STABILITY OF MICROSTRUCTURES DURING COOLING PROCESSES OF Al LIQUID METAL ①

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ABSTRACT From the molecular dynamics simulation on the microstructural transitions of Al liquid metal during rapid cooling processes, it is demonstrated that various aggregates are formed accidentally and randomly in both liquid state and glassy state, however, once they have been formed, some of them are relatively stable and can not be dissociated in the following runs. As an example, the stability of icosahedral aggregates can be expressed quantitatively by their lifetime or repeating times, some aggregates can be created repeatedly in both isothermal process and rapid cooling processes. The lifetimes of these aggregates generally increase with decreasing temperature, and increase remarkably below the glass transition temperature T_g. The number of aggregates having a longer lifetime also increases with decreasing temperature.

Key words stability microstructure liquid metal rapid cooling computer simulation

1 INTRODUCTION

It is well known that the macroscopic properties of metals and alloys are mainly determined by their microstructures, and the microstructures mainly determined by their cooling processes from liquid states. In order to understand the relations between the microstructures and macroscopic properties, as expected for a long time, a tracking research of the cooling processes should be made. However, under present experimental conditions, it is very difficult to perform such a tracking research. Therefore, the stability of microstructures of liquid metals cannot be fully studied in detail at this moment.

With rapid development of computer technique, the tracking research has been simulated by molecular dynamics methods, and some important results have been obtained for liquid metals Al, In, Ga and Mg-Ca by Wang *et al*[1-4]. The physical origins of the microstructure transitions of liquid metals are still not fully understood. Thus it is worth making further study and discussion.

For this purpose, based on the author's previous works[1,2], the stability of the microstructural configurations of Al liquid metal was investigated by tracking its rapid cooling processes using molecular dynamics simulation. A picture was obtained to show how the metal atoms gather to form aggregates and how the aggregates further evolve to form some new types of aggregates during the cooling processes. The stability of the icosahedral aggregates formed in both the liquid state and the glassy state was studied quantitatively with the lifetimes of aggregates, namely the repeating times during the isothermal processes and the rapid cooling processes. Some discussions were given for the results obtained.

2 SIMULATION CONDITIONS AND METHODS

A molecular dynamics simulation was performed at constant pressure on the microstruc-

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tural transitions of the liquid metal system consisting of 500 Al atoms during the isothermal processes and the rapid cooling processes.

The simulation conditions were as follows: place 500 Al atoms in a cubic box and let the system run with periodic boundary conditions. The interacting interatomic potential adopted here is the pair effective potential function of the generalized energy independent nonlocal model-pseudopotential theory developed by Wang *et al*[5, 6]. The function is

$$V(r_{ij}) = (Z_{\text{eff}}^2/r_{ij})[1 - (2/\pi)\int_0^\infty F(q)\sin(r_{ij}q)/q\,dq] \quad (1)$$

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 Ref. [5] and [6] The pair potential was cut off at 20.0 a.u. (atomic unit). This distance is enough for considering the interatomic action for more than 10 atomic distances. The time step in the simulation was 10^{-15} s. The cooling rate was chosen as 4×10^{12} K/s.

The simulation was started at 943 K (the melting point of Al is 933 K). The curve of the effective pair potential function at this temperature is shown in Fig. 1. At first, the system was run for 20 000 time steps at the same temperature to get an equilibrium liquid state. Secondly, the temperature was decreased to the following temperatures: 883, 833, 780, 730, 675, 550, 500, 400, 300, 200 and 100 K. Then, the system was allowed to run for 4 000 time steps at every given temperature to obtain the recorded structural configurations. In the running of 4 000 time steps, the structural configurations of the system, that is, the spatial coordinates of each atom were recorded for each 200 time steps, and 20 recorded data obtained. Finally, the types and indexes of the bonds between the related atoms are detected by means of the index method of Honeycutt-Andersen (HA)[7, 8].

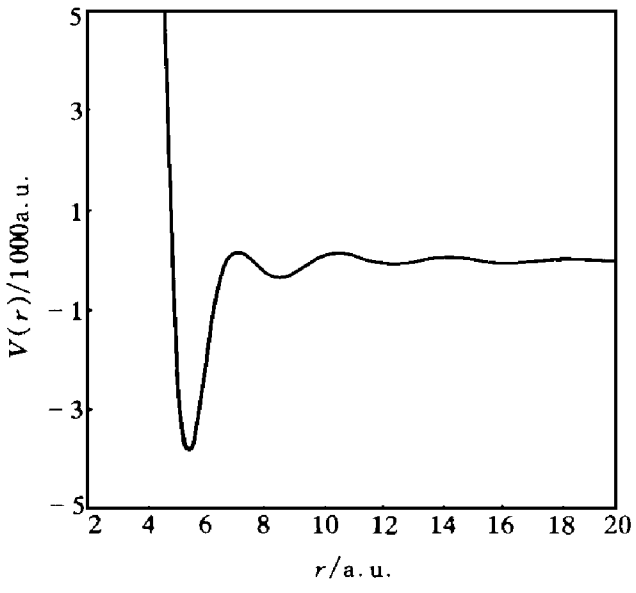

Fig. 1 Potential curve for Al liquid metal at 943 K

3 RESULTS AND DISCUSSION

First of all, we inspected the pair distribution function $g(r)$ of the system obtained from the simulation, and found out that it is in good agreement with the corresponding experimental results given by Waseda[9], as shown in Fig. 2. This implies that the effective pair potential function used here is highly accurate for the present study, and it can be expected that the results from the present simulation should, in a certain degree, reflect the physical nature of this system.

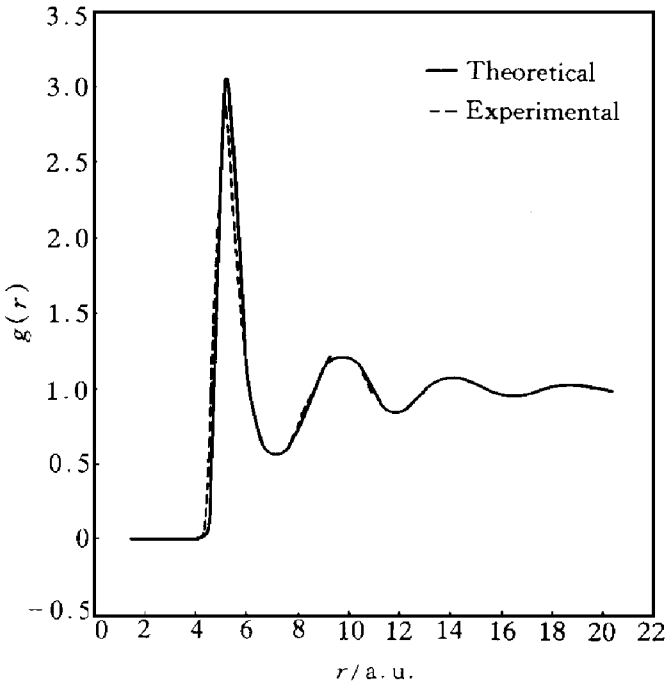

Fig. 2 Pair distribution function for Al liquid metals at 943 K

According to the index of HA, the icosahedral structure, being related to 1551 bond-type, plays a critical role for the microstructural transitions during the cooling process of Al liquid metal, as shown in Fig. 3. Thus we selected the icosahedral structure as the main representative to analyze the simulation results. As we know, the icosahedral structure consists of a central atom and twelve surrounding atoms that are interconnected with pentagon structure. In this simulation, the maximum permissible deviation from the bond angle and bond length of the ideal icosahedron is not more than 1%.

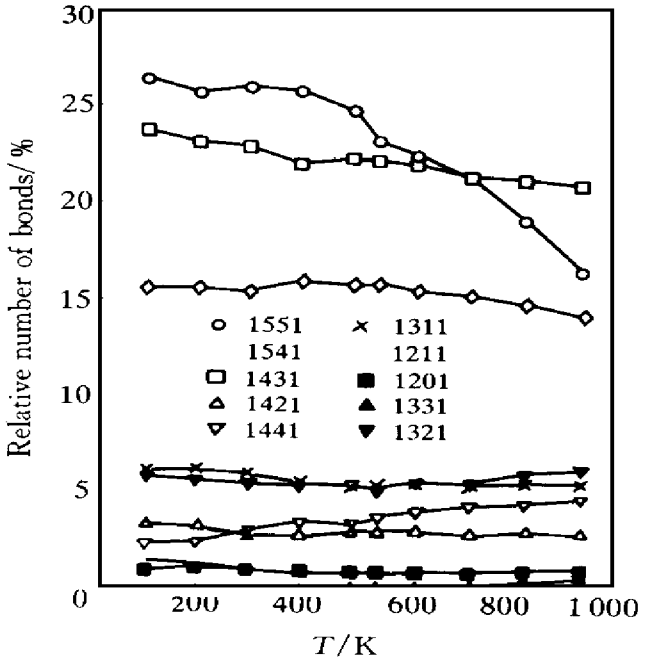

Fig. 3 Relationship of relative number of various HA bond-types with temperature during rapid cooling process of Al liquid metal

Having analyzed a great number of structural data from this simulation, we find that the stability, namely the lifetime, of a microstructural configuration could be expressed quantitatively by its repeating times during the isothermal processes and the rapid cooling processes. When the system makes isothermal run at each given temperature, among the 20 recorded data, some icosahedral aggregates can appear again and again with the same central atoms and the same surrounding atoms, as shown in Table 1. Following the decrease of temperature, the repeating times, namely the lifetime of the icosahedral aggregates are increased remarkably. Finally, the repeating times could be increased to 20, that is to say, these icosahedral aggregates could exist in the whole isothermal processes. For short, we only give the number of the central atoms that repeated more than 3 times, as shown in Table 2.

From this simulation, some new results can be clearly seen:

(1) During the isothermal processes, whether in liquid state or in glassy state, it can be clearly seen that which atom can become the central atom of an aggregate and which aggregate can be repeated are entirely accidental and random. However, once an atom becomes the central atom of an aggregate, the aggregate would appear with the same central atom and the same surrounding atoms in all the isothermal runs at different temperatures, namely, the ag-

Table 1 Repeated icosahedral aggregates with numbered central atom and surrounding atoms

Numbered central atom	Numbered surrounding atoms											
84	121	122	206	233	252	259	289	315	349	373	379	463
86	42	139	147	248	288	298	307	310	330	452	470	475
137	27	32	126	201	291	354	357	360	389	454	464	468
171	104	224	335	345	375	386	392	403	429	469	482	483
173	129	162	278	279	288	290	310	413	422	426	436	475
248	86	108	141	147	154	247	249	264	307	330	452	470
284	62	112	114	125	163	184	221	283	332	350	377	486
354	27	43	137	223	255	271	291	357	435	464	468	490

Table 2 Relationship between temperatures and variations of icosahedral aggregates during rapid cooling process of Al liquid metal

Temperature range/ K	Number of icosahedral aggregates	Number of icosahedral aggregates repeated	Number of icosahedral aggregates not repeated	Repeating times, central atoms numbered in brackets
943~ 883	48	10	26	3(40, 392)
883~ 833	57	10	34	4(122) , 3(48)
833~ 780	112	25	31	6(225, 376) ; 5(146, 223, 324) ; 4(310) ; 3(24, 68, 122, 181, 185, 235, 292, 490, 492)
780~ 730	154	38	38	7(46, 361) ; 6(431) ; 5(620) ; 4(9, 84, 234, 373, 487) ; 3 (21, 115, 132, 165, 241, 282, 298, 385, 474, 495)
730~ 675	129	30	37	8(335) ; 7(388) ; 6(36, 182) ; 4(261, 350, 471) ; 3(293, 371, 374, 456)
675~ 550	218	45	47	10(469) ; 8(84, 173, 220, 363) ; 6(309, 405) ; 5(94, 356, 458) ; 4(18, 162, 193, 282, 409, 413, 420, 444) ; 3(8, 20, 131, 166, 198, 205, 248, 277, 498)
550~ 500	306	54	18	16(137) ; 14(379) ; 13(84, 173, 387) ; 12(98) ; 10(44, 82) ; 9(477) ; 6(248, 349) ; 7(42, 251, 389) ; 6(285, 413, 434, 444, 465, 491) ; 5(172, 436) ; 4(14, 56, 205, 263, 272, 357, 457) ; 3(72, 404, 474)
500~ 400	297	51	21	15(379) ; 14(248) ; 11(171) ; 10(18, 137, 483) ; 8(116, 180, 441) ; 7(172, 264, 284, 306, 465) ; 6(106, 154, 357, 487) ; 5(15, 44, 84, 323, 330, 412, 438, 488) ; 4(39, 56, 75, 107, 121, 141, 229, 272, 291, 389, 444, 497) ; 3(109, 118, 296, 298)
400~ 300	331	43	22	20(164, 248) ; 19(323) ; 18(386) ; 17(171, 200, 434) ; 16 (392) ; 14(354) ; 11(285) ; 8(86, 335) ; 9(251) ; 7(56, 137, 173, 400) ; 6(106, 339, 448) ; 5(84, 154, 284, 497) ; 4(296, 415) ; 3(15, 123, 177, 192, 246, 307, 379)
300~ 200	365	37	11	20(105, 164, 171, 180, 192) ; 19(392, 434) ; 18(248, 284) ; 17(137, 173) ; 16(354) ; 15(208) ; 13(483) ; 10 (386, 448) ; 9(379) ; 8(86, 369) ; 5(44, 106, 325, 497) ; 4 (107, 330, 488) ; 3(222, 400, 470)
200~ 100	391	35	5	20(86, 105, 109, 164, 171, 180, 248, 284, 339, 354) ; 19 (392) ; 18(137, 173) ; 17(392) ; 15(208) ; 14(448) ; 12 (483, 488) ; 11(208, 434) ; 8(448) ; 6(44) ; 5(172) ; 4 (70, 106, 325, 369) ; 3(15, 85, 307)

gregate would be relatively stable. Therefore, the numbered central atom can be considered as a label of an aggregate in the system. In this paper, we only write the icosahedral aggregates labeled by their numbered central atoms. For example, some repeated icosahedral aggregates, such as 84, 86, 137, 171, 173, 248, 284 and 354, are shown in Table 1. Those that can be repeated more than 10 times are shown in Table 2.

It is worth noting that the stability of the aggregates in liquid and glassy states as above mentioned is a significant feature of the microstructures of metals. Just this feature will play an important role for understanding the concrete mechanism of the microstructural transitions of liquid metals during the isothermal processes.

(2) During the rapid cooling processes, when the temperature decreases from the initial liquid state (943 K) to the glass transition temperature T_g (in the range of 550~ 500 K for metal Al[2]), the total number of the icosahedral aggregates increases rapidly, from 48 in the range

of 943~ 883 K to 306 in the range of 550~ 500 K, a five-fold increased. The number of the repeatable icosahedral aggregates also increases from the minimum 10 to the maximum 54, a four-fold being increased. The number of non-repeatable icosahedral aggregates increases from 26 in the range of 943~ 883 K to 47 in the range of 675~ 550 K.

However, when the temperature is below 550 K, the total number of icosahedral aggregates would increase gradually from 306 in the range of 550~ 500 K to 391 in the range of 200 ~ 100 K, and in the same ranges of temperature, the total number of repeated aggregates and the number of non-repeatable aggregates decrease, respectively, from 54 to 35 and from 47 to 5. In the last case, it can be seen that the number of non-repeatable aggregates only occupied 2% of the total number of aggregates in the system. That is to say, 98% of the aggregates can be repeated for more than two times. From this, we can say that aggregates possess a certain stability.

(3) From Table 2, the stability of aggregates can be also clearly seen from icosahedral aggregates repeated for more than 3 times, the repeating times increase rapidly with the decrease of temperature, from 3 times in the range of 943~ 883 K to 16 times in the range of 550~ 500 K, a five-fold being increased. After this, the repeating times increase to 20 times in the ranges of 400~ 300 K, in this case, the 20 times being the maximum of the repeatable times, namely the saturation value of this simulation. As expected, it can be further seen that the number of aggregates with a saturation value of 20 times also increases rapidly from 2 in the range of 400~ 300 K to 10 in the range of 200~ 100 K, the system being in a deep cooling state. For example, some aggregates, such as 84, 86, 137, 171, 173, 248, 284 and 354, cannot be dissociated for a longer time. The stability of these aggregates would be higher and higher with decreasing temperature.

(4) From Table 2, it can be clearly seen that, in general, the aggregates that can be repeated during an isothermal process at a given range of temperature are not easy to be repeated continuously during the next isothermal process at another range of temperature. Only a few aggregates can be repeated continuously. For example, the aggregate numbered 84 can appear from the range of 780~ 730 K to the range of 400~ 300 K, and the aggregate numbered 137 can appear from the range of 550~ 500 K to the range of 200~ 100 K, and so on. However, it can be also clearly seen that the number of these continuously repeated aggregates also increases with decreasing temperature. In the last three ranges of temperature, there are more than 10 aggregates, such as numbered 86, 106, 137, 164, 171, 173, 248, 284, 339, 354, 379 and 434, that can be repeated continuously in different ranges of temperature, respectively.

From this result, it is worth noting that the continuity of aggregates in different ranges of temperature can be considered as the heredity of aggregates. It is this heredity that maybe play an important role in forming various microstructures of metallic materials during the rapid cooling processes.

(5) From Table 2, It can also be seen that the stability of the system microstructures increases rapidly for temperatures below the glass transition temperature T_g, however, the microstructural configurations have not yet been frozen completely even down to 100 K. A few atoms still diffuses from one position to another due to thermal vibration (though vibration amplitudes are small at low temperatures), so that some microstructural configurations are broken down or distorted at low temperatures. This result is very important for understanding the microscopic processes of the structure transitions at low temperatures.

(6) It is entirely accidental and radom in the system, which atom can be the central atom of an aggregate and which aggregate can be repeated in both the isothermal runs and the rapid cooling processes. For the reason to the above fact we think that the physical origin should be the themodynamical fluctuation in energy or velocity of the atoms in the system. It is well known that, in general, in a liquid or a supercooled state, the atoms having lower velocity or lower vibrational frequency around their instan-

taneous equilibrium positions would have a larger collection probability to form aggregates with each other, that is, they would be preferential in forming aggregates[10, 11]. For the same reason, among all the aggregates, only those consist of the atoms having the lowest velocity and vibrational frequency would be the most stable during the isothermal processes and the cooling processes, that is, they would possess the most excellent stability and continuity (heredity). Therefore, with decreasing temperature, the probability of forming aggregates for atoms and that to appear repeatedly for aggregates would increase remarkably. The relative stability and continuity (heredity) of aggregates would also increase.

From that mentioned above, we can get a very clear picture about the forming mechanism of the initial aggregates, and the microscopic process of aggregate continuation and evolution during the rapid cooling processes of Al liquid metal.

4 CONCLUSIONS

(1) Various microstructural (e. g., icosahedral) aggregates are formed in both the liquid state and the glassy state. However, which atom can become the central atom of an aggregate and which aggregate can be repeated during both the isothermal process and the rapid cooling process are accidental and random. Some of aggregates would be relatively stable and cannot be dissociated in the following runs.

(2) The stability of aggregates can be expressed quantitatively by their lifetime or repeating times.

(3) The lifetime or repeating times of aggregates increase, in general, with the decrease of temperature. The number of aggregates having a longer lifetime also increases remarkably with the decrease of temperature. Especially, they increase remarkably below the glass transition temperature T_g.

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