



Solid–solid phase transition of tungsten induced by high pressure: A molecular dynamics simulation

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Abstract: The phase transition of tungsten (W) under high pressures was investigated with molecular dynamics simulation. The structure was characterized in terms of the pair distribution function and the largest standard cluster analysis (LSCA). It is found that under 40–100 GPa at a cooling rate of 0.1 K/ps a pure W melt first crystallizes into the body-centred cubic (BCC) crystal, and then transfers into the hexagonal close-packed (HCP) crystal through a series of BCC–HCP coexisting states. The dynamic factors may induce intermediate stages during the liquid–solid transition and the criss-cross grain boundaries cause lots of indistinguishable intermediate states, making the first-order BCC–HCP transition appear to be continuous. Furthermore, LSCA is shown to be a parameter-free method that can effectively analyze both ordered and disordered structures. Therefore, LSCA can detect more details about the evolution of the structure in such structure transition processes with rich intermediate structures.

Key words: molecular dynamics (MD) simulation; rapid solidification; solid–solid phase transition; largest standard cluster analysis; topologically close-packed cluster

1 Introduction

An important goal of condensed matter science is to design and prepare materials with excellent properties. Pressure or cooling rate may have a profound effect on chemical and physical reactivity (such as electronic structure and atom size) and their different combinations could result in new phases or states [1]. For example, under the high pressures different crystals have been found for Ba [2], Na [3], Ca [4] and Mg [5]; and the

irreversible evolution of superconductivity in PdB_2 can be induced by pressure [6]. The diamond anvil cell (DAC) is a unique device that produces ultra-high static pressure; and the maximum compressive strength of diamond limits the highest achievable pressure. Due to the huge pressure enhancement, the maximum compressive strength of the DAC is theoretically predicted to be 900 GPa in an early study [7]. Three decades ago, it was reported that the static high pressure determined by ruby pressure calibration scale was 0.55 TPa [8]. Recently, in the carefully prepared DAC for observing solid metal

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hydrogen, the static high pressure is also as high as 495 GPa [9]. To date, the more generally accepted pressure range obtained in DAC is 350–400 GPa [10].

With high hardness and density, tungsten (W) is usually used under dynamic pressure, such as hard materials, kinetic energy penetrators, cannon shells and missiles to create supersonic shrapnel. W is recently believed to be a promising candidate for plasma-facing materials for future fusion reactors and is planned to be used for diverter armour of the international thermonuclear experimental reactor (ITER) [11], where the W surface could be melted repeatedly under high thermal stress. Thus, it is of great significance to investigate the property of W under high pressure and temperature. It is reported that the relative electrical resistance of W decreases with increase of pressure from 0 to 30.8 GPa [12]. For pure W sintered body, high-pressure torsional deformation improves the room temperature fracture strength by 2–3 times [13].

However, the mechanism for the changes of these properties associated with high pressure has not been fully understood, due to the difficulty in obtaining the structural details of the disordered systems in the experiment, such as liquids, super-cooled liquids and amorphous solids. Computer simulation is an effective tool [14–16] to overcome this difficulty. Molecular dynamics (MD) [17–19] and first-principles simulations [20–23] are both effective methods for high-pressure research. Comparing with the first-principles calculations, MD simulation can be applied to a large number of atoms enough for studying phase transitions between ordered and disordered systems. However, limited by the capability of current computers, solid melting or melt solidification is usually investigated under extremely high heating or cooling rates. With the development of cooling technology and computational science, the cooling rate gap between simulation and experiment is gradually decreased. In fact, for example, the A15 phase of Zr has been found at high pressure (>60 GPa) by classic MD simulations [18].

In order to investigate the effect of pressure on structure evolution during rapid solidification and to search possible high-pressure phases of W, rapid solidifications of liquid metal W under the pressure

of 40–100 GPa have been conducted with MD simulation. The structures of the simulated systems were characterized by the pair distribution function and the largest standard cluster analysis (LSCA) [24–26], and the results revealed that the ambient-condition stable BCC (body-centred cubic) phase of W becomes a high-temperature metastable phase under high pressure during rapid cooling at 0.1 K/ps, and finally transforms into a hexagonal close-packed (HCP) phase. The liquid-BCC transformation may experience intermediate stages, similar to some alloys [27,28]. While the first-order BCC–HCP transformation looks like a continuous process because there are lots of intermediate states. In addition, as a parameter-free structural analysis method for both ordered and disordered systems, LSCA can probe more structural details by calculating new indexes, such as the mean cut-off distance.

2 Methods

2.1 Computational methods

The MD simulation of the rapid solidification of liquid W was conducted using a large atomic and molecular parallel simulator (LAMMPS) software package [29]. The W–W interaction potential used here was proposed by WANG et al [30], and the calculation formulas are as follows:

$$E_{\text{tot}} = \sum_i^N F(\rho_i) + \frac{1}{2} \sum_{ij, i \neq j}^N V(r_{ij}) \quad (1)$$

where the embedding energy $F(\rho)$ is given by

$$F(\rho_i) = -A\sqrt{\rho_i} \quad (2)$$

And

$$\rho_i = \sum_{j, j \neq i} f(r_{ij}) \quad (3)$$

The pairwise potential function and electronic density function are respectively represented by a series of polynomial functions:

$$f(r) = \sum_{n=1}^N (A_n + B_n r + C_n r^2 + D_n r^3 + E_n r^4 + F_n r^5 + G_n r^6 + H_n r^7) \theta(r_n - r) \theta(r - r_{n+1}), \quad r_1 < r \leq r_{n+1} \quad (4)$$

and

$$V(r) = \sum_{n=1}^{N'} (A'_n + B'_n r + C'_n r^2 + D'_n r^3 + E'_n r^4 + F'_n r^5 + G'_n r^6 + H'_n r^7) \theta(r'_n - r) \theta(r - r'_{n+1}), \quad r'_1 < r \leq r'_{n+1} \quad (5)$$

where $\theta(x)$ is a Heaviside step function, defined as $\theta(x)=1$ for $x \geq 0$ and $\theta(x)=0$ for $x < 0$.

The effect of pressure was not specifically considered in the development of this potential function [30]; therefore, before it was used to simulate the rapid cooling of melts under high pressures, we verified the applicability of this force field under different pressures by the pressure–specific volume (p – V/V_0) curve (see Fig. 1). Our calculation revealed that at 0 K, the calculated p – V/V_0 curves are in good agreement with the experimental and DFT calculated data. Furthermore, at $p < 30$ GPa the calculation based on the BCC crystal is slightly better than that based on the HCP crystal; while at $p > 30$ GPa the result based on the HCP crystal is much better than that based on the BCC crystal. This change is consistent with our simulation: at 40–100 GPa the final state is HCP rather than BCC that is stable at ambient conditions. Thus, this potential has sufficient accuracy under the high pressure.

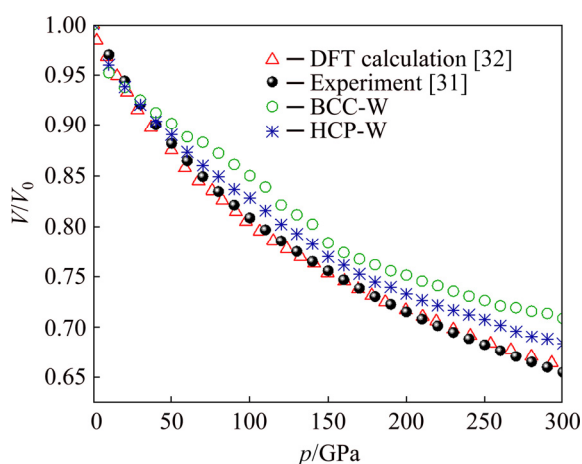


Fig. 1 Pressure dependence of specific volume of pure W at 2.5 K, compared with experiment at 293 K [31] and DFT calculation at 0 K [32] (V_0 is zero-pressure volume)

The simulation was subjected to the three-dimensional periodic boundary conditions and a constant time step of 1 fs. After randomly generating the positions and velocities of 16000 atoms in a cubic box, the equilibrium liquid was firstly obtained by relaxing the system for 2×10^6 time steps (2 ns) at 6000 K (well above the melting point of this potential, $T_m = (4100 \pm 50)$ K [30]). The system was then quenched to 300 K at a cooling rate of 0.1 K/ps. The quenching simulation was performed at the pressures of 40, 60 and 100 GPa with NPT ensemble [33]. The Nose–Hoover

thermostat method [34,35] for controlling temperature and the Parrinello–Rahman algorithm [36] for pressure were adopted in the simulation. The atom velocity, position and other necessary information were recorded every Kelvin for further analysis.

2.2 Structural analysis methods

For MD simulation, characterization methods are necessary to identify local structures in ordered or disordered systems. In the past, many methods have been proposed to quantify local structures, most of which require a pre-set cut-off distance (r_c) to determine neighbourhood between atoms, such as the Honeycutt–Andersen pair (HA-pair), the common neighbours analysis (CNA) [37], the bond orientation order (BOO) [38], the Voronoi tessellation [39], the atomic cluster alignment [40], the core-shell geometric analysis [41,42] and the SPRPG (a topological technique combining the Shortest-Path ring and planar graph) [43,44]. However, in a heterogeneous system r_c depends on individual environments; and then a certain r_c cannot accurately identify all local structures, especially during phase transitions [45,46] where various structures coexist and change remarkably.

The difficulties caused by a fixed r_c have been recently overcome in the largest standard cluster analysis (LSCA) by introducing a topological criterion [24–26]. In LSCA, a pair of atoms are bonded if their distance is less than r_c , and the local structure is composed of a central atom and all neighbours are called a cluster. An example is shown in Fig. 2(a), where the atom 9800 is the centre and other 14 atoms are neighbours. A part of such cluster is called a common neighbour sub-cluster (CNS) that comprises of a reference pair (RP, composed of the centre and one neighbour) and their common near neighbours (CNNs). In Figs. 2(b) and (c), the RPs are respectively the atom pair 9800–8914 and 9800–2788; and the atoms in Figs. 2(d) and (e) are the corresponding CNNs. The topology of a CNS can be systematically described by a CNS-index S_{ijk} , where “S” is just a prefix (the first letter of “sub-cluster”), i is the number of CNNs, j is the number of all bonds between CNNs, and k is the number of bonds in the longest CNN string formed by part or all of the j bonds.

Therefore, the CNS in Fig. 2(b) is indexed as S444 and that in Fig. 2(c) is S666. In the cluster

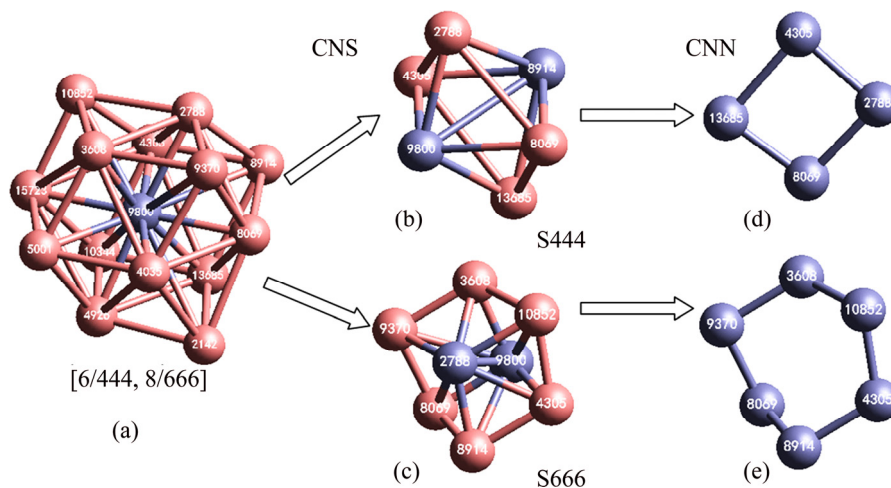


Fig. 2 Topology of BCC LSC [6/444, 8/666] centered at atom 9800 (a) and its two CNSs of S666 (b) and S444 (c), as well as their topologies (d) and (e), respectively

shown in Fig. 2(a) there are six S444 and eight S666, so the cluster is denoted as [6/444, 8/666]. The cluster shown in Fig. 2(a) is a standard cluster (SC), because the topology of each CNS in this cluster can be uniquely characterized by a CNS-index. With the increase of r_c , the number of neighbours around a certain atom increases and the bond between neighbours becomes complex rapidly; when r_c exceeds a certain critical value, there will be too many bonds between neighbours, resulting in the failure of the topological uniqueness denoted by the CNS-index (such as S566).

In practice, a pre-set initial r_s is large enough to invalidate at least one CNS-index in a cluster. In this case, the longest bond in the cluster will be removed and the previously bonded atom will be removed from the cluster. Then r_s decreases also. If all CNS-indexes in a cluster are valid, the critical r_s (assigned as r_c) is obtained and the resulting cluster is the largest standard cluster (LSC) [24]; otherwise, the longest bond in the remaining cluster will be removed again to check the validity of all CNS-indexes, till the r_c is obtained. Obviously, r_c varies and is determined by the individual local environment of atoms. But for each atom, the validity of CNS-indexes in the LSC around it can be guaranteed. Therefore, all atoms in a system can be classified according to LSC type based on a closed set of CNS-indexes. For example, the atom 9800 shown in Fig. 2(a) is identified as a [6/444, 8/666] atom, while on the other hand it can also be linked to BCC as such a cluster is the building block of the BCC crystal [24].

In supercooled metallic liquids, the primary CNSs are usually S421, S422, S433, S444, S544, S555 and S666 [18,25,26], among which S433 and S544 can be considered as the deformed S444, S555 and S666. S555 has good rotational symmetry, which is one of the densest 3D structural units [47] and the building block of icosahedron (ICO [12/555]) and other polyhedrons. S421, S422, S444 and S666 all have both transitional and rotational symmetries, therefore they can form a variety of crystal structures, such as HCP [6/421, 6/422], FCC [12/421] and BCC [6/444, 8/666] LSCs. Composed of ten S421 and two S555, the truncated decahedron (tDH), identified as [10/421, 2/555], usually acts as the five-fold twinned crystalline boundary [48,49].

Together with other Frank–Kasper clusters [49], ICO structures can form complex topologically close-packed (TCP) crystals, such as β -Ta [45] and A15 Zr [48,50]. Recently, we proposed the TCP LSC (or cluster) that consists of S444 ($\times n_4$), S555 ($\times n_5$) and S666 ($\times n_6$), where $n_5 \geq 1$ [45]. Based on the Euler theorem ($V+F-E=2$, where V , F and E are respectively the number of vertexes, faces and edges of a polyhedron.), it is easy to prove that a TCP LSC satisfies the equation of $2n_4+n_5=12$, and n_6 is free, just confined by the total coordination number (CN) of the centre atom. Thus, we have $n_4 \leq 5$ (due to $n_5 \geq 1$). Therefore, each TCP LSC can be simply, clearly and uniquely denoted by a TCP-index that is composed of a letter followed by an integer, standing as “ L_n ”, where the letter “ L ” is Z if $n_4=0$, or A–E if $n_4=1–5$, respectively, and the integer n is the CN of the central atom. For example,

the TCP LSC of $[1/444, 10/555, 2/666]$ is labelled as A13, because there is only one S444 ($n_4=1$), and there are 13 neighbours in total.

All TCP LSCs are close-packed, because they only include tetrahedral interstitials. The ICO and Frank–Kasper clusters are TCP LSCs, while $[6/444, 8/666]$ are not. Our study revealed that the TCP LSCs are ubiquitous in metal melts and metallic glasses [45,48], and the evolution of TCP cluster is crucial for phase transition: during liquid–solid transition if the number of TCP clusters rapidly changes, the resulting solid will be crystals, otherwise glasses.

3 Results and discussion

Figure 3 shows the average potential energy dependence of temperature (E – T curve) at the three pressures (40, 60 and 100 GPa) examined here. First, consistent with basic thermodynamics theory, the higher the pressure is, the higher the system energy is. Second, before the temperature decreases to 4000 K, the liquid–solid phase transition occurs in all three cooling processes. They are typical first-order phase transitions and may contain intermediate states. Third, the onset temperatures of the liquid–solid transition (T_s) under 40, 60, and 100 GPa are 4418, 5245 and 5018 K, respectively. Therefore, the pressure has a nonlinear relationship with T_s , which is consistent with the fact that the nucleation is a statistic process, and the transition temperature varies significantly in different runs of such brute-force MD simulations. The melting point under pressure should be higher than T_s because in MD simulation nucleation can only occur in the supercooled regime. All these T_s are higher than 4100 K, the melting point of this potential under ambient conditions; thus, pressure increases the melting point of metal W. In addition, the end temperatures (T_e) of the liquid–solid transition under 40, 60 and 100 GPa are 4410, 5090 and 4815 K, respectively. Fourth, at $T < T_e$, the slope of the E – T curve is constant over a rather wide temperature range, and the accelerated decrease in potential energy in the low-temperature section should indicate another phase transition.

The most interesting observation is the shape of the E – T curves at the low-temperature end, where the system potential energy accelerates down as the temperature decreases. What happened

during this stage? To answer this question, the rest of this work will focus on the structural evolution during rapid cooling under 100 GPa, because it includes a distinct intermediate state that may provide more information about phase transition. In fact, our analysis revealed that as shown by the E – T curves, structural evolution is similar at the low-temperature end under different pressures.

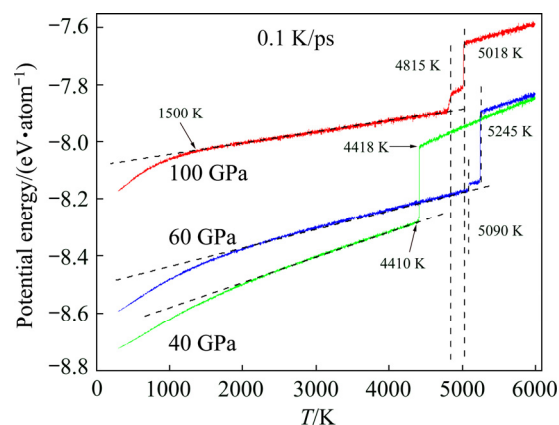


Fig. 3 Evolution of average potential energy per atom during cooling process of liquid W at 0.1 K/s under 40, 60 and 100 GPa

3.1 Liquid–solid phase transition

As shown in Fig. 3, the slope of E – T curve under 100 GPa has two drop-offs at 5018 and 4816 K respectively and a smooth change at $T < 1500$ K. Therefore, there may be at least two first-order phase transitions and one continuous phase transition. The pair distribution function (PDF or $g(r)$) for the sample at 5012 K (see Fig. 4) is very similar to that at 5019 K for the supercooled liquid, indicating the order degree of the system at 5012 K is rather low even if crystallization has started. The typical characteristics of the crystal

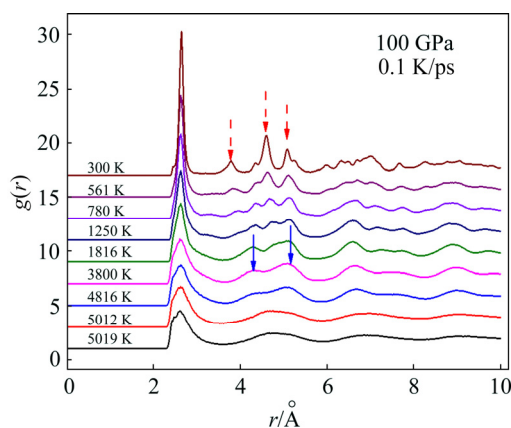


Fig. 4 $g(r)$ curves at several temperatures during cooling process of liquid W

become distinct at 3800 K, where in addition to the primary peak there are many small peaks.

With the further decrease of temperature, the peaks become sharper and narrower; thus, the degree of order is increasing. However, both the shape and the position of the peaks of the $g(r)$ curve at 300 K are much different from those at 3800 K (highlighted by arrows in Fig. 4(b)), thus the W crystal at 300 K is different from that at 3800 K.

In order to quantify the key structural characteristics of the system in the vicinity of the first phase transition, we studied the 8 LSCs that have the highest number in each sample of the system. From 1501 samples (one every degree from 5500 to 4000 K), there were 27 LSCs which consisted of only 7 CNSs, as listed in Table 1. As shown in the compact denotation in the rightmost

column of Table 1, there are 3 crystal LSCs and 9 TCP LSCs, and the others are slightly deformed TCP LSCs. Therefore, the topological close-packed structure is the essential characteristic of metals whether in liquids and supercooled liquids. For more details about this denotation, please refer to the text and supplementary of Refs. [45,48].

According to the evolution pattern of the number of LSCs, the 27 LSCs are divided into 4 groups: 7 FCC-, 5 BCC-, 3 HCP-, and 12 TCP-types (see Table 1), and their amount as a function of temperature is plotted in Fig. 5. One can find that from 5400 to 4000 K there are two critical temperatures (5018 and 4815 K) and four evolution patterns.

(1) The number of FCC-type LSC increased rapidly at about 5018 K, then kept unchanged for

Table 1 Structural details of 27 LSCs

No.	CN	S421	S422	S433	S444	S544	S555	S666	Label
1	12	12							FCC
2	12	8		2		2			1-FCC
3	13				5		2	6	E13
4	13			1	3	3	3	3	1-D13
4	13	3		2	2	4		2	BCC HCP
6	14				4		4	6	D14
7	14			1	3	3	3	4	1-D14
8	13				5	4		4	F14-V4
9	13			2	3	6		2	1-BCC-V4
10	13	1		2	3	4		3	1+(BCC HCP)
11	14				6			8	BCC
12	14			2	4	2		6	1-F14
13	12	6	6						HCP
14	12	4	4	2		2			1+FCC
15	15				5		2	8	E15
16	12			2		2	8		1-Z12
17	13				1		10	2	A13
18	13				3		6	4	C13
19	13			2	1	2	6	2	1-C13
20	13			2	2	2	4	3	1-C13
21	13			1	1	3	7	1	1-A13
22	14				2		8	4	B14
23	14				1		10	3	A14
24	14				3		6	5	C14
25	14			1	1	3	7	2	1-B14
26	14			1	2	3	5	3	1-C14
27	15				2		8	5	B15

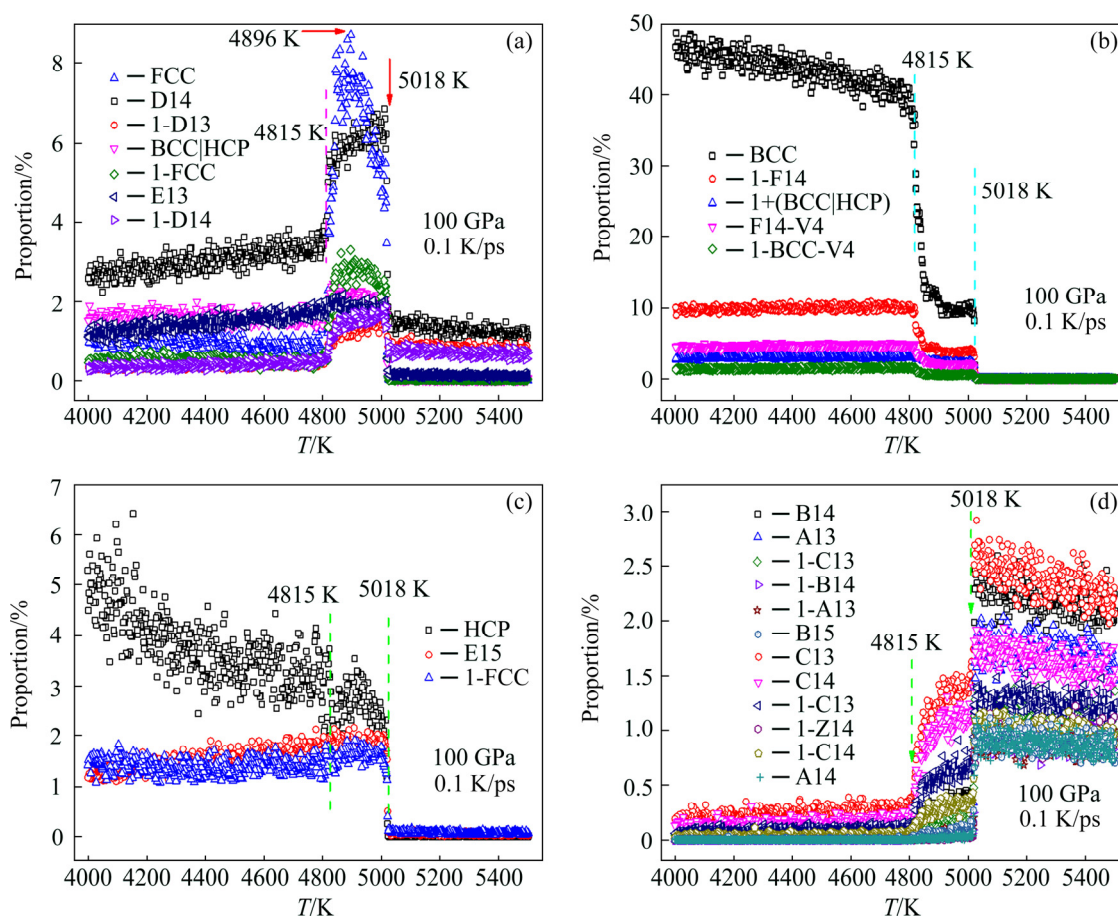


Fig. 5 Temperature dependence of number percentage of 27 LSCs in vicinity of liquid–solid transition: (a) FCC-type; (b) BCC-type; (c) HCP-type; (d) TCP-type

about 200 K (5018 to 4815 K), and finally decreased to a rather low level (Fig. 5(a)). The number of FCC atoms increased linearly from 5108 to 4896 K, accounting for about 8% of all the atoms in the system, and then decreased remarkably to about 4% at 4815 K.

(2) The number of BCC-type LSC increased rapidly at two critical points and then increased linearly (see Fig. 5(b)). As a stable structure under ambient conditions, BCC atoms only increased to about 10% from 5018 to 4815 K and then levelled off for about 200 K. By 4815 K the percentage of BCC atoms burst up to about 40%.

(3) At 5018 K the HCP LSC rapidly increased to about 3%, then slowly increased; while other two HCP-type LSCs increased to about 2%, then slowly decreased (Fig. 5(c)).

(4) The TCP-type LSC experienced two sudden drops at 5018 and 4815 K respectively. It decreased to almost zero at 4815 K, and then slowly decreased (Fig. 5(d)).

In brief, in the range of 4815–5018 K, the

number of FCC-type atoms reached the maximum and then decreased; the HCP-type atoms continued to grow slowly; the evolution of the number of BCC-type atoms was opposite to that of TCP-type ones: the BCC-type atoms experienced two jump-ups, while the TCP-type atoms had two drop-offs. At $4000\text{ K} < T < 4815\text{ K}$, BCC atoms dominated the system, and this liquid–solid phase transition can be called BCC-crystallization.

Phase transition is a dynamic process under certain thermodynamic conditions, such as temperature, pressure and energy. Generally, thermodynamic conditions determine whether liquid–solid crystallization occurs, and dynamic factors determine the location, time and manner of nucleation. The classical nucleation theory argues that the formation of crystal nucleus must overcome a certain energy barrier that is jointly affected by the volume-free energy and interface-free energy. In rapid cooling the system could be non-equilibrium, and the local environments of different atoms could be rather different, so various crystallizations with

similar energy barriers may occur simultaneously. Crystal nuclei may disintegrate under thermodynamic fluctuations. In general, unless the nucleation rates of various crystals are very different, with lower potential energy, there will be more nuclei and the nuclei will also be more stable.

In the present simulation, under 100 GPa when temperature decreases to 5018 K, BCC, FCC and HCP nuclei appear in the system almost at the same time, which is consistent with the fact that they have almost equal potential energy (less than that of the system, see Fig. 6(a)). When the temperature is between 4850 and 5018 K, the potential of FCC and BCC atoms is basically equal, but the percentage of BCC atoms is 10% which is a bit higher than that of FCC (8%), as shown in Figs. 5(a) and (b). This may be linked with the potential fluctuation: the smaller the potential fluctuation, the more stable the structure. With the maximal potential fluctuation, the number of HCP nuclei is the smallest (~3%, see Fig. 5(c)). When the temperature decreases further, another smaller energy decrease of the system occurs between 4850 and 4815 K. Around 4815 K the potential energy of FCC atoms is sometimes more than the system, and correspondingly the number of FCC atoms decreases (Fig. 5(a)); while the BCC atoms increase rapidly (Fig. 5(b)), due to the fact that the potential energy of BCC atoms is distinct less than the system, and fluctuates slightly.

The position and distribution of the nucleus are usually determined by dynamic factors, such as the fluctuation in structure and energy, the atomic velocity and distribution. Visualization is the most direct and effective way to present such effects with a series of snapshots. As shown in Fig. 7, at the

initial stage of BCC crystallization at 5012 K, BCC, FCC and HCP atoms were evenly distributed in the system, and many small crystal regions with rough edges were formed (see Figs. 7(a)–(c)). Between 5012 and 4896 K, there was almost no change in the number and distribution of HCP and BCC atoms (Fig. 7(b) vs Fig. 7(e) and Fig. 7(c) vs Fig. 7(f)); while between 4896 and 4700 K, the amount of BCC atoms increased rapidly. The number of FCC atoms reached the maximum at 4896 K (see Figs. 7(a), (d) and (g)). Figures 7(g)–(i) show that at 4700 K BCC atoms dominated the system, and the nuclei composed of HCP atoms were heterogeneous (Fig. 7(h)).

3.2 Solid–solid phase transition

As shown in Fig. 8(a), at $2100\text{ K} < T < 4815\text{ K}$ the number of BCC, FCC and HCP atoms increased monotonically, where the number of BCC atoms was much higher than those of the other two kinds of atoms. At 2100 K the amount of BCC atoms reaches a maximum of 60%, and those of HCP and FCC atoms are 3% and 10%, respectively. Obviously from 4815 to 2100 K BCC atoms dominated, and the system should be basically a BCC crystal. When $T < 2100\text{ K}$ the evolution of the number of FCC, HCP and BCC atoms changed remarkably. BCC atoms decreased rapidly; oppositely HCP and FCC atoms increased exponentially. Finally, at 300 K, the percentages of HCP, FCC and BCC atoms are respectively about 60%, 12% and 12%. Therefore, the final solid should be mainly an HCP crystal. In fact, under 40 and 60 GPa, the evolution of the numbers of HCP, BCC and FCC atoms is similar. As the

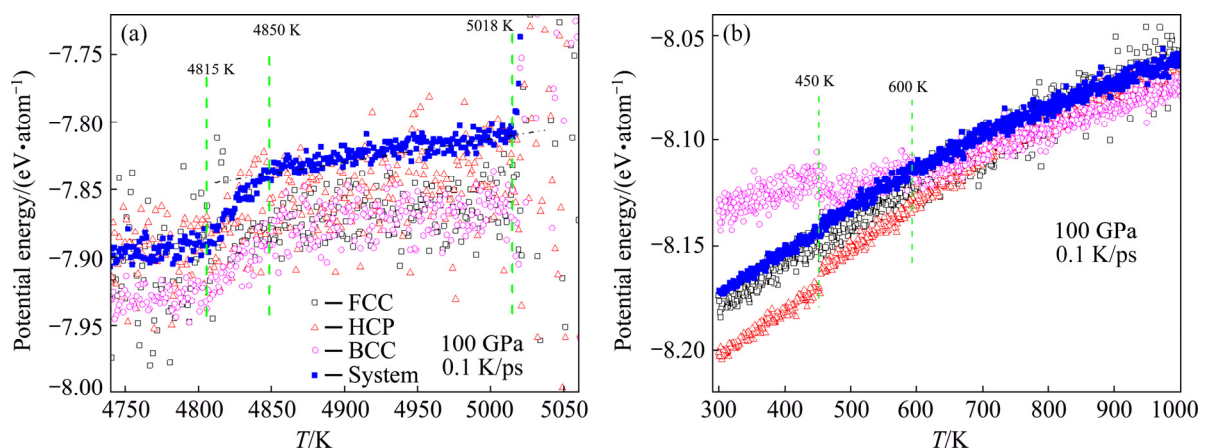


Fig. 6 Energy evolution of FCC, HCP and BCC atoms, compared with system energy from 5050 to 4750 K (a) and from 1000 to 300 K (b)

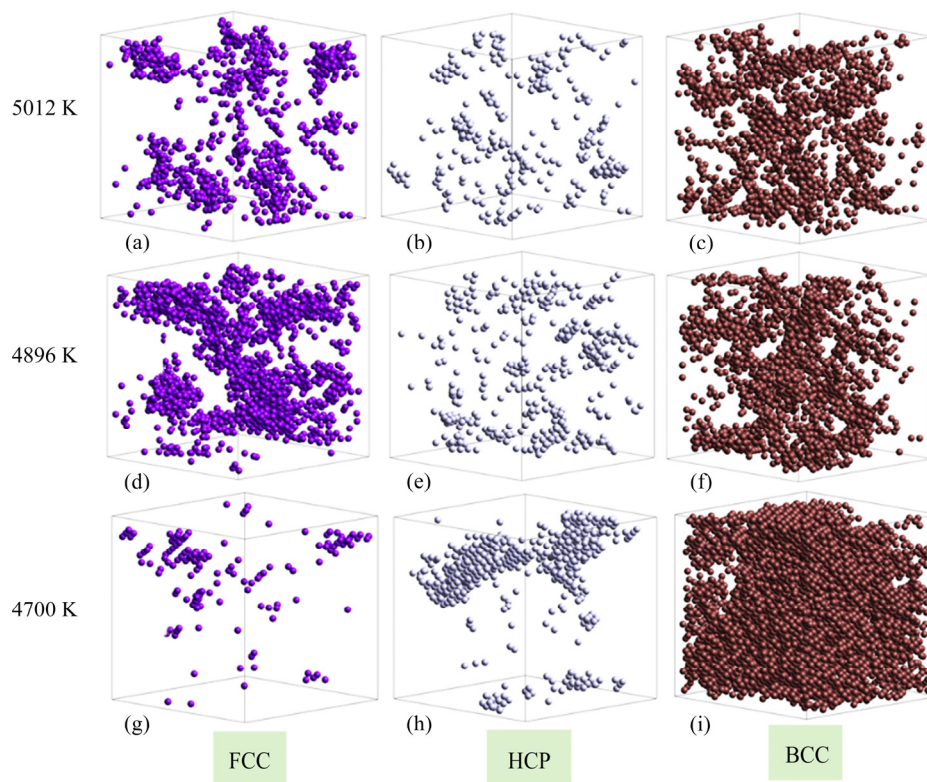


Fig. 7 Distribution of FCC, HCP and BCC atoms at the first stage of BCC-crystallization at 5012 K (a–c), 4896 K (d–f) and 4700 K (g–i)

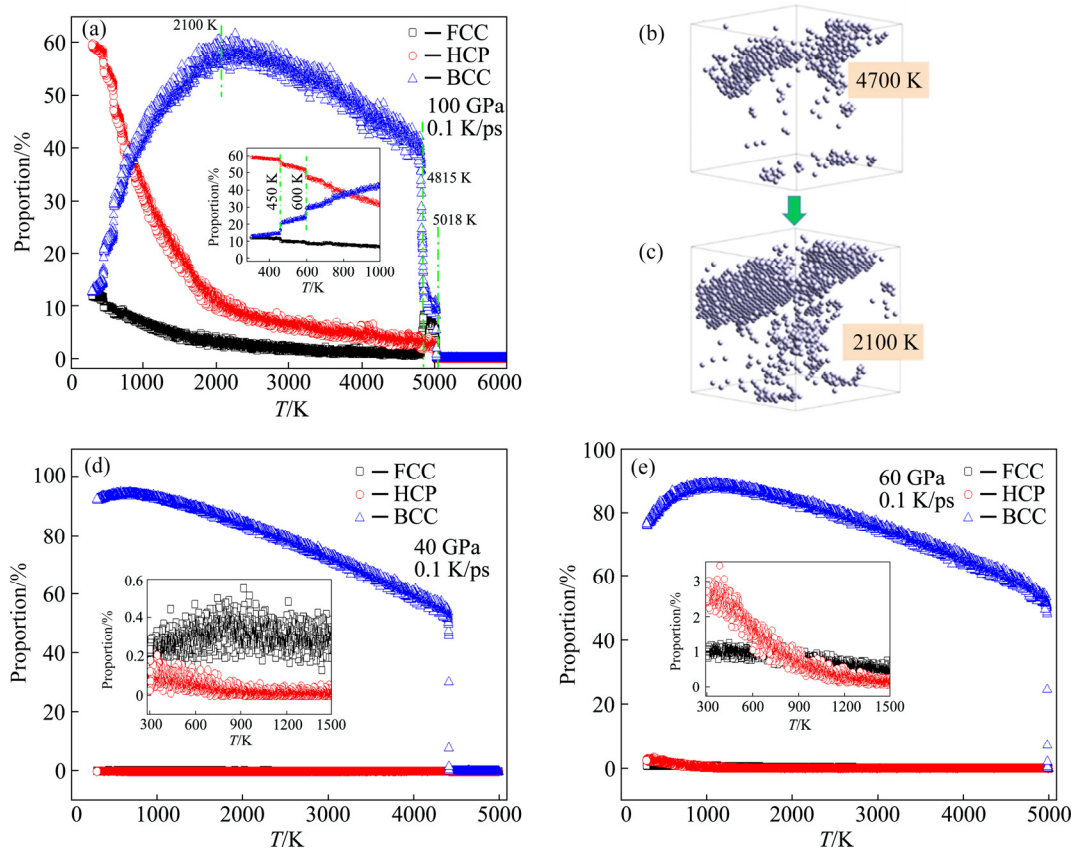


Fig. 8 Evolution of number percentage of BCC, FCC and HCP atoms during rapid cooling of liquid W under 100 GPa (a), 40 GPa (d) and 60 GPa (e) at cooling rate of 0.1 K/ps, and spacious distribution of HCP atoms at 4700 K (b) and 2100 K (c)

temperature decreased, the number of BCC atoms decreased, and that of HCP atoms increased. The higher the pressure, the more the HCP and FCC atoms (see Figs. 8(d) and (e)).

Under ambient conditions, the stable phase of W is a BCC crystal when $T < 3695$ K. In our present simulation the amount of BCC atoms reached up to 60% at 2100 K. But is it stable under high pressure? For simple metals that have two stable phases at high and low temperatures respectively, our previous work revealed that the stable phase at high temperature is very difficult to capture to room temperature [6]. For example, pure α -Zr will transform to β -Zr (the stable phase at low temperature) rapidly when the temperature is less than $T_\beta \sim 1136$ K, even if the cooling rate is as high as 10^{14} K/s that can vitrify almost all pure metals.

In order to quantify the stability of the BCC phase at high temperature, the sample was relaxed for 2000 ps at 3000 K (HCP and FCC atoms are about 7.4% and 2.0%, respectively), and the evolution of the number of three crystal atoms over time is shown in Fig. 9. One can find that at the beginning of this isothermal relaxation, the number of BCC atoms increased instantly, while that of FCC and HCP atoms decreased. Then their amount becomes very stable: BCC atoms are about 60%, and FCC and HCP atoms are less than 0.1% (see the inset of Fig. 9).

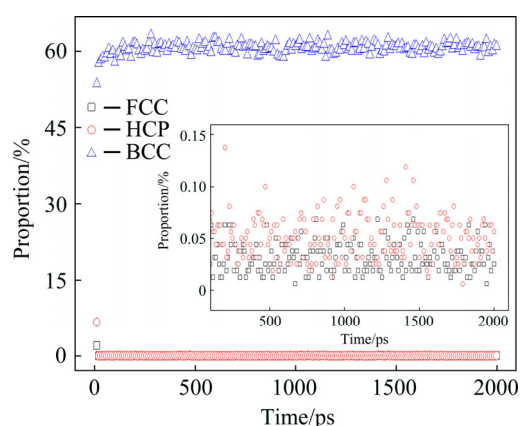


Fig. 9 Number percentage of FCC, HCP and BCC atoms as function of time in system during 2000 ps isothermal relaxation at 3000 K

Therefore, this BCC state of W should be a stable phase around 3000 K under 100 GPa, and the equilibrium transforming temperature from BCC to HCP phase should be higher than 2100 K that is the

onset temperature of such transition under rapid cooling. Therefore, BCC crystal is the stable phase of W at high temperature under 100 GPa, and there exists a $\text{BCC} \rightarrow \text{HCP}$ solid–solid transition beginning at around 2100 K at a cooling rate of 0.1 K/ps. Previous work has discussed the link between the distribution of new phase and the transition pathway upon a solid–solid phase transition under high pressures [18], and pointed out that near the end of the parent solid phase, if the new-phase atoms are randomly distributed, or the boundaries of the new-phase clusters are irregular, a single-intermediate-state crystallization (SisC) will happen; otherwise, it will be a multiple-intermediate-state crystallization (MisC). In the present work, the new phase was HCP crystal. HCP atoms aggregated together to form two crystal regions at 4700 K (see Fig. 7(h) and Fig. 8(b)). They gradually grew up and became more regular as shown in Fig. 8(c). Therefore, this BCC–HCP transition should be a MisC that undergoes a series of first-order phase transitions, which is shown in the inset of Fig. 8(a). Such a process includes a series of indistinguishable intermediate states, making it appear to be continuous (see Fig. 8(a)).

Certainly, a significant change in potential energy is accompanied by a remarkable change in the number of primary crystalline atoms. Figure 6(b) shows that at 600 K the average potential energy of BCC atoms becomes higher than that of the system, and another increase occurs at 540 K. Oppositely, the average potential energy of HCP atoms had a distinct decrease at 540 K. Therefore, the number of BCC atoms dropped off at 600 and 540 K, and correspondingly that of HCP atoms jumped up at the two temperatures (see Fig. 8(a) and the inset). These two discontinuous changes in the number of crystal atoms unveil that the BCC–HCP solid–solid transition is still a first-order phase transition.

What role does the FCC atom play in this solid–solid phase transition? It is found that the number of FCC atoms increased slowly (Fig. 8(a)), and most of them lay on several planes, as can be found in Figs. 10(b), (f) and (j)). These FCC planes are the boundaries of HCP grains (Figs. 10(a), (e) and (i)). They are criss-cross in space. Therefore, it is difficult for these FCC atoms to be converted into HCP atoms by layer slip, because layers perpendicular to each other will hinder layer slip.

3.3 TCP structure and cut-off distance

It is believed that amorphous metals are frozen liquids, so the primary structural characteristics of supercooled metal liquids should be closely related to metallic glass. Recently, we proposed that the TCP structure is the essential structural characteristic of metallic glass. After the liquid–solid transition begins, if the number of TCP structures decreases rapidly, the liquid will solidify into a simple crystal; otherwise a complex TCP crystal or amorphous solid will be obtained. Does this mechanism still apply under high pressure?

Figure 11 shows the evolution of the number percentage of TCP atoms in the simulated system during rapid cooling. The number of TCP atoms

gained the maximum percentage of 19% at 5075 K, which is 57 K higher than T_s of the liquid–solid transition. Thus, there is a strong competition between the vitrification and crystallization from 5075 to 5018 K. At 5018 K when the number of TCP atoms begins to avalanche, BCC crystallization begins.

The TCP atoms are usually located at the boundaries of crystal grains, and a remarkable structural change during crystallization will cause a distinct change in the type and amount of TCP structures. Therefore, as shown in Fig. 11(a) and the insets, at the critical points of 4815, 2100, 600 and 450 K, the decreasing rate of TCP atoms changed distinctly. Therefore, the evolution of the amount of

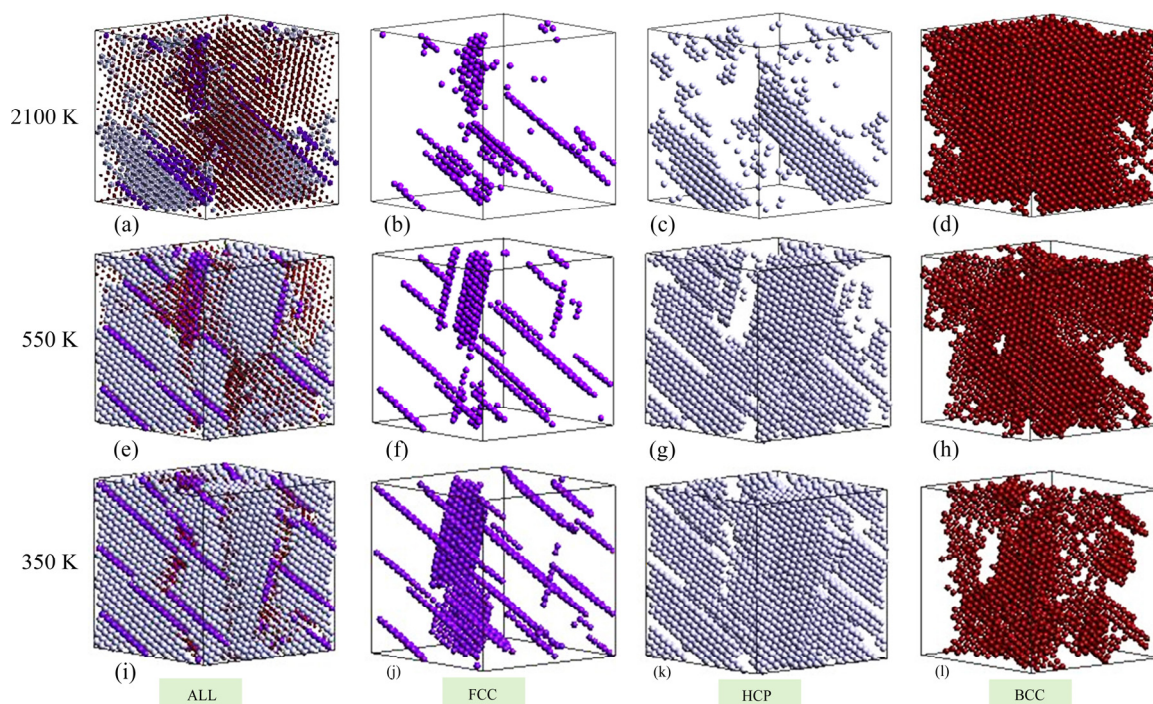


Fig. 10 Distribution of FCC, HCP and BCC atoms at three temperatures during solid–solid phase transition

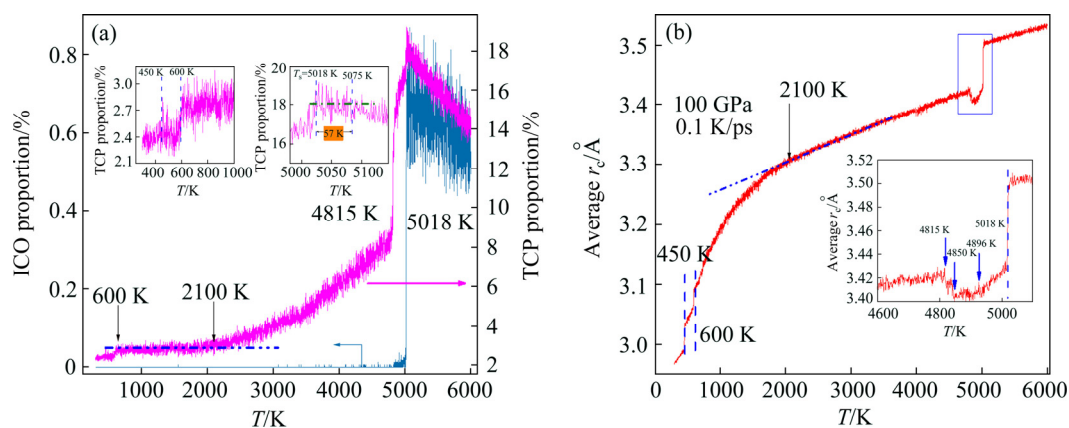


Fig. 11 Evolution of number percentage of ICO and TCP atoms (a) and average cut-off distance r_c (b) as function of temperature during rapid cooling

TCP atoms can not only reflect the competition between disordered and ordered structures at the beginning of crystallization, but also show more details during the crystallization process. In a word, TCP atoms are a good indicator of phase transition. On the contrary, ICO atoms cannot play this role. As shown in Fig. 11(a) the number of ICO atoms also reached the maximum at 5028 K, but it was less than 1% of all atoms in the system, and even dropped to zero immediately after crystallization began. Therefore, the structural evolutions at $T < 5018$ K cannot be detected from the perspective of ICO atoms.

One of the advantages of LSCA is that the local structure around atoms can be determined without setting the cut-off distance r_c in advance. In addition, LSCA can provide a statistical parameter (the average of r_c) over all atoms. Figure 11(b) shows that the average r_c changed remarkably at all critical temperatures (including 5018, 4815, 2100, 600 and 450 K) during rapid cooling. It is worth pointing out that more details about phase transition can be detected by the average r_c . For example, as shown in the inset of Fig. 11(b) when the FCC atoms reached the maximum number at 4896 K (see Fig. 5(a)), the average r_c decreased to the minimum; at 4850 K, when the system potential energy decreased faster (see Fig. 7(a)), the average r_c increased again; and at 4815 K, when the system potential energy slowly decreased again, the evolution of average r_c also reversed.

At around 5018 K, the average r_c suddenly decreased because the average distance between neighbouring atoms decreased remarkably when the crystal structure was rapidly formed in the liquid. However, why is there a deep valley between 4815 and 5018 K? If the atom is regarded as hard spheres, the FCC and HCP structures will occupy the smallest volume, followed by BCC and amorphous ones. Therefore, when the FCC/HCP atom number reaches the maximum, the average r_c reaches the minimum. When some FCC/HCP atoms are converted to BCC atoms, the average r_c increases accordingly [23]. Therefore, the average r_c is also a good indicator to quantify the local structure evolution during vitrification and crystallization.

4 Conclusions

(1) Several solidifications of pure W liquid

metal at 40–100 GPa and a rapid cooling rate of 0.1 K/ps have been simulated with LAMMPS. The analysis of local structures reveals that it is a crystallization with the pathway of the super-cooled liquid (SCL) through the BCC phase to the HCP crystal.

(2) The BCC phase, which is stable under ambient conditions, becomes a high-temperature metastable phase under high pressure, and finally transforms into an HCP crystal. Due to the dynamic factor, the SCL $\rightarrow$ BCC transition may include intermediate stages, and the first-order BCC $\rightarrow$ HCP transition includes many intermediate stages.

(3) The evolution of the number of TCP structures and the average r_c exported by LSCA can provide more details about phase transitions, such as the competition between crystalline and amorphous structures before the start of crystallization, the abrupt change of the distance between the neighbouring atoms during the phase transition.

(4) These findings provide a clear physical picture at the atomic level of the crystallization pathway of W under rapid cooling and high pressures. It can improve the fundamental understanding of phase transition of pure W as well as other related metals and alloys, especially for those having different stable phases at high temperature and low temperature, respectively.

Acknowledgments

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高压下金属钨固-固相变的分子动力学模拟

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摘要: 采用分子动力学模拟研究高压下金属钨快速凝固过程中的相变, 并用双体分布函数和最大标准团簇分析法(LSCA)对其结构进行分析。在冷却速率为 0.1 K/ps、压强 40~100 GPa 下纯钨熔体首先结晶成体心立方(BCC)晶体, 然后经过一系列 BCC-HCP 共存的中间态, 转变成六方密排(HCP)晶体。动力学因素可能导致液-固相变过程包含中间态; 而在 BCC 向 HCP 转化的过程中, 纵横交错的晶界导致很多难以区分的中间相, 从而使本为一级相变的固-固转变看起来像是连续相变。作为一种与参数无关的结构分析方法, LSCA 能识别拓扑密堆结构和计算其平均截止距离等参数来探测无序体系中的关键结构演变。

关键词: 分子动力学模拟; 快速凝固; 固-固相变; 最大标准团簇分析法; 拓扑密堆团簇

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