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Simulation study on transition mechanisms of microstructures during forming processes of amorphous metals①

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[Abstract] For the first time, a molecular dynamics simulation study of 50000 atoms has been performed for the transition mechanisms of the microstructure configurations of liquid metal Al during forming processes of amorphous state by rapid cooling. Not only have various bond-types been researched, but also icosahedra, defective icosahedra and Frank-Kasper polyhedra cluster structures were discussed. A very clear picture of how the metal atoms gather to form clusters and how the clusters evolve further has been obtained. Some discussion corresponding to the microscopic mechanisms of the simulation results was also given. These will give an important enlightenment to understand the forming mechanisms and their microscopic processes of amorphous structures.

[Key words] amorphous metals; microstructures; transition mechanism; computer simulation
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1 INTRODUCTION

It is well known that amorphous metals and alloys prepared by melt quenching possess various excellent properties, which are mainly determined by their special microstructures. For understanding the relationship between the structures and properties, it is very important both in theory and practice to find out the transition feature of the microstructural configurations by tracking the forming process of amorphous metals. However, under the present experimental conditions, it is very difficult to perform such a tracking research. With the rapid development of computer technique, it is possible to make such a simulation study. We have used the molecular dynamics method to study the instantaneous processes of microstructural configurations of a small liquid metal system consisting of 500 Al atoms, and obtained a very clear physical picture of these processes and some important results[1~7]. However, owing to the application of periodic boundary conditions in simulation studies, for the small system consisting of 500 Al atoms, some serious influences of the boundary conditions will happen during researching the constructions of clusters possessing various bond-types and plural shells. For this reason, on the basis of the author's work[1~7], this paper is devoted to performing a tracking research for a larger liquid metal system consisting of 50 000 Al atoms during rapid cooling processes by using molecular dynamics and parallel algorithm. From the above research, we have got a series of new results.

2 SIMULATING CONDITIONS AND METHODS

Based on the author's work, the supercomputer YH—III in a national key laboratory was utilized to perform a simulation study on the microstructural transitions in a larger liquid metal system consisting of 50 000 Al atoms during rapid cooling process by using molecular dynamics and parallel algorithm. The conditions for simulating calculation were as follows: 50 000 Al atoms were placed in a cubic box and the system run under periodic boundary conditions. The interacting interatomic potential adopted here was the effective pair potential function of the generalized energy independent nonlocal model—pseudopotential theory developed by WANG et al[8,9], and the function is

$$V(r) = (Z_{\mathrm{eff}}^2/r)\cdot \left[1-\left(\frac{2}{\pi}\right)\int_0^{\infty}\mathrm{d}qF(q)\sin(rq)/q\right] \quad (1)$$

where Z_{eff} and $F(q)$ are, respectively, the effective ionic valence and the normalized energy wave number characteristic, which were defined in detail in references[8, 9]. This pair potential was cut off at 20.0 au (atomic unit). The time step of these runs was chosen at 10^{-15} s. The cooling rate was 3.4×10^{13} K/s. The simulating calculation started at 943 K (the melting point of Al is 933 K). The system run first for 750 steps at the same temperature to reach an

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equilibrium state. (We judge whether the system is in an equilibrium state by the changing degree of energy in the system during the running, in this case, the system has been actually in an equilibrium state after 100 steps). Secondly, the system temperature decreased at a cooling rate of 3.4×10^{13} K/s to some given temperatures: 883, 833, 780, 730, 675, 625, 550, 500, 400 and 300 K. Then let the system run 10 time steps at each given temperature to keep it in a quasi-equilibrium state. The structural configurations of this system, i.e. the space coordinates of each atom were recorded. Finally, the bond-types and their indexes between related atoms were detected by means of the index method of Honeycutt-Andersen (HA)[10]. By analyzing and comparing these results, the transforming rules of microstructures in the system during rapid cooling processes from liquid to amorphous states are discussed in detail.

3 DESCRIPTION OF SIMULATING CALCULATION RESULTS

At first, we inspect the pair distribution function $g(r)$ of the system obtained from the above simulation, and find it consistent very well with the experimental results given by Waseda[11], as shown in Fig. 1. On the other hand, the second-peak of $g(r)$ is gradually split with decreasing temperature, as shown in Fig. 2. It is well known that the splitting second peak is one of the important characters for forming amorphous structures. From these, it can be clearly seen that the effective pair potential function adopted here is very successful reflecting on the objective physical nature of this system in the microstructural formation of amorphous metals.

From the bond-type indexes expressed in Table 1, the followings can be clearly seen.

1) The relative numbers of 1551 and 1541 bond-types related to the icosahedral configuration occupy 16.95% and 15.89% at 943 K, respectively, and the total number of them amounts to 32.84% of the total number of all bond-types. The relative number of 1551 bond-type increases remarkably with decreasing temperature, finally, the increment amounts to 75%. On the contrary, the relative number of 1541 bond-type alone has less increment, being about 5.4%. While the temperature decreases to 300 K, the relative numbers of 1551 and 1541 bond-types have amounted to 46.35% of the total number of bond-types. From these results, we can consider that the 1551 bond-type plays an important role during the process of forming amorphous structures from liquid metal.

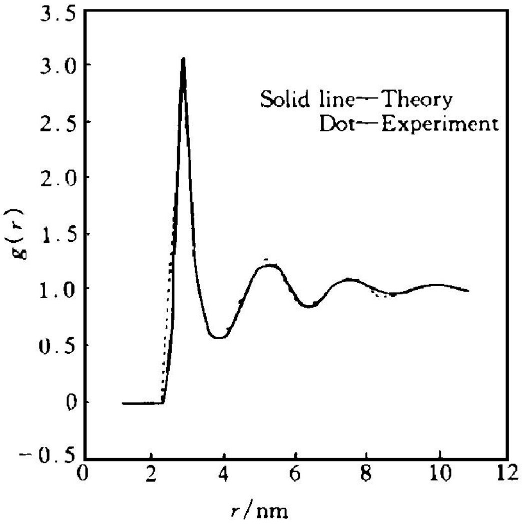

Fig. 1 Pair distribution function $g(r)$ of liquid Al at 943 K

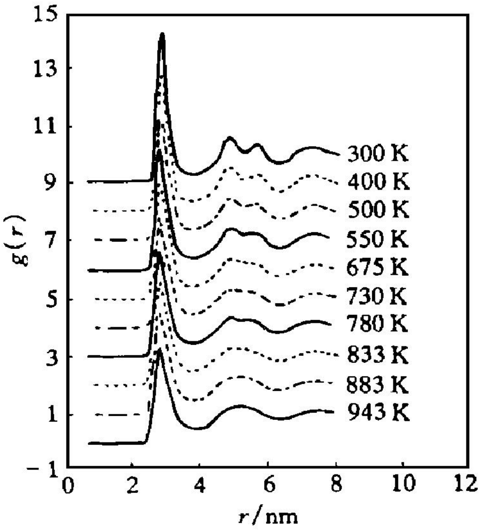

Fig. 2 Pair distribution function $g(r)$ of liquid supercooled and solid state Al

2) The relative numbers of 1441, 1431, 1421 and 1422 bond-types related to the tetrahedral structures occupy, respectively, 4.78%, 21.47%, 3.47% and 6.91%, and the total number of them amounts to 36.63% of the total number of bond-types at 943 K. Although the numbers of the four bond-types are decreased, respectively, very slowly with decreasing temperature, the total number of them still amounts to 31.89% at 300 K. It can be seen that these bond-types have quite a slow change during all cooling process.

3) The relative numbers of both 1321 and 1311 bond-types related to the rhombohedral structures decrease with decreasing temperature, and the total number of them amounts to 13.36% at 943 K, and 9.37% at 300 K, respectively.

4) The relative number of 1661 bond-type related to hexahedral and bcc structures retains about 5% ~ 6%, with few changes at any temperature. It is surprising that there is a little peak (< 1%) at 625~500 K.

5) The relative number of 1201 and 1211 bond-types being almost in free states decrease evidently with decreasing temperature. The total relative num-

ber is not a large one, being 2.5% at 943 K, 1.67% at 300 K, respectively.

6) The total number of all bond-types is about 95% at 943 K, 98% at 300 K, respectively. This result indicates that more than 95% of atoms are still in the structures with different degrees of ordering, and the number of atoms being really in free states is less than 5% at any temperature, no matter whether the system is in liquid, supercooled liquid or solid state.

With regard to the disordered systems of liquid and amorphous states, the specific kinds and numbers of bond-types can form various cluster structures at different levels. In this paper, we adopt a cluster bond-type index method (CBTIM —we give it this name) first introduced by Qi and Wang[12], who had adopted this method to express Frank-Kasper polyhedra, Bernal polyhedra and other defective icosahedra, and used four integers to express a kind of cluster. According to the CBTIM, we get the statistic numbers of various types of clusters related to icosahedra, defective icosahedra and Frank-Kasper polyhedra at given temperatures, as shown in Table 2. From Table 2, it can be clearly seen that: the icosahedra expressed by (12 0 12 0), will play an important role in the microstructure transition during the rapid cooling process, whose structures are shown in Figs. 3(a) and (b). With regard to Fig. 3, it can be obviously seen that the icosahedral structures in melted state

Table 1 Relations of relative numbers of various bond-types with temperature

Temperature / K	Bond-types/ %										
	1201	1211	1311	1321	1421	1422	1431	1441	1541	1551	1661
943	1.32	1.29	6.68	6.68	3.47	6.91	21.47	4.78	15.89	16.95	5.03
883	1.25	1.17	6.44	6.43	3.17	6.64	21.47	4.81	16.06	18.19	5.20
833	1.14	1.12	6.08	6.26	3.07	6.55	21.30	4.72	16.07	19.11	5.27
780	1.08	1.02	5.66	5.98	2.99	6.26	21.42	4.74	16.37	20.35	5.46
730	0.95	0.94	5.36	5.70	2.90	6.07	21.09	4.79	16.40	21.54	5.66
675	0.83	0.84	4.96	5.46	2.77	5.94	20.97	4.74	16.76	22.65	5.81
625	0.77	0.84	4.71	5.34	2.74	5.75	20.99	4.64	16.77	23.91	5.86
550	0.77	0.81	4.65	5.20	2.63	5.66	21.09	4.48	16.84	25.07	5.86
500	0.75	0.82	4.56	5.15	2.58	5.56	20.99	4.28	16.85	26.04	5.74
400	0.70	0.79	4.33	5.10	2.34	5.35	20.64	3.96	16.76	28.36	5.60
300	0.72	0.95	4.17	5.20	2.19	5.20	20.65	3.85	16.75	29.60	5.54

This Table does not include those bond-types whose data are less than 1%.

Table 2 Relations of numbers of various type clusters with temperature

Types of clusters	Temperature/ K										
	943	883	833	780	730	675	625	550	500	400	300
(12 0 12 0)	186	216	275	337	455	525	621	785	915	1236	1474
(13 1 10 2)	110	140	146	190	229	286	325	348	365	453	499
(12 2 8 2)	60	72	72	71	115	106	105	126	106	117	77
(14 1 10 3)	34	32	42	49	64	71	88	111	119	143	143
(14 0 12 2)	14	8	28	29	26	39	50	58	41	69	64
(13 3 6 4)	66	77	70	62	88	86	104	105	108	112	100
(14 2 8 4)	42	55	61	77	87	115	116	138	127	162	174
(11 2 8 1)	14	15	18	14	10	10	14	5	15	12	1
(13 2 8 3)	31	33	23	46	43	50	48	61	66	46	60
(15 1 10 4)	11	10	14	26	22	37	29	40	55	72	72
(14 3 6 5)	14	26	33	44	36	37	54	47	47	43	44
(15 0 12 3)	2	4	5	10	8	10	14	21	22	24	23
(16 2 8 6)	3	4	4	2	5	6	5	12	6	7	9
Total numbers	648	773	862	1055	1318	1481	1713	1970	2109	2600	2866
Icosahedrons expressed by (12 0 12 0) amounting to percentage of total numbers of all clusters	28.7	27.9	31.9	31.9	34.5	35.4	36.2	39.8	43.4	47.5	51.4

The four integers of cluster bond-type index method used in this Table express in turn as: the first integer represents the number of surrounding atoms which have a central atom to form a cluster. The second, third and fourth integers further represent the numbers of 1441, 1551 and 1661 bond-types, respectively, by which the surrounding atoms are connected with the central atom in the cluster. For example, the (12 0 12 0) expresses an icosahedron that is composed of 13 atoms (one is the central atom) connected with 12 1551 bond-types.

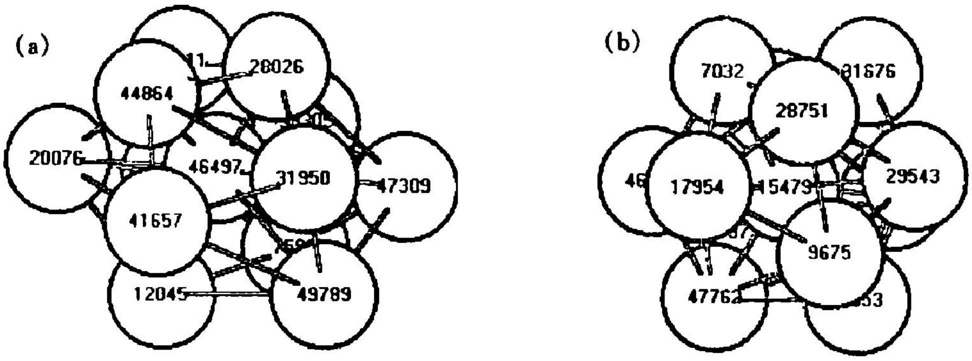

Fig. 3 Structure of icosahedron with atom of 46497 as center at 943 K (a) and structure of icosahedron with atom of 15479 as center at 300 K (b)

(at 943 K) are not standard, but those in solid state (at 300 K) are very standard. The numbers of icosahedron sharply increase from 186 at 943 K to 1474 at 300 K, namely 19162 atoms (amounting to 38.32% of total numbers) are formed in icosahedra by 1551 bond-type. At the same time, a lot of distorted or defective clusters can be formed with different numbers of 1441, 1551 and 1661 bond-types.

Especially in our simulating, the larger and various dimension cluster structures composed of various kinds of clusters are found; moreover, the size and amount of them increase with decreasing temperature. Because the situation is very complex, it will be discussed as a special topic in other papers. The small cluster, as shown in Fig. 4, is composed of three different polyhedra, namely, one icosahedron (12 0 12 0) and two polyhedrons (13 2 8 3).

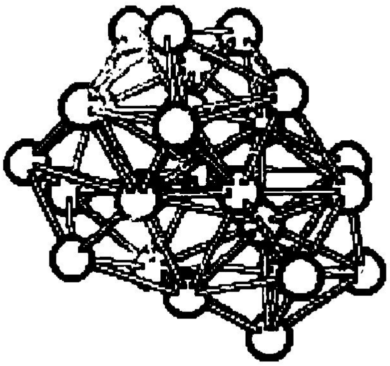

Fig. 4 Structure of small cluster consisting of 26 atoms within three polyhedra at 943 K (consisting of icosahedron (12 0 1 0) with atom of 218 as center, a polyhedron (13 2 8 3) with atom of 13283 as center and a polyhedron (13 2 8 3) with atom of 2816 as center)

4 DISCUSSION

In order to deeply understand the physical origins of the characteristics mentioned above, it is necessary to understand the relations of the structural models represented by the HA bond-type index with the typical crystal structures and the ordering degree.

Firstly, according to the work of Honeycutt and Andersen[10], for a small cluster consisting of 19 atoms, there are three different configurations, such as icosahedron, hcp and fcc. They in turn have different binding energies such as 3.8242, 3.6342 and 3.6288 (in reduced atomic unit), respectively. The stability of these clusters also decreases in turn. From the relations between the ordering degree and energy, it is well known that the higher the bonding energy, the higher the stability of the cluster. Thus the ordering degree of the icosahedral cluster will be the highest among these three clusters. Secondly, according to the definitions of HA bond-type index[10], after investigating the relationships of all the structures represented by the root pairs of atoms and their related near-neighbors with the degree of ordering, we can clearly find that: the greater the number of atoms involved in a bond-type (namely the second number of the HA index) and the greater the number of the near-neighbors connected to each other (namely the third number of the HA index), the higher the degree of ordering of the structure involved by the bond-type.

On the basis of the above discussion, we can propose the viewpoint: each structure of all the small clusters represented by the HA bond-type index corresponds to a certain ordering degree. For all the bond-types in this paper, their degrees of ordering decrease in the following order: 1661, 1551, 1541, 1441, 1431, 1422, 1421, 1321, 1311, 1211 and 1201. For the clusters mentioned in this paper, the ordering degree of the icosahedral cluster expressed by (12 0 12 0) in cluster bond-type index method is one of the highest.

According to this viewpoint, from the simulation results, we can obtain a clear physical picture on the microstructure transition from liquid to amorphous metal during the rapid cooling process.

1) With decreasing temperature, the kinetic energy of atoms in the system will be decreased, thus the probabilities of collision and diffusion of those atoms to each other will also be decreased. Therefore, the bond-types with a lower degree of ordering would be easily gathered each other and transformed into the bond-types with a higher degree of ordering.

In this paper, an important transition has happened from other bond-types to the 1551 bond-type with a higher degree of ordering. Thus the degree of ordering of this system would be increased continuously with the decrease of temperature. This is just the expected result from thermodynamics theory. We think the main reason why this transition is not favoring to form 1661 bond-type with the highest degree of ordering should be the factors in dynamics. Since the 1661 bond-type demands 6 near-neighbor atoms and those should be bonded to each other, in general case, this condition is not easy to be created, so the relative number of 1661 bond-type has only a few change and keeps at 5% ~ 6% of the total bond-types. Moreover, the reason for appearing a small peak value for the number of 1661 bond-type between 625~ 500 K (namely the glass transition temperature region) is attributed to the transformation of the system from liquid to amorphous state at this moment. In this case, the microstructural configurations in the system have a significant reorganization and the 1661 bond-type has a more chance to be formed.

2) The relative numbers of 1541 and 1431 bond-types are both greater ones. The total number of them has less change from liquid to amorphous state. Moreover, the changing direction of them are opposite, so the sum of them can be kept up about 37.3%. In this case, both the 1541 and 1431 bond-types can be considered in a kinetic equilibrium, namely, themselves will transform to the 1551 bond-type with a higher ordering degree. At the same time, the other bond-types, such as 1531, 1421 and other bond-types with a lower ordering degree, will transform to 1541 and 1431 bond-types with a higher degree ordering again. Finally, the dynamic equilibrium comes true in the system.

3) During the forming process of amorphous metal by rapid cooling, the system comes through the transition from liquid, supercooled liquid to amorphous state. Various kinds of polyhedral cluster structures can be formed from some specific kinds and numbers of bond-types. The icosahedral structures with the highest degree of ordering will play an important role during the transitions of microstructural configurations. Finally, almost 38.32% of all atoms are used to form icosahedral clusters by 1551 bond-type. The various kinds of polyhedral cluster structures will be combined each other to form some new larger cluster structures with different dimensions.

4) With the rapid cooling of temperature, the atoms almost in or near free states in the system will be decreased remarkably, from about 5% at 943 K to 2% at 300 K. The other atoms are still in the structures with a different degree of ordering.

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