD annealing simulation of Ni [26]. However, in the present study, the number of SIAs is limited and the dislocations are mainly stair-rods during the MD annealing simulation for up to 400 ns (Fig.5e). Hence, the formation and growth of SFTs does not necessarily need the presence of SIAs and the formation of dislocation loops as shown by Fig.5 and the supplementary movie 1. The diffusion and aggregation of individual vacancies and small vacancy clusters at the elevated temperature result in the formation and growth of

1 SFTs in the irradiated microstructure of the TiAl alloy. Hence, fast diffusion of defects at
2 high temperatures promotes the formation and growth of the SFTs in the irradiation
3 microstructure.
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7 During the MD irradiation simulation, both interstitials and vacancies are introduced into
8 the system, and the recombination of the two defects at 873 K was also dramatically
9 enhanced. For example, after the same MD irradiation simulation for 40 ns for the single γ -
10 TiAl phase, there are 327 vacancies and interstitials each at 300 K, while only 133 defects
11 each at 873 K. The remaining defect concentration in the irradiated microstructure at room
12 temperature is 2.5 times that at the elevated temperature of 873 K. The accelerated
13 recombination of the two defects at the elevated temperature greatly reduced their
14 concentrations in the irradiated microstructure. Hence, the recombination of the two defects
15 at the elevated temperature slows down the formation and growth of SFTs. Small imperfect
16 SFTs are observed after 200 ns MD irradiation simulation as shown in Fig.6.
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34 **4.2 Strengthening mechanisms of lamellar interfaces in the radiation damage process at** 35 **elevated temperatures** 36 37

38 During ion or neutron irradiation, the microstructural features such as precipitates and
39 phase interfaces can act as sinks to absorb the interstitial atoms and vacancies. The
40 accumulation of interstitials and vacancies at the interfaces offers more chance for the
41 recombination of the two types of defects, and effectively suppresses the formation of defect
42 clusters [5]. Especially at high temperatures, the movements of interstitials and vacancies as
43 well as the matrix atoms are accelerated due to the increased diffusion. The majority of
44 vacancies move to the interfaces, leading to a reduced number of vacancies in the regions
45 near the interface and refining the SFTs in these regions, especially for the α_2/γ lamellar
46 interface (Figs.7-10).
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The refinement effect of the α_2/γ lamellar interface can be estimated using the number of the vacancies included in the perfect SFTs. For example, in the projection direction $\langle 110 \rangle$ (Fig.4e), the base and the height of the projection triangle are along the $\{002\}$ and $\{110\}$ planes. The length of the base and height for the triangle include five $\{110\}$ and $\{002\}$ planes, and the d-spacing of $\{110\}$ and $\{002\}$ are 0.2832 nm and 0.2035 nm, respectively, and consequently the base and heights have the length of 1.416 nm and 1.0175 nm, respectively. On the basis of this, the vacancy number of SFTs in the experimental TEM and STEM images of Fig.7 can be estimated. If the base and height of the projection triangle in the direction $\langle 110 \rangle$ of a SFT contain $n\{110\}$ and $n\{002\}$ planes, their length are $0.2832n$ nm and $0.2035n$ nm. SFTs 1 and 2 in Fig.7 are typical SFT in the region near the α_2/γ lamellar interface and that away from the interface. The height and base length are approximately 6.895 nm and 8.902 nm, respectively, for the SFT 1, and 24.02 nm and 27.799 nm, respectively, for the SFT 2. The average values of n for SFTs 1 and 2 are calculated as approximately 33 and 108. The magic number of vacancies in the n^{th} plane is the sum of first n natural number [26], and hence the total vacancy number in a perfect SFT is the sum of the sum of first n natural number i.e. $(n*(n+1)*(n+2))/6$. It can be calculated that the SFTs 1 and 2 contain approximately 6545 and 215820 vacancies, respectively, if they are perfect SFTs. Thus, the SFTs in the region away from the α_2/γ interface are approximately 33 times those near the interface in the additively manufactured TiAl alloy. Hence the α_2/γ lamellar interfaces absorb a majority of vacancies and dramatically refine the vacancy-type SFTs, enhancing the radiation damage tolerance of the material.

The introduction of vacancies and dislocations in the interface areas greatly increase the sink strength of the microstructure not only at room temperature [5] but also at high temperatures. The lamellar microstructure with initial defects at the α_2/γ interface (Fig.10) has fewer defects in the matrix than that with perfect interface (Fig.9). These results again

confirm that the initial defects in the interface areas of the start microstructure play an important role in attracting the point defects and defect clusters during irradiation at the elevated temperature. Also, more defects are present at the α_2/γ interface than the γ/γ interface, and the α_2/γ lamellar interface can act as stronger sinks than the γ/γ interface to absorb more primary point defects and defect clusters at the elevated temperature (Figs.7, 8 and 10). The additively manufactured TiAl alloy in the present study contains very high amounts of defects at the α_2/γ lamellar interfaces, resulting in an approximately 70 nm width SFT-refinement zone and hence enhancing its radiation tolerance.

5. Conclusions

The TEM specimen of the GTAW-ALM additively manufactured TiAl alloy was in-situ irradiated with 1 MeV Kr^{2+} ions at the elevated temperature of 873 K. The post-irradiation microstructure was further examined ex-situ using advanced analytical TEM. TEM image simulation and molecular dynamic simulation were conducted to investigate the atomic origins and the formation and growth of the radiation-induced defects and interfacial strengthening in the radiation damage process at elevated temperature. The experiment and simulation results have led to the following conclusions:

- (1). During Kr-ion irradiation at 873 K, volume defects were observed within the FCC γ -TiAl phase, and the volume defects became large with increasing irradiation dose. Defect-refinement zones with a width of approximate 70 nm formed near the α_2/γ lamellar interfaces.
- (2). The volume defects exhibit triangle or large hexagon shapes under the zone axes of $\langle 110 \rangle$ in the TEM and STEM images, and white and dark contrast in the BF and DF images respectively. These microstructural characteristics in combination with the EDX composition analyses revealed that the volume defects were vacancy clusters. The HREM morphologies showed that the rows of the $\{111\}$ plane atoms at the bottom of the triangle were a lateral

shift away from the top of the triangle. All these features indicated that the volume defects are vacancy-type stacking fault tetrahedrals.

(3). The MD annealing and irradiation simulations confirmed the origin of the volume defects as SFTs, and revealed the formation and growth of SFTs via a vacancy agglomeration mechanism. Due to the increased diffusion coefficient for vacancies at the elevated temperature of 873 K, the vacancies became mobile, especially in small clusters. The small vacancy clusters could grow to become large and stable SFTs by absorbing individual vacancies or small vacancy clusters. Hence, fast diffusion of defects at high temperatures promoted the formation and growth of SFTs in the irradiation microstructure.

(4). At the elevated irradiation temperature of 873 K, the lamellar interfaces with initial defects could effectively act as strong sinks to absorb primary point defects and defect clusters, and fast diffusion also accelerated the accumulation of interstitials and vacancies at the interfaces as well as the recombination of the two types of defects. The reduced concentration of defects near the interfaces resulted in the formation of SFT-refinement zones, especially near the α_2/γ interfaces. More initial defects at the interfaces of the additively manufactured TiAl alloy can enhance its radiation damage tolerance at the high irradiation temperature.

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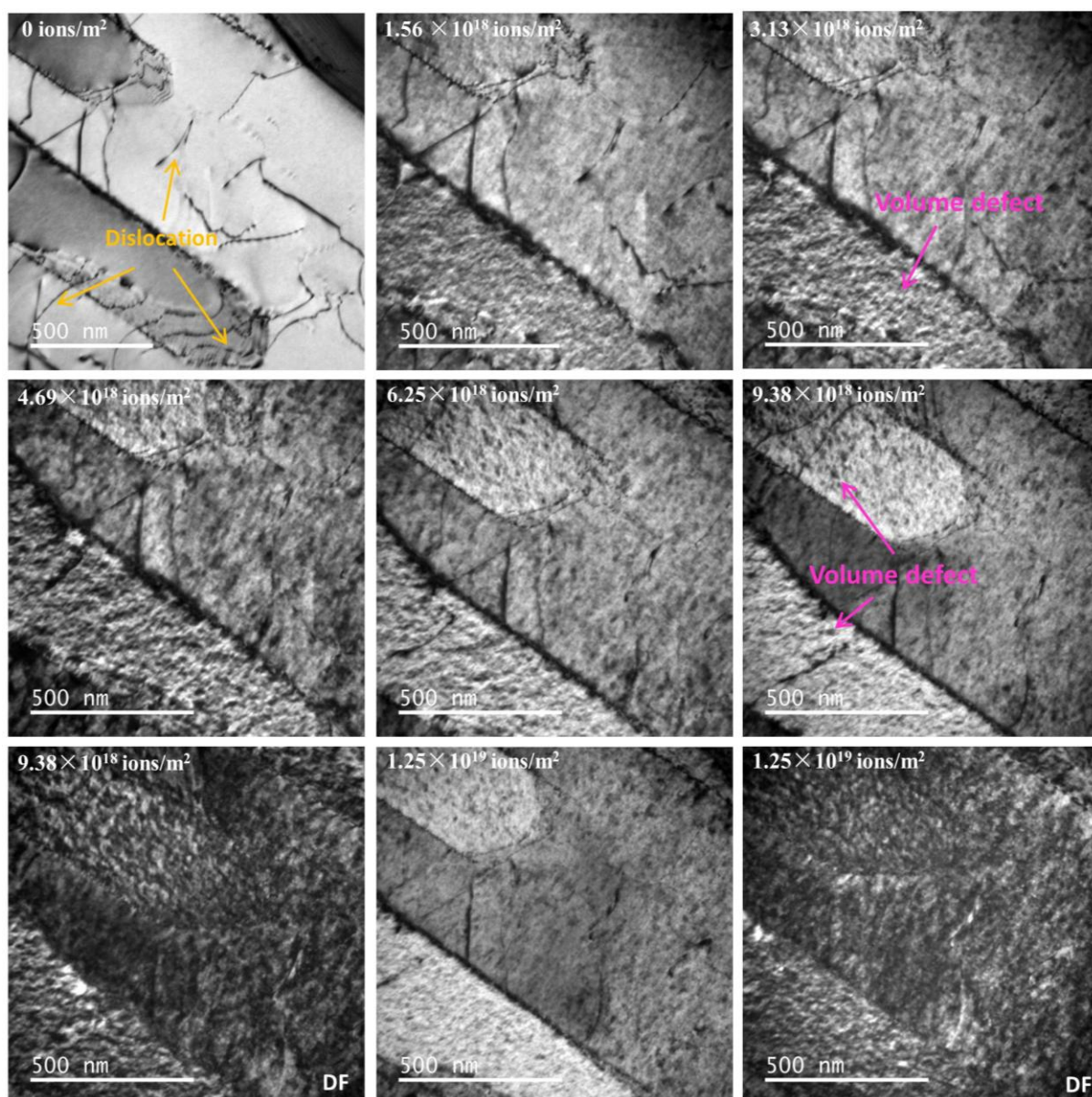


Figure 1: TEM micrographs of the Kr-ion irradiated microstructure of the additively manufactured TiAl alloy irradiated at 873 K. The micrographs show defect development with the corresponding iterative increase in radiation dose.

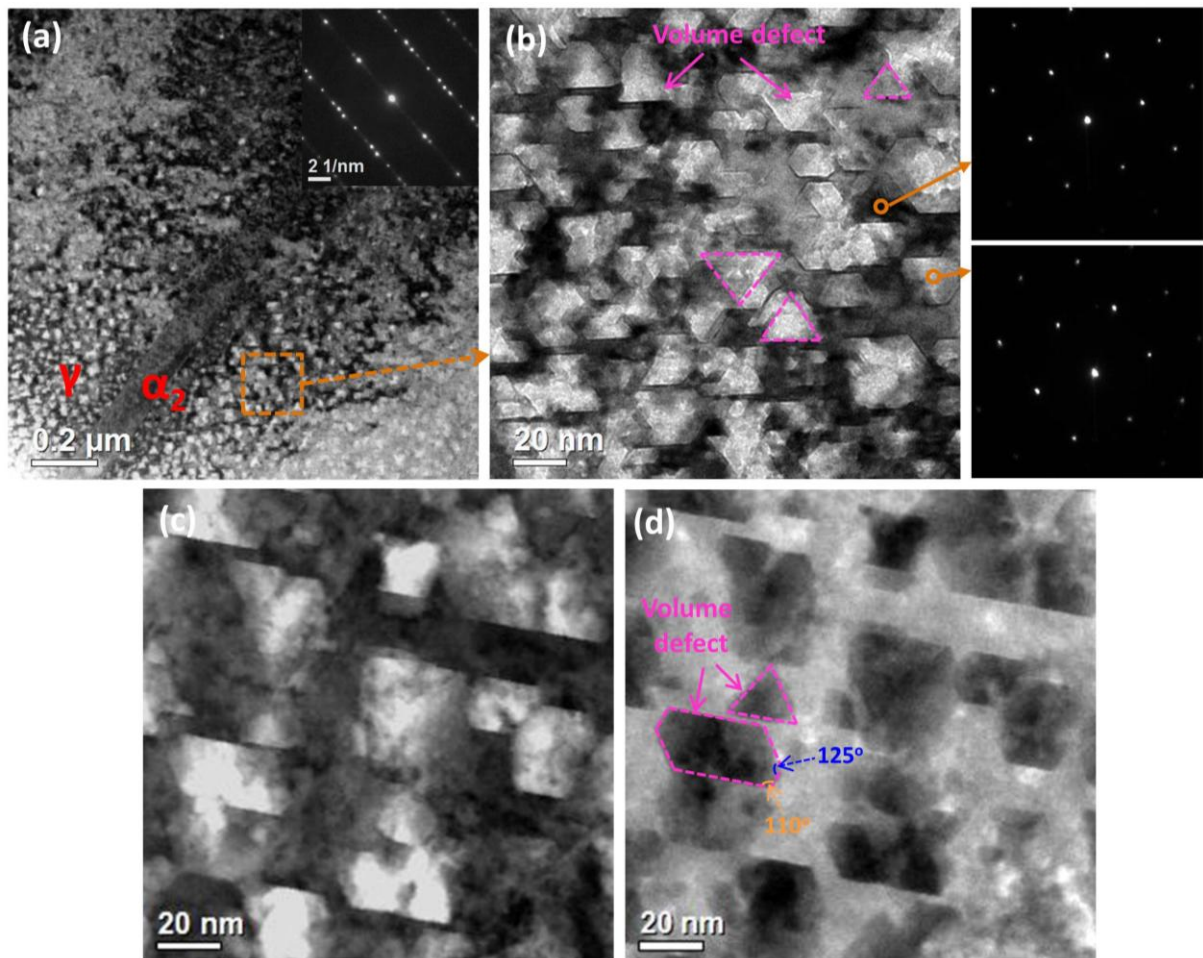


Figure 2: Microstructural characteristics of volume defects. (a) and (b) TEM morphologies of the irradiated microstructure with SAD patterns, and STEM morphologies of volume defects in the γ phase under (c) BF and (d) HAADF conditions.

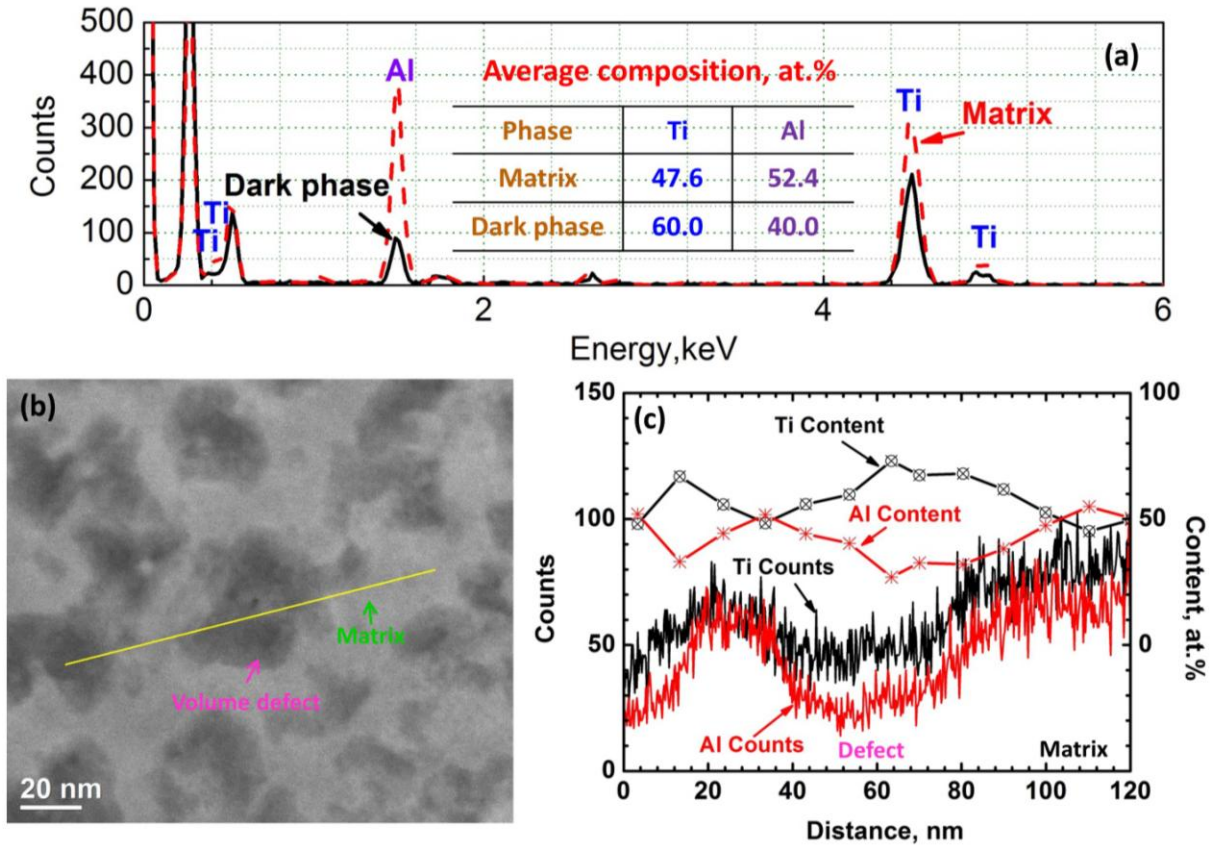


Figure 3: The distribution of chemical elements across volume defects. (a) The chemical compositions of volume defects and their surrounding matrix, (b) HAADF-STEM image, and (c) STEM line scan counts (line curves) and chemical element contents (line curves with scatter data) of Ti and Al elements across the volume defects of (b).

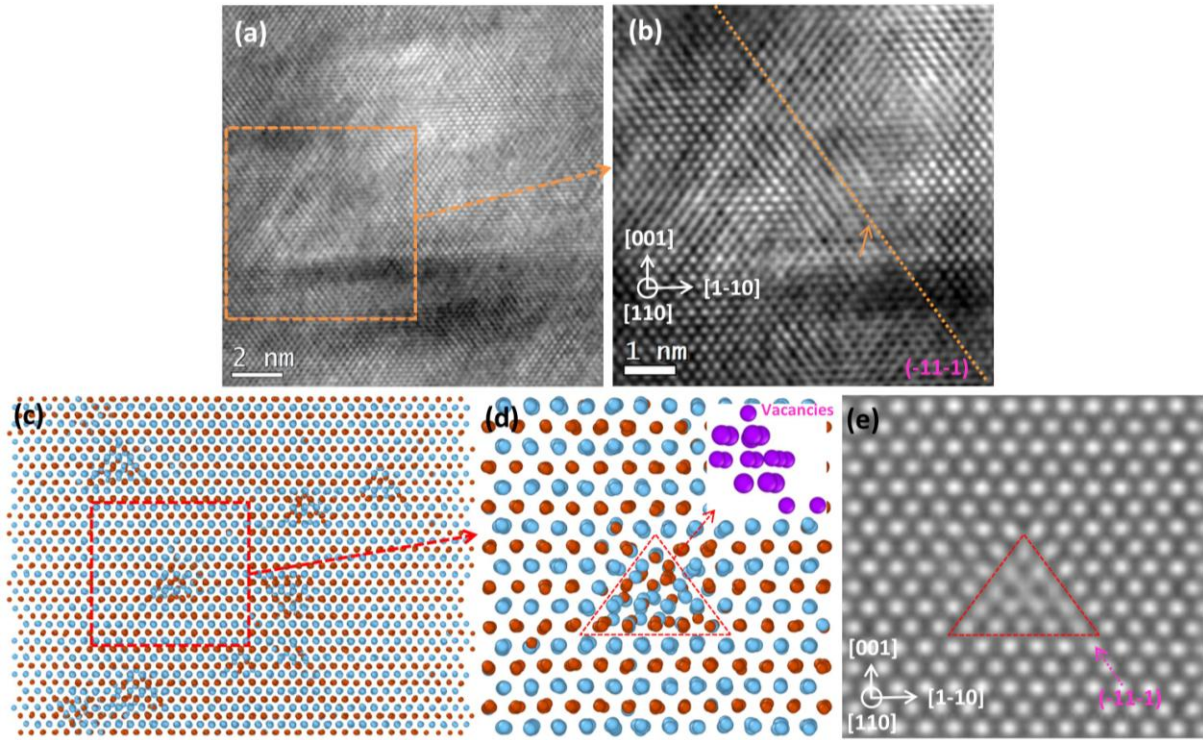


Figure 4: HREM morphologies and image simulation of SFTs. (a) and (b) HREM images of a SFT, (c) a selected snapshot of the simulated microstructure of the TiAl system with 152 initial vacancies after the MD annealing simulation for 427 ns at the annealing temperature of 873 K, (d) the selected area with a SFT for TEM image simulation together with the snapshot showing the vacancies contained in the SFT, and (e) simulated HREM image of (d), the sample thickness (t) and defocus (d) for the HREM image simulation are $t=1.9$ nm and $d=132$ nm, respectively.

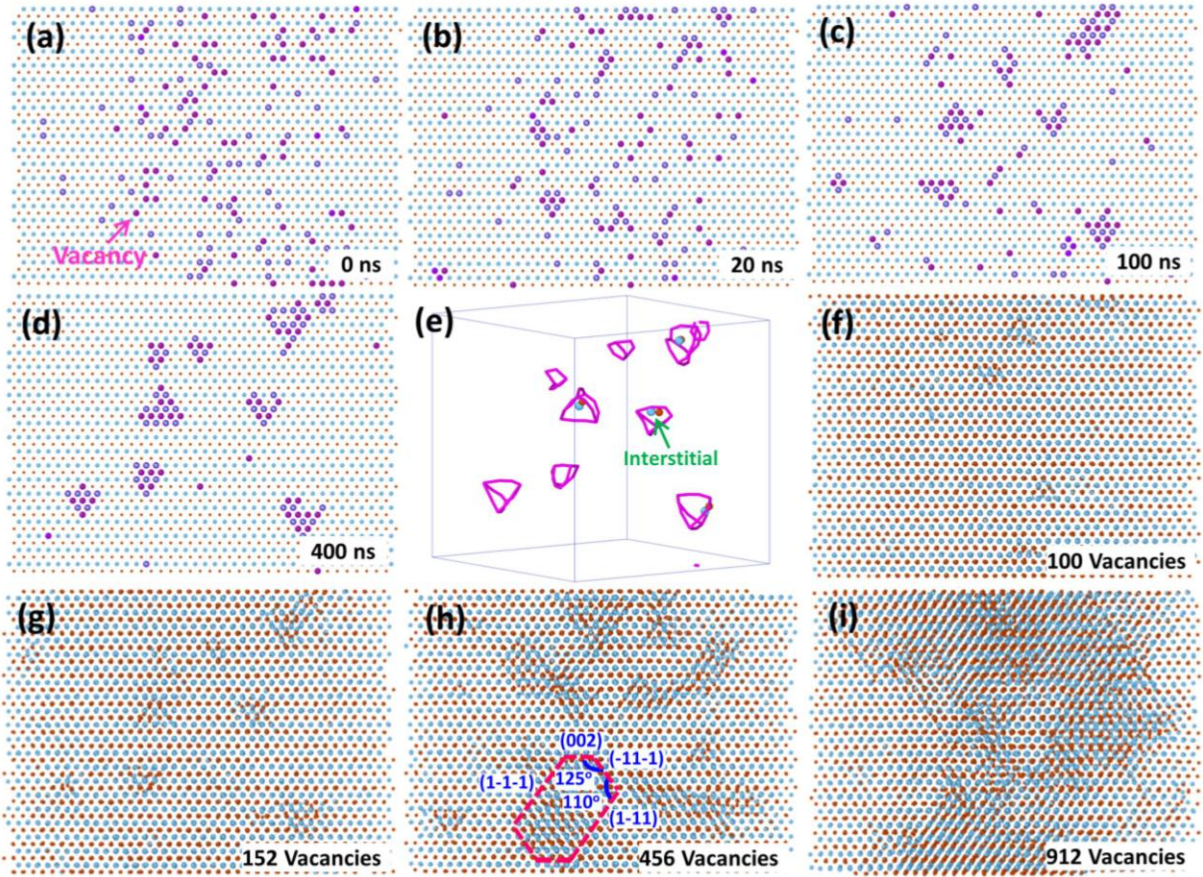


Figure 5: Selected snapshots of the MD annealing simulation showing the effects of the simulation duration and initial vacancies in the start microstructure on the formation and growth of SFTs in the γ phase annealed at 873 K. The distribution of vacancies in the start microstructure with 152 initial vacancies after simulation time of (a) 0 ns, (b) 20 ns, (c) 100 ns, (d) 400 ns and (e) dislocations and interstitials of (d), vacancies are represented with large spots, and the simulated microstructure for the γ phase with initial vacancies of (a) 100, (b) 152, (c) 456 and (d) 912 after the MD annealing simulation for 200 ns.

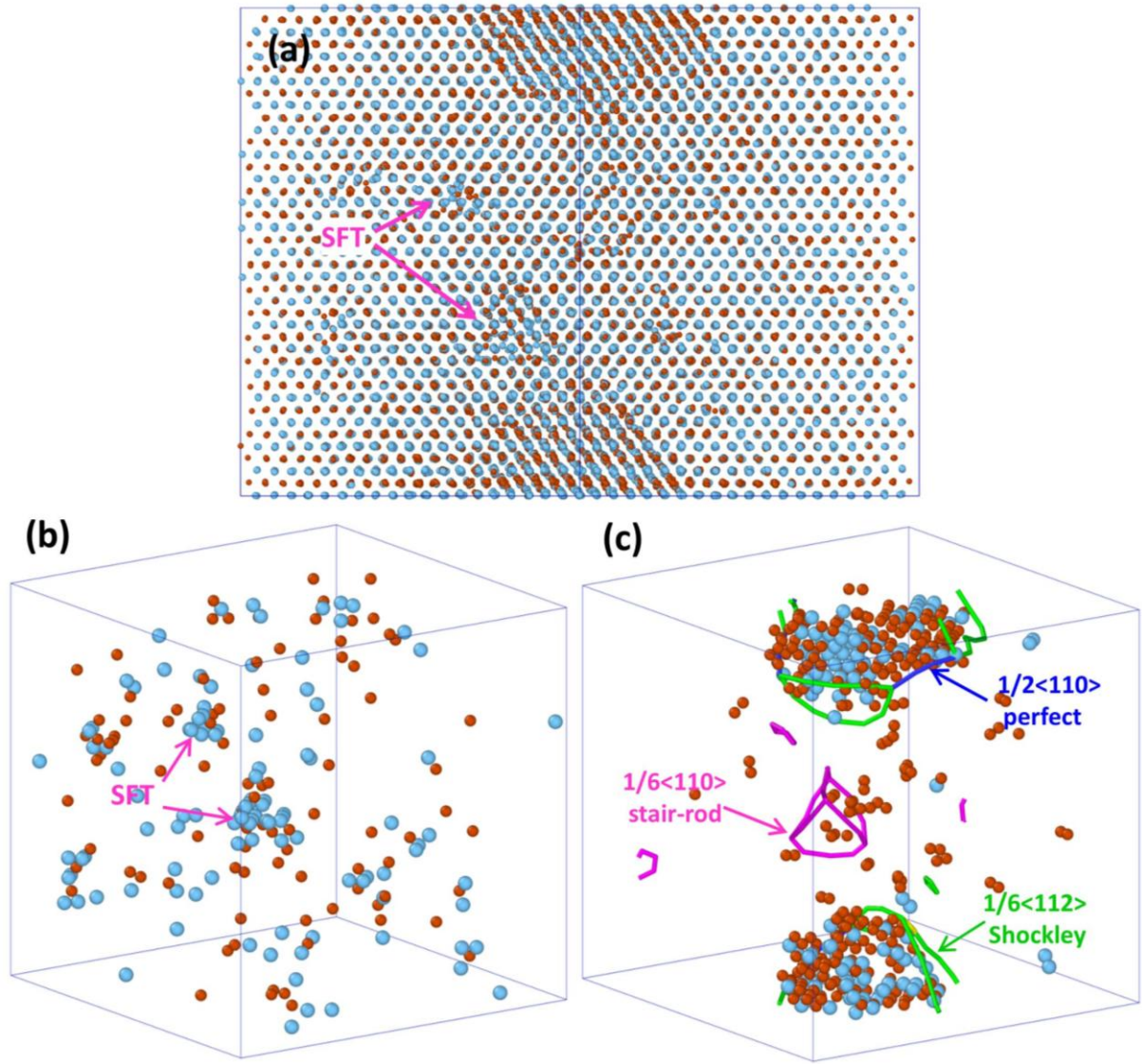


Figure 6: Selected snapshots of the MD irradiation simulation for the γ phase after simulation for 100 ns at the irradiation temperature of 873 K. (a) The simulated irradiation microstructure, and the distribution of (b) vacancies (Ti and Al atoms represent the vacancy sites formed when they were removed from their substrate sites), and (c) interstitials and dislocations in the simulated unit.

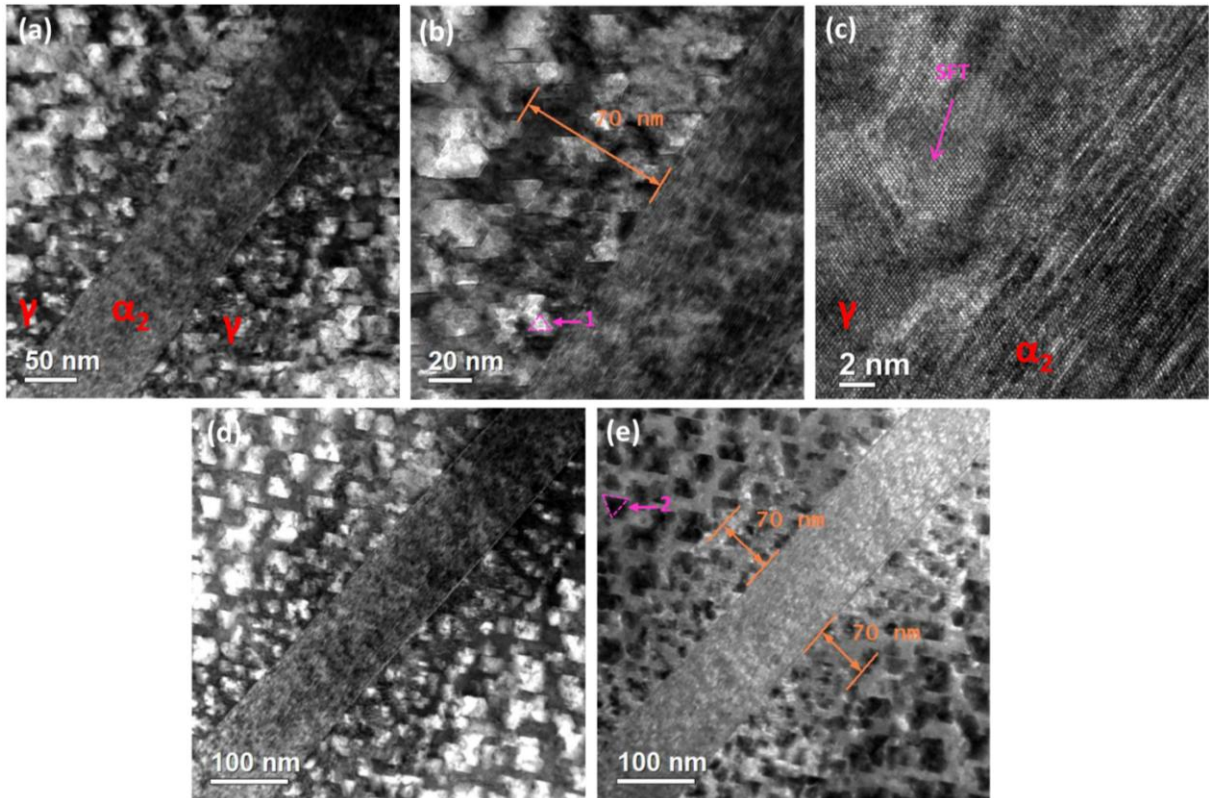


Figure 7: TEM and STEM morphologies of volume defects near the α_2/γ lamellar interfaces in the Kr-ion irradiated microstructure of the additively manufactured TiAl alloy irradiated at 873 K. (a) and (b) TEM, (c) HREM, (d) BF-STEM and (e) HAADF-STEM.

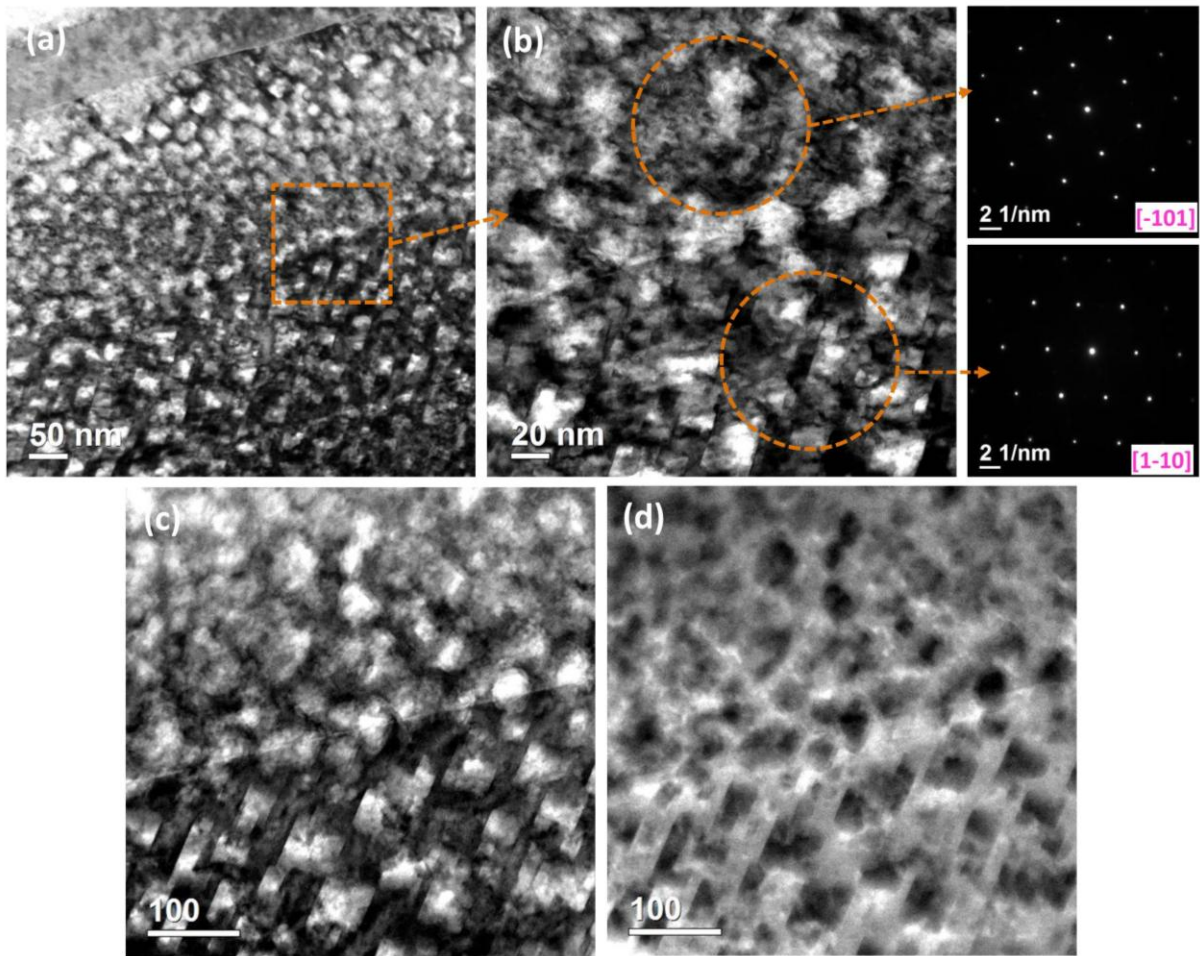


Figure 8: TEM and STEM morphologies of volume defects near the γ/γ lamellar interfaces in the Kr-ion irradiated microstructure of the additively manufactured TiAl alloy irradiated at 873 K. (a) and (b) TEM with SAD patterns, (c) BF-STEM and (d) HAADF-STEM.

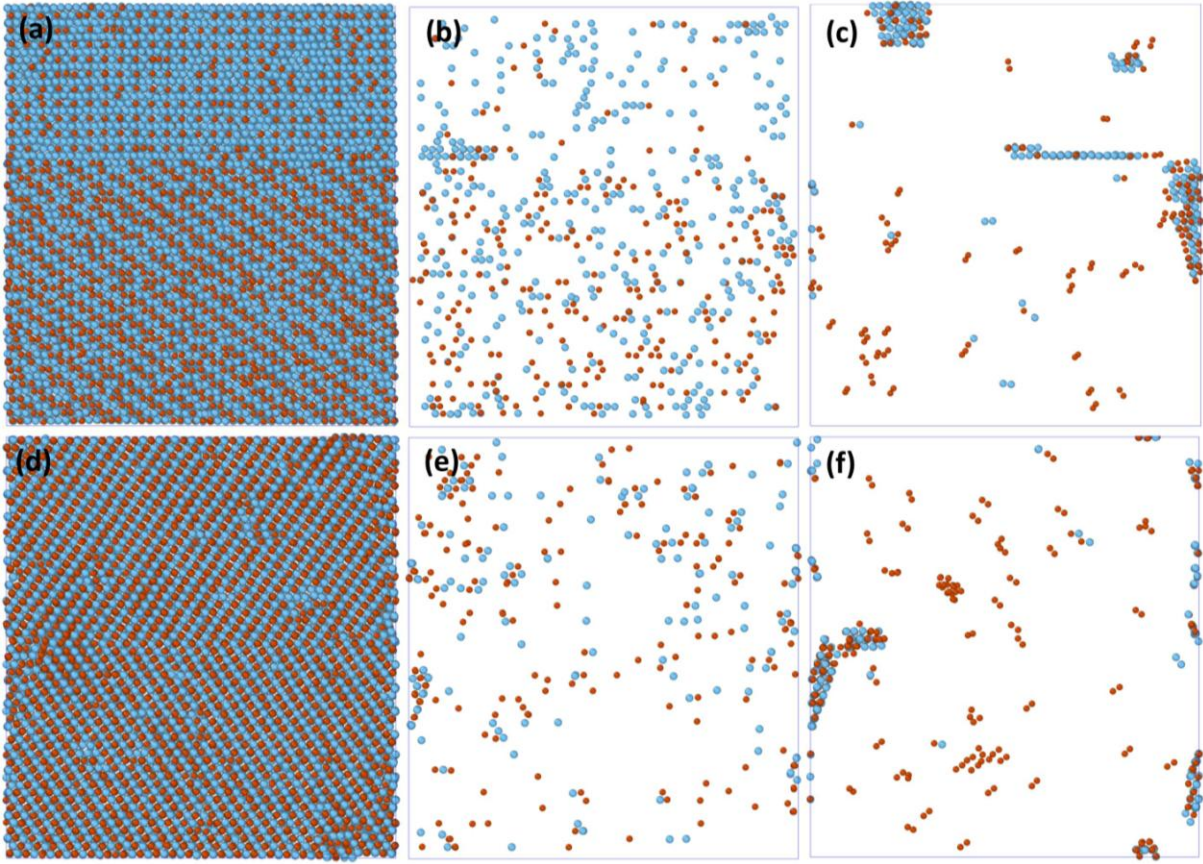


Figure 9: Selected snapshots of the MD irradiation simulation for the lamellar microstructure with perfect lamellar interfaces after simulation for 40 ns at the irradiation temperature of 873 K. (a) The simulated irradiation microstructure with the α_2/γ lamellar interface, and corresponding (b) vacancies and (c) interstitials, and (d) the simulated irradiation microstructure with the γ/γ true twin interface, and corresponding (e) vacancies and (f) interstitials.

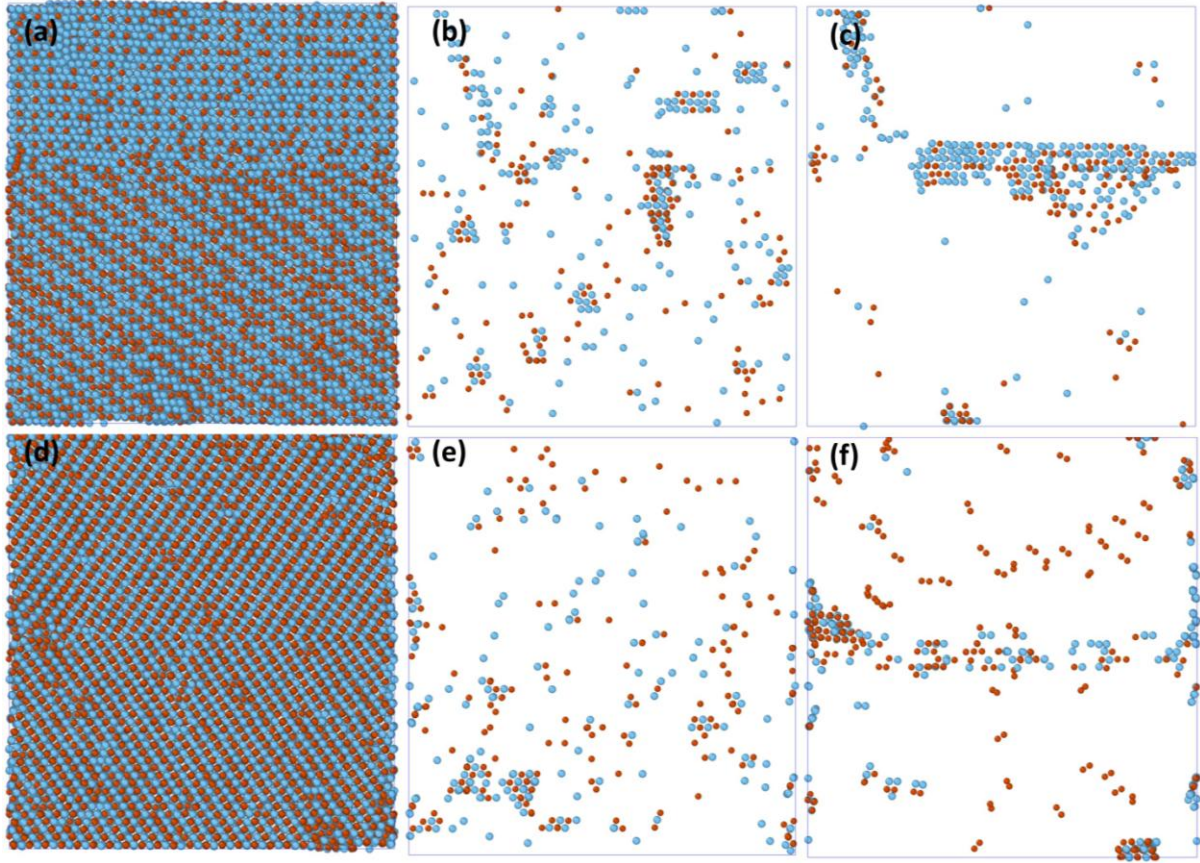


Figure 10: Selected snapshots of the MD irradiation simulation for the lamellar microstructure with defect interfaces after simulation for 40 ns at the irradiation temperature of 873 K. (a) The simulated irradiation microstructure with the α_2/γ lamellar interface, and corresponding (b) vacancies and (c) interstitials, and (d) the simulated irradiation microstructure with the γ/γ true twin interface, and corresponding (e) vacancies and (f) interstitials.

Supplementary Material

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