

Structural evolution of five-fold twins during the solidification of Fe₅₆₀₁ nanoparticle: a molecular dynamics simulation

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Abstract In the current study, we provide a structural evolution process of isolated Fe nanoparticle with 5601 atoms during solidification. Five-fold twinned structure has been found in the final configuration of the nanoparticle. Furthermore, detailed formation process has been visualized and carefully discussed. During the formation of five-fold twinned structure, two main stages have been identified, including *i*) liquid–solid phase transition at solidification point, in which the main part of the five-fold twinned structure formed, and *ii*) structural relaxation, in which twinning boundaries and five-fold axis were transformed to eliminate the dislocation between two adjacent five-fold twins.

Keywords Five-fold twins · Iron nanoparticle · Molecular dynamics · Structural evolution

Introduction

Multiply twinned particles (MTPs) have attracted enormous interest as they exhibit unique properties in nanocrystals. Five-fold twins, a kind of MTPs, have been extensively studied for decades [1–6], especially face-centered cubic (*fcc*) metals and alloys.

Few reports focus on five-fold twins formed by molecular dynamics (MD). Zhu et al. believed that five-fold twins could not be predicted by MD because of the uniaxial stress

condition used in MD [7]. However, Cao and his colleagues [8] obtained five-fold twins by MD with pretwins. Furthermore, Chui et al. [9] achieved five-fold twins in gold nanoparticle with 10,179 atoms.

To our knowledge, the majority of reports focus on formation mechanism of five-fold twins, such as, experimental or simulating methods in nanoparticles and thin films. However, not much emphasis was placed on the detailed structural evolution during solidification, especially the growth and moving of twinning boundary (TB) in a five-fold structure. Here, we demonstrate the structural evolution of five-fold twins in Fe nanoparticle during solidification process by molecular dynamics.

Computational details

All MD simulations of nanoparticle were performed with NVT ensemble using DL_POLY3 package [10]. The velocity verlet algorithm [11] and Berendsen thermostat [12] was used. The time step was set to 2 fs. The Finnis and Sinclair [13] potentials were employed and the parameters used here are $\varepsilon=0.0006$ eV, $a=0.36467$ nm, $n=15$, $m=4$, $c=1104.7351$, which were obtained by fitting the experimental data, such as lattice parameter, cohesive energy and bulk modulus of γ -Fe (*fcc* structure). These parameters have been proven very successful to simulate the melting and solidifying phase transitions between bulk γ -Fe (*fcc*) and liquid-Fe [14, 15].

The Fe nanoparticle was dug out from bulk crystal with the digging radius of 2.5 nm, in which 5601 atoms included, and then completely melted at 2,000 K for 100 ps to get the initial configuration for cooling process. Seven cooling rates ranged from 0.125 K/ps to 25 K/ps have been employed. Based on our observation, Fe₅₆₀₁ tend to form five-fold twins with a lower limit of 0.25 K/ps (this work will be

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detailed discussed in another paper). With a purpose that the detailed structural evolution of five-fold twins can be presented as clearly as possible, a cooling procedure with a temperature interval of 25 K per 100 ps (0.25 K/ps) from 2000 K to 300 K have been employed in this paper. The whole MD simulation was carried out with no boundary condition.

A cluster-type index method [16] (CTIM-2) based on Honeycutt-Anderson (H-A) Index [17] has been applied in order to explore structure evolution. Considering high temperature causing violent thermal motion of atoms, coordinated atoms in the form of standard *bcc*, *fcc* or *hcp* are not stable. We enlarged the region of the characteristic indices based on standard CTIM-2 index to identify the perfect and similar solid atoms, respectively (see in Table 1).

Results and discussion

The variation of potential energy versus temperature during the solidification process is illustrated in Fig. 1, where four stages can be identified: *i*, a liquid state from 2000 K to 1400 K; *ii*, a liquid–solid transition at 1375 K; *iii*, structural relaxation from 1350 K to 700 K; and *iv*, an equilibrium configuration below 700 K. The division at 700 K is clearly identified from the structure evolution as shown below.

As temperature decreased, potential energy decreased along the liquidus to 1400 K. Then, a significant drop, indicating a liquid–solid phase transition, appeared at 1375 K. The potential energy was still slightly higher than solidus after the drop. The difference between the potential energy curve and solidus can be regarded as the driving force for the subsequent structural relaxation. The equilibrium configuration is formed at approximately 700 K, where the difference disappeared. According to our data, the temperature of 700 K is unlikely to be a rigorous cutoff point as the difference has fallen to a negligible value, 0.1 %, when the temperature was close to 700 K.

The twinning boundaries (TB), composed of *hcp* atoms, have been illustrated in Fig. 2. *fcc* atoms or amorphous are not shown. Four twinned five-fold twins shared twinning

boundaries with each other, are involved and labeled as α , β , γ and δ according to their birth sequence in solidification process. The TBs and twinning axes were colored as yellow and brown dots, whereas other *hcp* atoms not participating in the five-fold twins were blue. This represents a form of typical five-fold twins, in which five TBs join together with an enclosed angle of about $2\pi/5$ ($\sim 70.53^\circ$).

The percentage variation of *fcc*, *hcp* and amorphous atoms are shown in Fig. 3. At the solidification point of 1375 K, when liquid–solid transition occurred, the percentages of *fcc* and *hcp* atoms dramatically increased from 0 to 25.66 % and 15.39 %, respectively, whereas amorphous atoms depleted from 100 % to 58.95 % correspondingly.

The structural relaxation occurred at the temperature ranging from 1375 to 700 K. For *fcc* atoms, the percentage was nearly doubled from 25.66 % to 47.40 %, whereas *hcp* atoms increased from 15.39 % to 20.47 %. On the basis of the configuration snapshot, *hcp* atoms were observed to be in the form of TBs or other grain boundaries (see Fig. 2). Furthermore, most of *hcp* atoms acted as TBs during structural relaxation and a mass of newly formed *fcc* atoms, nearly 1/4 of the entire particle, were crystallized into blocks surrounded by TBs.

At the temperature of <700 K, the percentage curves flattened since most *fcc* and *hcp* atoms have been previously formed. Amorphous atoms remained at a percentage of 30.70 %, most of which were surface atoms.

For example, Fig. 4 shows the formation process of the first five-fold twin, α , as labeled in Fig. 2. Meanwhile a video file is included to visually demonstrate a liquid–solid transition, formation and growth of nucleus, and structural relaxation. As temperature reached 1375 K, the atomic thermal motion decreased consequently and the quantity of *fcc* and *hcp* atoms increased significantly. In order to clearly identify the formation of five-fold structure in the particle, we present only the *fcc* and *hcp* atoms involved in the formation of α from 24 ps to 100 ps in Fig. 4. Atoms, which were not involved in the formation of α , regardless of *fcc*, *hcp* or amorphous, are not shown.

A cluster consisting of nearly 20 atoms was formed at 24 ps in α by the assembly of *fcc* and *hcp* atoms, which can

Table 1 Standard and extended CTIM-2 indices for the determination of *bcc*, *fcc* and *hcp* atoms

	Standard index ^a					Extended index ^b	
	Coordination number	$n_{(1441)}$	$n_{(1551)}$	$n_{(1661)}$	$n_{(1421)}$		$n_{(1422)}$
<i>bcc</i>	14	6	0	8	0	0	$4 \leq n_{(1441)} \leq 8, 6 \leq n_{(1661)} \leq 10$
<i>fcc</i>	12	0	0	0	12	0	$9 \leq n_{(1421)} \leq 15$
<i>hcp</i>	12	0	0	0	6	6	$4 \leq n_{(1421)} \leq 8, 4 \leq n_{(1422)} \leq 8$

^a $n_{(i)}$ means the number of the *i*-indexed bond type and coordination number = $n_{(1441)} + n_{(1551)} + n_{(1661)} + n_{(1421)} + n_{(1422)}$

^b Characteristic indices could change at a certain region with coordination number unchanged

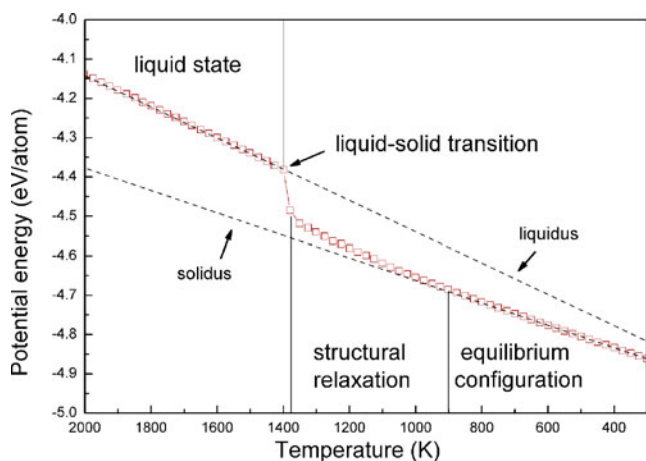


Fig. 1 The variation of potential energy versus temperature

be regarded as the rudiment of the nucleus. Then a TB1, consisting of *hcp* atoms, was formed as a grain boundary at 60 ps. At 64 ps, TB2 began to form. One of its endpoints jointed with TB1, but another was not arrayed because of the existence of amorphous atoms. Subsequently, a lamellar twined structure with two *hcp* planes was formed at the bottom left of the particle at 66 ps. The upper *hcp* plane extended to the joint of TB1 and TB2 can be recognized as an early stage of TB3, forming three-fold twins. And the lower one partially disappeared at 68 ps, whereas TB2 and TB3 were still growing. At the three-fold joint point, *hcp* atoms were arranged into a closed five-membered ring at the twinning axis, and the early stages of TB4 and TB5 were formed. Finally, the entire five-fold twins were formed at 72 ps. The reason that five-fold twins were formed could be explained by the surface energy of the particle, which played a similar role with the pretwins and provided additional stress in simulation cells, ultimately leading to the formation of five-fold twins as shown in Cao et al.'s work [8].

When the aforementioned process happened, other five-fold twined structures were formed simultaneously. In Fig. 4, we labeled α and β with blue and red lines,

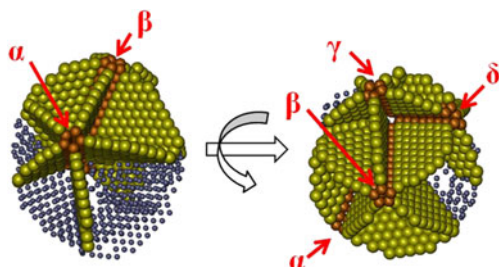


Fig. 2 Five-fold twinning structures in Fe_{5601} , while only *hcp* atoms (composing twinning boundary) are shown, and *fcc* or amorphous atoms are not shown

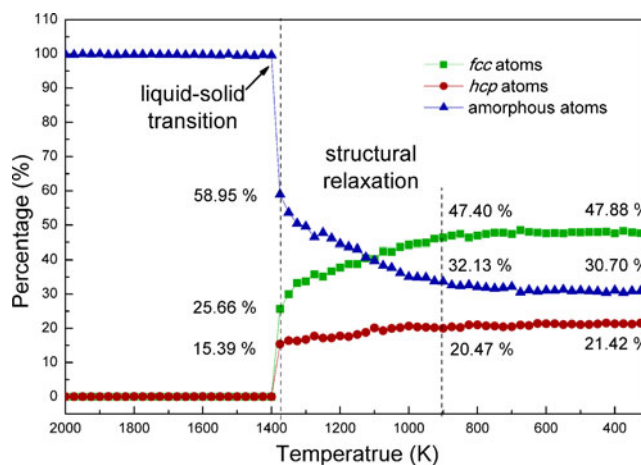


Fig. 3 Percentage variation of three atom categories versus temperature

respectively, for their directing TBs. Compared with the final configuration, in which α and β share one TB perfectly as shown in Fig. 2, a dislocation was found between these two adjacent five-fold twins after the solidification at 1375 K. It could be inferred that the dislocation could be eliminated at the next stage, in which structural relaxation occurs from 1350 K to 700 K.

Based on our observation, dislocation elimination consists of three steps. Step 1 occurred at 1350~1300 K, as shown in Fig. 5a. TB5 kept growing with its intrinsic direction, whereas TB- β shrank distinctly. The remaining four TBs stayed with their own direction. A significant transformation appeared in step 2 (see Fig. 5b). TB5 moved toward right where TB- β exited. The atoms forming TB5 before were transformed to *fcc* atoms and consequently formed a TB5-new. This is mainly due to a 7.35° gap in an ideal five-fold twinning process, which is accommodated by elastic strain [18, 19]. Moreover, a mass of *fcc* atoms were crystallized as discussed above and, as a results, an extrusion between crystals arose, which caused atomic rearrangement. Simultaneously, TB3-new was formed in the same symmetrical way as TB5 did. At this moment, the stress balance among five TBs was perturbed and the closed five-membered ring at the center five-fold structure became hardly recognized. Step 3 occurred while the temperature decreased from 1150 to 1125 K (Fig. 5c). TB2 and TB4 moved in the same way as TB3 and TB5 did, therefore, TB2-new and TB4-new were formed, while TB1 remained its own position. Furthermore, as a result of four newly formed TBs, the original five-fold joint was no longer available while a new five-fold axis was formed to accommodate the new TBs system.

According to the birth sequence, five-fold twins γ and δ were formed later than α and β . As illustrated in Fig. 6, a rudiment of γ containing three TBs was formed at a liquid–solid transition temperature of 1375 K, whereas its full

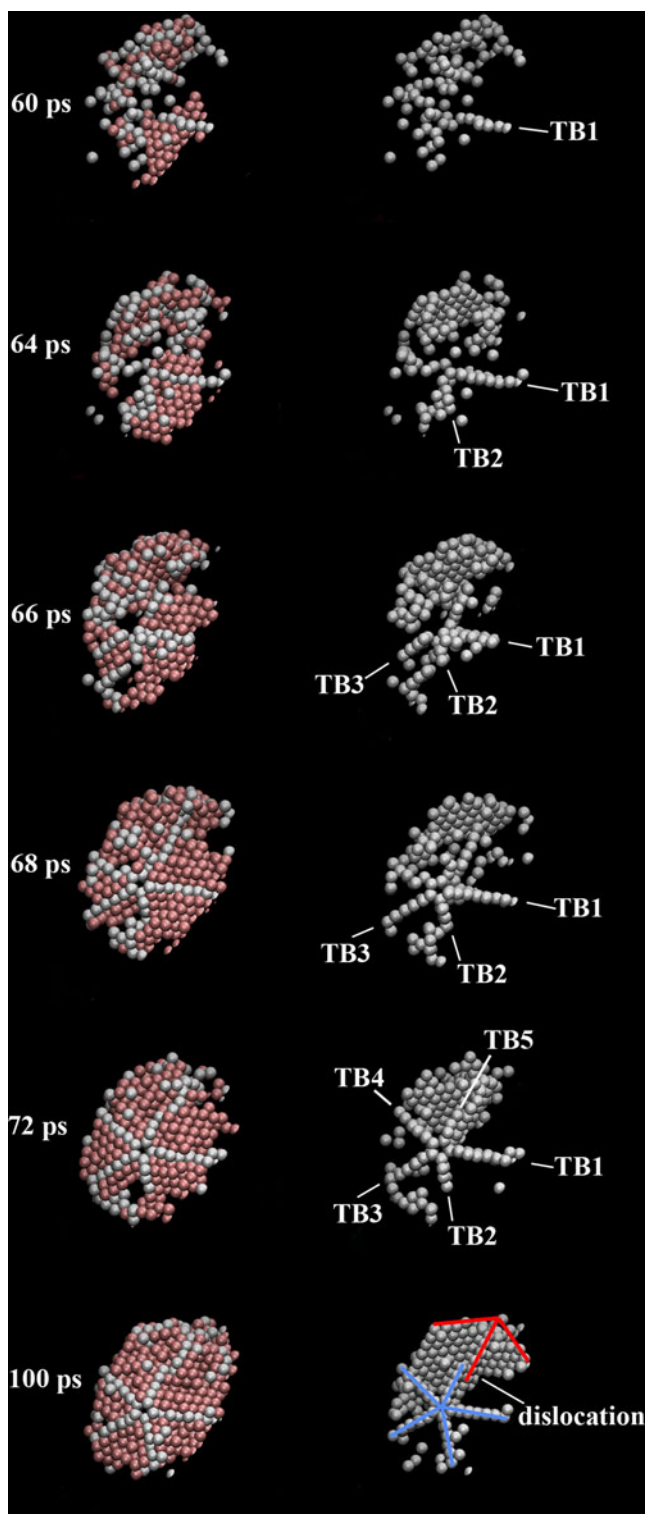


Fig. 4 The structure evolution of a twinning structure α at 1375 K. *fcc* fragments and *hcp* planes are shown on the left and the evolution of the *hcp* twinning plane network on the right

structure was formed at 1325 K. Lastly, at a temperature of 1250 K, δ was formed as a consequence of structural relaxation.

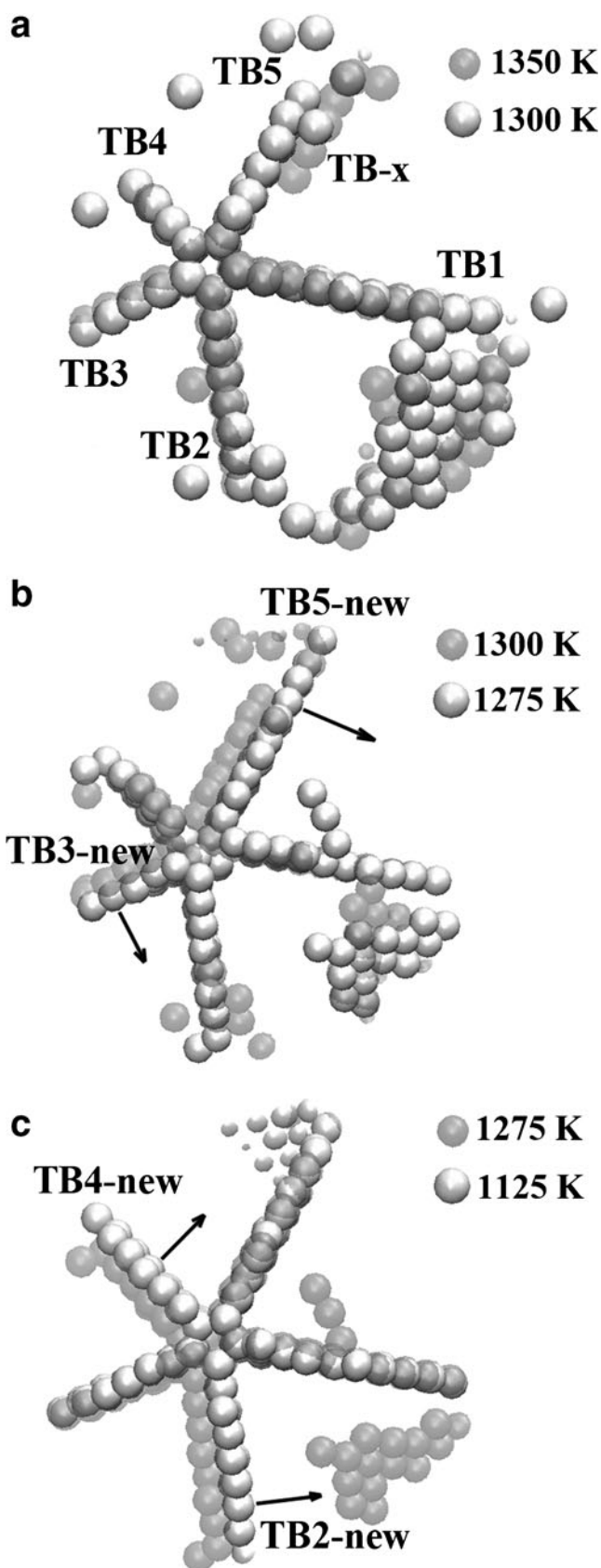


Fig. 5 The structure evolution of the five-fold structure α with *hcp* atoms from 1350 K to 1120 K

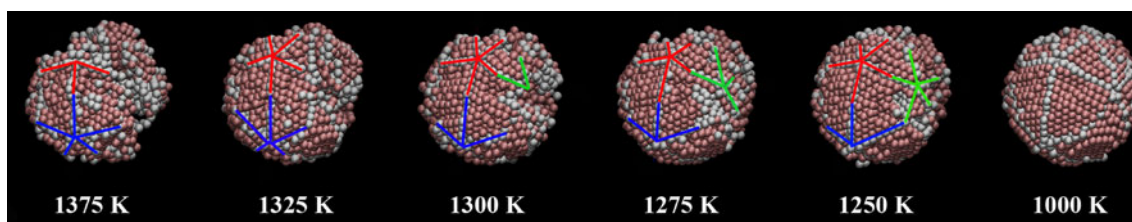


Fig. 6 The formation process of five-fold structures γ and δ . The TBs of β , γ and δ are marked with *blue, red and green lines*

Conclusions

In summary, four five-fold twins, α , β , γ and δ , have been found in Fe nanoparticle with 5601 atoms during solidification. Detailed structural evolution has been presented in this study. Liquid–solid phase transition and structural relaxation have been shown to play a major role in the formation of five-fold twins.

During liquid–solid phase transition at 1375 K, two five-fold twins (α and β) were formed. Twinning boundaries consisting of *hcp* atoms were formed when liquid–solid phase transition finished. Finally, as a result of the growth of TBs, a dislocation has been found between two adjacent five-fold twins, α and β .

Structural relaxation occurred during the temperature range of 1350~700 K and two more five-fold twins (γ and δ) were subsequently formed. Besides, with more amorphous atoms transformed into solid atoms (*fcc* and *hcp*), stress concentrated on TBs, which caused changes in atomic arrangement as shown in the snapshot. The new five-fold axis was formed to accommodate the new TBs system. Dislocation disappeared consequently and two adjacent five-fold twins shared one TB perfectly.

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