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Thermal contraction phenomenon of cluster structure of indium melt①

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[Abstract] The structure of liquid indium was studied at 280, 390, 550, 650, 750 ℃, respectively, by using an elevated temperature X-ray diffractometer. The diffraction intensity, structure factor, pair distribution function, radial distribution function, nearest interatomic distance and coordination number were obtained. The results show that the structure of In melt can be approximately described by the random closed packed hard-sphere model with hard-sphere diameter d= 2.86 Å, packing density η= 0.45. The cluster structure of In melt transforms from quasi-face-centered-cubic lattice into random closed packed structure above melting point. It has been found that the nearest interatomic distance r_1 and coordination number N_s decrease with increasing temperature from 280 ℃ to 750 ℃, r_1 decreases from 3.25 Å to 3.18 Å and N_s decreases from 12.771 to 6.648, and thermal contraction phenomenon of atom cluster occurs. Thermal contraction of In melt cluster is not homogeneous in whole measured temperature range. The sudden transformation and the biggest contraction have been found in the range of 390~ 550 ℃.

[Key words] melt; cluster structure; thermal contraction; X-ray diffraction
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1 INTRODUCTION

With the development of modern science and technology, the structure and properties of solid state have been deeply understood. However, up to now, the liquid metal has been less understood than the solid. The reason is that most metals' melting point is so high that the properties of metal melt can not be measured easily and the melt can not be explained by traditional solid physics and solid physical chemistry based on space lattice because of the short-range order in liquid metals rather than long-range order in crystals. However, the structure of liquid metals has an important effect on the structure and properties obtained from melts solidification. So, it is worthy to study the structure of liquid metals.

In recent years, great improvement has been acquired in the study of liquid metals. For example, it has been found that there exists relativity, namely heredity between liquid and solid of many metals and alloys[1, 2]; there exists medium-range order rather than only short-range order in alloy melt[3~5]; there exists nonlinear temperature dependence of the structure in liquid Al and Sn[6]. Micro-inhomogeneous structure of liquid alloys has been found[7]. The effect of different thermal histories on liquid structure has been studied[5, 8]. It has also been found that temperature dependence of the specific heat for superheated Al-10Sr alloy melts is affected by the heating rate[9].

Whether solid or liquid, it is a usual phenomenon that metal will expand when heated. In the case of liquid metal, Ref. [10] shows that the volume of metal will increase linearly with changing temperature. It is also believed that the interatomic distance of metals and alloys will increase with increasing temperature[11], so that the thermal expansion phenomenon of liquid metal is caused. But, it is not sure that whether this phenomenon exists in all metals.

Metal indium has been applied widely in the fields of electric instruments, bearing alloys, solder, coat, atomic energy industry and medical treatment because of its excellent properties from it was found in 1863. But there were few reports about structure of liquid In. In this paper liquid In is studied by using X-ray diffraction and the temperature dependence of cluster structure of In melt is posted.

2 EXPERIMENTAL PROCEDURE

The θ-θ liquid metal X-ray diffractometer used in this experiment was made in Metal Physics Institute of Ukraine National Academic. MoK_α radiation (wavelength λ= 0.071 nm) is reflected from the free surface of the specimen, and reaches the detector through a graphite monochromator in the diffraction beam. The accuracy of the angle is 0.001°, scattering angle 2θ ranges from 5° to 90°. The magnitude of the wave vector Q ($Q = 4\pi\sin(\theta)/\lambda$) is then from about

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5 to 120 nm^{-1}. The scanning step was set down according to the range of 2θ, at intervals of 0.5° between 5° and 11°, 0.2° between 11° and 19°, 0.5° between 19° and 45°, 1° between 45° and 90°.

The specimen of pure In (99.999%) was settled in sample room after pretreatment and the sample room was vacuumized to about 2×10^{-6} Pa, then pure He (99.99%) was puffed to 1.3×10^5 Pa. The specimen was heated to 900 ℃ in a crucible of the size 24 mm × 18 mm × 11 mm in this atmosphere and maintained for 1 h at 900 ℃, then cooled down to the measured temperature. 20 min was waited before X-ray diffraction experiment. Measurements were made at 280, 390, 550, 650 and 750 ℃, respectively.

3 DATA PROCESSING

The details of the data processing can be referred in Ref. [12]. To the convenience of discussion, the main parts are given here. Firstly the sum of the two or three sets of data is gotten, then proper polarization and absorption are done. The scattering intensity measured can be converted into the coherent scattering intensity per atom in an electron unit $I_{eu}^{coh}(Q)$, using the generalized Krogh-Moe-Norman method. Compton scattering is also corrected using the values reported by Cromer and Mann. The coherent intensity can be written as

$$I_{eu}^{coh}(Q) = \sum_i c_i f_i^2 + \int_0^\infty 4\pi r^2 [\sum_i \sum_j c_i f_i f_j \rho_{ij}(r) - (\sum_i c_i f_i)^2 \rho_0] \frac{\sin(Qr)}{Qr} dr \quad (1)$$

The total structure factor is

$$S(Q) = \frac{I_{eu}^{coh}(Q)}{\langle f^2(Q)\rangle} = c_1 k_1^2 S_{11}(Q) + c_2 k_2^2 \cdot S_{22}(Q) + 2(c_1 c_2)^{1/2} k_1 k_2 S_{12}(Q) \quad (2)$$

In Eqn. (2), the partial structure factors are

$$S_{ij}(Q) = \delta_{ij} + \int_0^\infty 4\pi r^2 [\rho_{ij}(r) - c_j \rho_0] \frac{\sin(Qr)}{Qr} dr \quad (3)$$

where $Q = 4\pi\sin(\theta)/\lambda$, 2θ is the scattering angle, λ is wavelength of the incident X-ray beam. $c_i = N_i/N$, c_i, N_i are concentration and number of the atom type i in the melt. N is the total number in the scattering volume. f_i is the atomic scattering factor of atom type i. i, $j = 1, 2$.

The radial distribution function (RDF) can be written as

$$4\pi r^2 \rho(r) = 4\pi r^2 (c_1 k_1 + c_2 k_2)^2 \rho_0 + \frac{2r}{\pi} \cdot \int_0^\infty [S(Q) - 1] Q \sin(Qr) dQ \quad (4)$$

where $k_i = f_i / \langle f^2(Q)\rangle^{1/2}$, $\langle f^2(Q)\rangle = \sum_i c_i f_i^2$, $\rho(r)$ and ρ_0 are atomic total density function and mean density.

The pair distribution function is calculated using equation

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q[S(Q) - 1] \cdot \sin(Qr) dQ \quad (5)$$

The coordination numbers were calculated using equation

$$N_{min} = \int_{r_0}^{r_{min}} 4\pi r^2 \rho(r) dr \quad (6)$$

where r_0, r_{min} are the nearest zero to the left and the first minimum to the right of the first peak of the RDF.

4 RESULTS

The structure factors of liquid In at different temperatures are shown in Fig. 1. It is found from Fig. 1 that the main peak shows obvious symmetry. The corresponding pair distribution function ($g(r)$) and radial distribution function (RDF) are shown in Figs. 2 and 3, respectively.

Temperature dependence of the nearest interatomic distance r_1 calculated from $g(r)$ is shown in Fig. 4, r_1 is the position of the first peak of $g(r)$

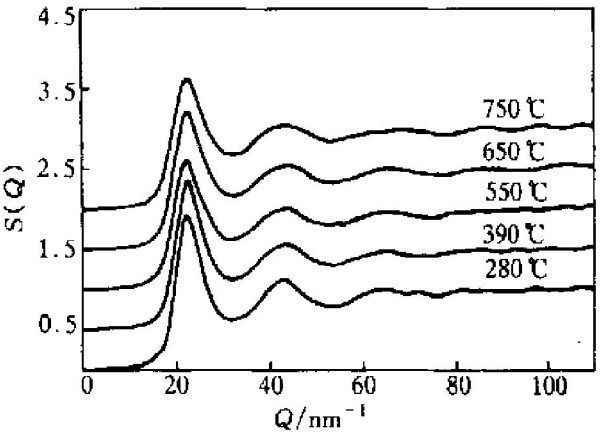

Fig. 1 Structure factors of In at different temperatures

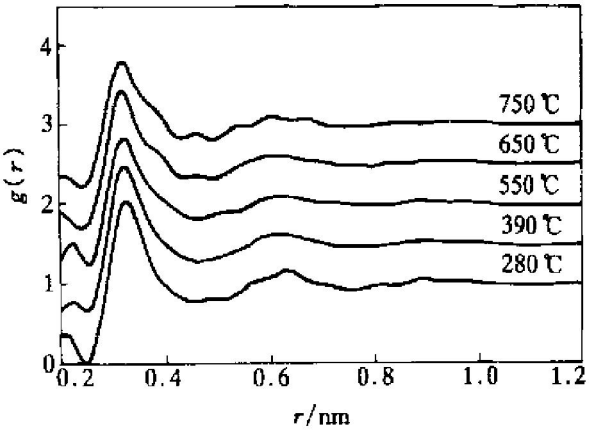

Fig. 2 Pair distribution function of In at different temperatures

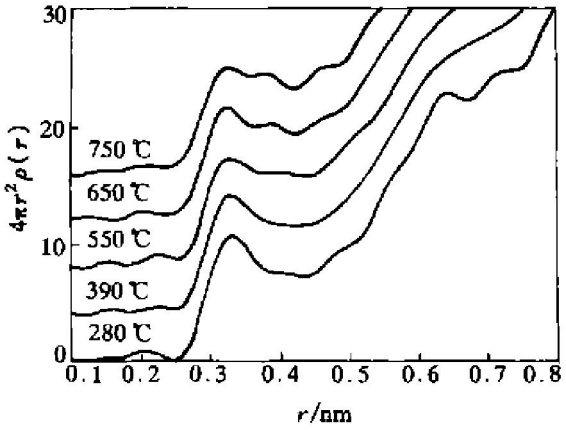

Fig. 3 Radial distribution function of In at different temperatures

. Fig. 4 shows that r_1 decreases with increasing temperature.

Fig. 5 shows the temperature dependence of coordination numbers N_s which is the area under the first peak of RDF. It is found that N_s decreases with increasing temperature.

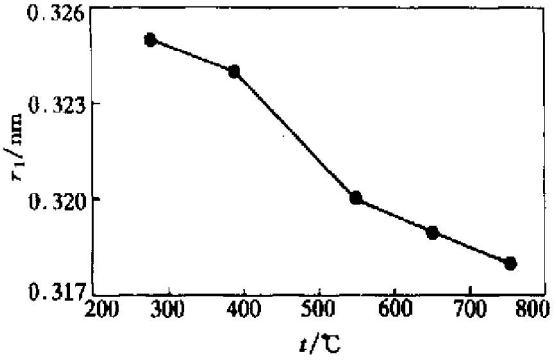

Fig. 4 Position of first peak of $g(r)$ of In at different temperatures

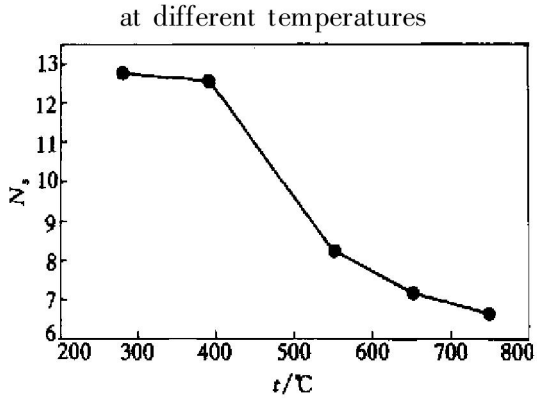

Fig. 5 Coordination numbers of In at different temperatures

5 DISCUSSION

The random closed packed hard-sphere model presented by Bernal[13] can be used to describe the structure of liquid metal. In order to show the characteristic of the structure of melts that accord with hard-sphere model, the equation $\eta = \pi\rho_0 D^3/6$[14] is used, here, η is packing density, ρ_0 is atomic density, D is hard-sphere diameter. According to this equation and the calculated atomic density $\rho_0 = 0.038\,3$, it can be concluded that the structure of liquid In can be approximately described by the random closed packed hard-sphere model with hard-sphere diameter $D = 2.86$ Å, packing density $\eta = 0.45$. The structure factor curves of In at 280 ℃ and 390 ℃ coincide well with that obtained from this random closed packed hard-sphere model[15]. The closest packing density $\eta_c = 0.74$, $\eta_c/\eta = 1.65$, which is identical to the value for a quasi-face-centered-cubic lattice model of a liquid. The coordination number calculated in this paper (12.771 at 280 ℃, 12.584 at 390 ℃) is in agreement well with this model. That In exhibits "closest-packing" in the liquid state can be taken as evidence that the partial covalent bonding present in the solid state is destroyed upon melting. So, it is believed in this paper that the structure of liquid In is quasi-face-centered-cubic lattice at low temperature above melting point and transforms into random closed packed structure with increasing temperature.

The structure of liquid is not disorder entirely but exists many short-range order atom clusters. It can be concluded from Figs. 4 and 5 that the size of atom cluster decreases with increasing temperature, namely, thermal contraction phenomenon of cluster appears. This phenomenon can be explained by the free volume theory presented by Eying[16]. Doolittle[17] thought that free volume is the increased part of volume of liquid because of thermal expansion in the case of absence of phase transformation. Cohen[18] inherited and developed the free volume theory of liquid and used it to analyze the structure of liquid and correlative physical properties with the assumption that redistribution of free volume does not consume local area free energy. With increasing temperature, the free volume expands and redistributes and the vacancy concentration between clusters increases, so that the contraction of clusters is caused.

The volume of In melt expands, but atom cluster contracts. The structural changes happened in melt are that the big clusters split into small clusters or the big clusters reconstitute into more small clusters due to enhanced thermal movement and increased atomic diffusivity. The clusters in whole melt "disperse", whereas the arrangement of atoms within clusters transforms disperse structure into compact structure.

The decrease in r_1 with increasing temperature is related to the decrease in N_s. When temperature elevates, the ratio of potential energy to kinetic energy of atoms decreases gradually, the influence of the long-range part of potential energy on the structure

diminishes, so the structure begins to adjust gradually. When temperature is high enough, the kinetic energy will overcome the long-range potential barrier, those atoms with high kinetic energy will slip the leash of central atom and escape, so that coordination number of this cluster decreases. Adding to gravitation of central atom, the "collapse" of atomic cluster and the decrease in r_1 are resulted in. In the case of In, coordination number decreases from 12.771 to 6.648, decreased nearly a half, with increasing temperature from 280 ℃ to 750 ℃. The decrease in coordination number plays a more important role than the thermal expansion in determining the interatomic distance.

It is noticeable that this kind of thermal contraction of cluster structure of In melt is not homogeneous with increasing temperature. The sudden transformation and the biggest contraction have been found in the range of 390~ 550 ℃. This can be found from the transition of curves in Figs. 4 and 5. The whole measured temperature can be divided into three ranges: 280~ 390 ℃, 390~ 550 ℃, 550~ 750 ℃. In these ranges, the contraction of cluster structure of In melt is not same. In the range of 280~ 390 ℃, the decrease in r_1 is very small (from 3.25 Å to 3.24 Å) and the decrease in N_s is also very small (from 12.771 to 12.584), which shows the contraction of cluster is very small. In the range of 390~ 550 ℃, the decrease in r_1 is biggish (from 3.24 Å to 3.2 Å) and the decrease in N_s is about 1/3 (from 12.584 to 8.274), which shows the contraction of cluster is obvious. In the range of 550~ 750 ℃, the decrease in r_1 is biggish (from 3.2 Å to 3.18 Å) and the decrease in N_s is about 1/5 (from 8.274 to 6.648), which shows the contraction of cluster is biggish.

In order to describe the liquid structure, Bernal[19] put forward a geometric model considering several kinds of structure units. Different short-range structure can be obtained by combination of structure units. The sudden transformation of cluster structure of In melt can be explained by the sudden change of relative number of structure units.

6 CONCLUSIONS

1) The structure of In melt can be approximately described by the random closed packed hard-sphere model with hard-sphere diameter d = 2.86 Å, packing density η = 0.45. The cluster structure of In melt transforms from quasi-face-centered-cubic lattice into random closed packed structure above melting point.

2) The nearest interatomic distance r_1 and coordination number N_s of liquid In decrease with increasing temperature and thermal contraction phenomenon of atom clusters occurs.

3) Thermal contraction of In melt cluster is not homogeneous in whole measured temperature range. The whole measured temperature can be divided into three ranges: 280~ 390 ℃, 390~ 550 ℃, 550~ 750 ℃. The sudden transformation and the biggest contraction have been found in the range of 390~ 550 ℃.

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