Structures of bulk amorphous $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}Be_{22.5}$ alloy in amorphous, crystalline, supercooled liquid and liquid states [①]

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[**Abstract**] The amorphous and crystal structures of $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}Be_{22.5}$ alloy have been analyzed with X-ray diffractometer. The structures of bulk amorphous $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}B_{22.5}$ alloy in solid, supercooled liquid and liquid states are almost of the same structure. The RDFs (Radius Distribution Function), the first coordination number, the first coordination radius, the correlation radius and atom number of the cluster were calculated for bulk amorphous $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}B_{22.5}$ alloy in different states. The first coordination sphere radii and the first coordination numbers are 0. 312 nm, 11. 2 in solid state, 0. 301 nm, 10. 932 in supercooled liquid region and 0. 305 nm, 11. 296 in liquid state. The crystal structure of $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}B_{22.5}$ alloy is consisted of several intermetallic compounds which are $CuZr_2$, Be_2Zr, etc. The reason of formation glass for this alloy is that there is a larger resistance for atoms to rearrange and form intermetallic compounds in a long range order.

[**Key words**] bulk amorphous; liquid structure; crystal structure

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1 INTRODUCTION

The bulk amorphous alloys of Mg-TM-Ln, Ln-Al-TM, Zr-Al-TM, Hf-Al-TM and Ti-Zr-TM were prepared by Inoue and his co-workers since 1990[1]. The critical cooling rates of these alloys are 10 ~ 100 K/s. These alloys can be prepared in an ingot with a large size. For example, Inoue et al[2] successfully prepared a bulk amorphous $Mg_{65}Cu_{25}Y_{10}$ alloy in 1991. Its shape was a cylinder with a size of d 4 mm × 50 mm. In 1993, the bulk amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy was prepared by Peker and Johnson[3]. Its critical cooling rate was 10 K/s. Its shape was also cylinder and its size was d 14 mm × 40 mm. And it was reported later that its critical cooling rate was about 1 K/s[4]. In 1996, Xing[5] reported that the bulk amorphous Zr-Ti-Al-Cu-Ni system alloy was prepared, and its cooling rate was 10~ 100 K/s. HE et al[6] also studied this system on its formation.

Because amorphous alloys have good properties, the GFA (Glass Form Ability) of the bulk amorphous alloy were studied all over the world.

The ratio of the glass transform temperature (T_g) and molten temperature, T_m, i. e. T_g/T_m was regarded as the GFA of bulk amorphous alloy[5, 7~ 9].

If the $T_g/T_m > 0.65$[5] or $T_g/T_m > 0.66$[7], the alloy will form glass. The increase of the T_g/T_m indicates the increase of the GFA.

All above works have described the technologies for preparing the bulk amorphous alloys. In order to understand the forming mechanisms of bulk amorphous alloys, it is important to study the structures of the alloy in bulk amorphous and in crystal states.

With the intensity curves of TEM, the structure factors and the pair distribution functions of bulk amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy and its crystallizing process were calculated by Wang et al[10]. And the structures of the alloy in different solid states were analyzed. For understanding the GFA, the structures of crystalline phases have been studied for many types of bulk amorphous alloy after being annealed[5, 11~ 13].

As we know, the bulk amorphous alloys are cooled from liquid state, and sometimes that will be crystallized. It is important for understanding the mechanism of glass formation to study the structures of the bulk amorphous alloys in different states and the correlation between the structures.

2 EXPERIMENTAL

2. 1 Sample preparation

Amorphous alloy ingots, with nominal composition $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$, were prepared from a mixture of the elements of purity ranging from 99.9% to 99.999% by electric arc melting under a Ti-gettered Ar atmosphere. The ingot was remelted in a silica tube under pure Ar atmosphere and the melt was injected in a copper mold with an external size of d 90 mm × 100 mm and an inner casting cavity of 10 mm × 20 mm × 60 mm. The amorphous state of the alloy was measured with X-ray diffractometry and differential scanning calorimetry. The results indicated that the alloy ingot is amorphous. Fig. 1 shows the intensity of X-ray diffraction and Fig. 2 shows the DSC result. The ingot was cut into several samples with the size of 9 mm × 20 mm × 25 mm for X-ray diffraction in solid, supercooled liquid and liquid states, and several samples with the size of 5 mm × 10 mm × 10 mm for analyzing the crystal structure of this alloy.
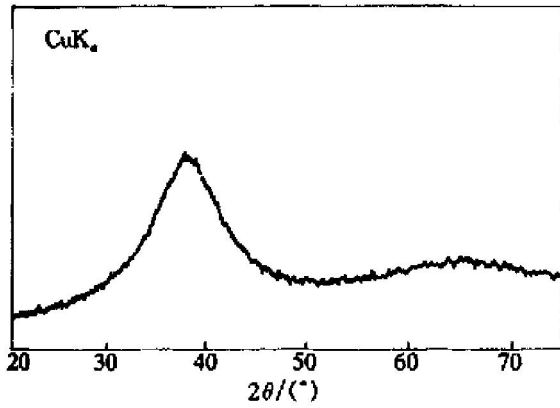

Fig. 1 X-ray diffraction spectrum of bulk amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy

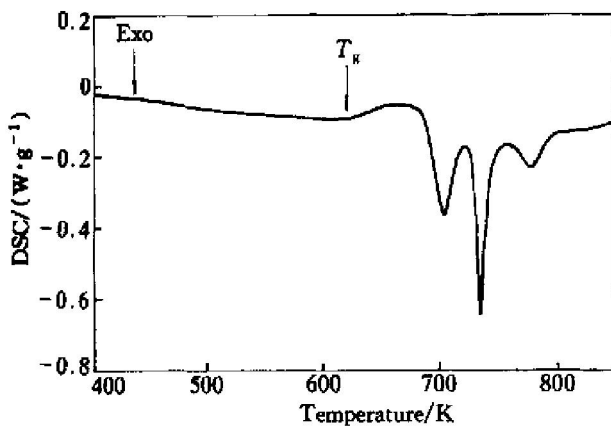**Fig. 2** DSC curve of amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy
(Mass is 43 mg and heating rate is 10 K/min)

2.2 Experiments

The structural analysis on the amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy was carried out at 303 K, 643 K and 1 273 K with high a temperature θ-θ X-ray diffractometry for liquid metals. The different tem-

peratures were corresponding to the different states: solid, supercooled liquid and liquid.

In order to obtain the crystal state of this bulk amorphous alloy, the sample with size of 5 mm × 10 mm × 10 mm was heated to 800 K and held for 10 min. The X-ray diffraction analysis was carried out on the crystal sample.

3 RESULTS

3.1 Structures in solid, supercooled liquid and liquid states

The X-ray diffraction intensities were measured on the samples of bulk amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy with a size of 9 mm × 20 mm × 25 mm at different temperatures. The results are shown in Fig. 3.
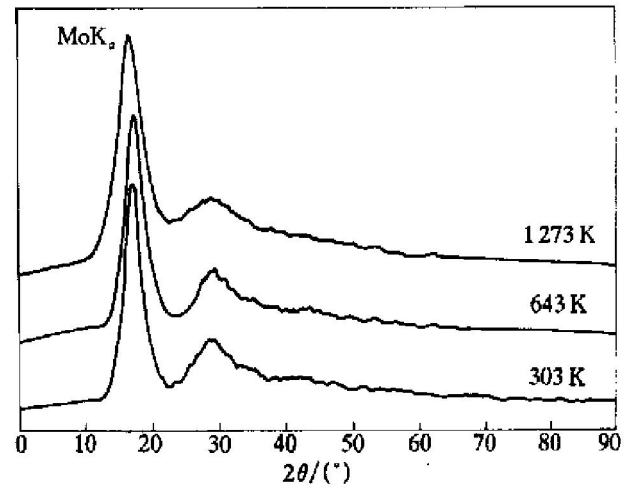

Fig. 3 X-ray diffraction spectra of amorphous alloy at different temperatures

For calculating the first coordination sphere radius (r_{max}) and the first coordination number (N_c), first of all the structure factor and the RDF are necessary.

The structure factors can be obtained with normalizing the X-ray diffraction intensities on the samples of amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy at different states. The normalizing process is made as Eqn. (1)[14].

$$S(Q) = [I(Q) - (\langle f^2 \rangle - \langle f \rangle^2)]/\langle f \rangle^2 \quad (1)$$

where $S(Q)$ is structure factor, $Q = 4\pi\sin\theta/\lambda$, 2θ is the scattering angle, λ is the X-ray wave length, $I(Q)$ is X-ray diffraction intensity in electron units, f is atom scatter factor.

$$\langle f^2 \rangle = \sum_{i=1}^{n} c_i f_i^2 \quad (2)$$

$$\langle f \rangle^2 = (\sum_{i=1}^{n} c_i f_i)^2 \quad (3)$$

$$\rho(r) = \sum_{i=1}^{n}\sum_{j=1}^{n} c_i f_i f_j \rho_{ij}(r)/\langle f \rangle^2 \quad (4)$$

where c_i is the atomic fraction of i-type atoms;

$\rho(r)$ is the average number of density function and $\rho_j(r)$ corresponds to the number of j-type atoms found at a radial distance r from an i-type atoms at the origin, and in this paper $n = 5$; Zr, Ti, Cu, Ni and Be are elements.

On the other hand, $I(Q)$ is given by the following Eqns., using Faber-Ziman form

$$I(Q) = \langle f^2 \rangle - \langle f \rangle^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] \cdot$$
$$\frac{\sin(Qr)}{Qr} dr \qquad (5)$$

By the Fourier transform, Eqn. (1) will become the following,

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ \qquad (6)$$

Eqn. (6) is RDF. Fig. 4 shows the RDFs of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy in solid, supercooled liquid and liquid states.
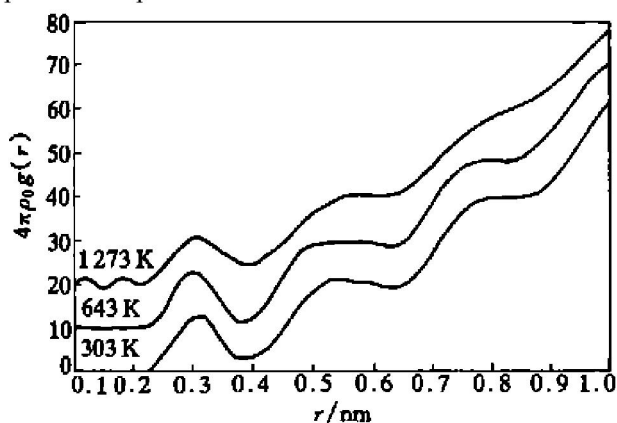

Fig. 4　RDFs of amorphous alloy at different states
(Where 303 K is in solid state, 643 K in undercooled liquid region and 1 273 K in liquid state)

According to the RDFs of amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy, the r_{max} and N_c can be calculated. They are 0.312 nm and 11.23 in solid (303 K), 0.301 nm and 10.932 in supercooled liquid (643 K), 0.305 nm and 11.296 in liquid (1 273 K).

3.2　Crystal structure of alloy

Fig. 5(a) shows the result of the intensity curve of X-ray diffraction on the crystal sample of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy with size of 5 mm × 10 mm × 10 mm. It is known that the crystal structure of the alloy is consisted of (Cu, Ni)Zr_2, Be_2Zr and other phases[5], as shown in Fig. 5(a). Fig. 5(b) is the intensity of bulk amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy in amorphous state at room temperature.

To understand the thermal properties of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy, its melting temperature was measured by DSC method, as shown in Fig. 6. The melting temperature of this alloy is 923~1 001 K. It is largely lower than the melting temperature of every element in the alloy. For example, the melting
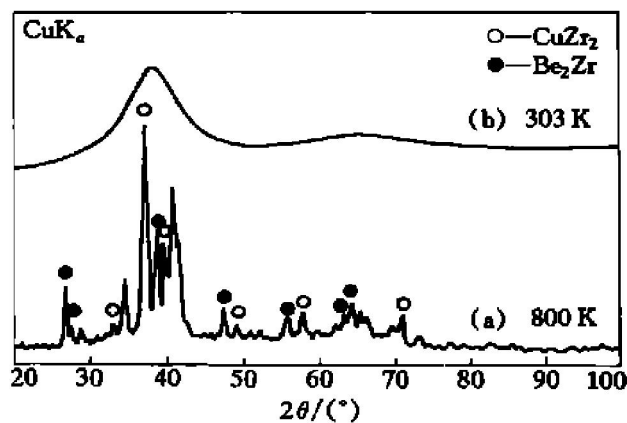

Fig. 5　X-ray diffraction spectra of alloy in crystalline and amorphous state
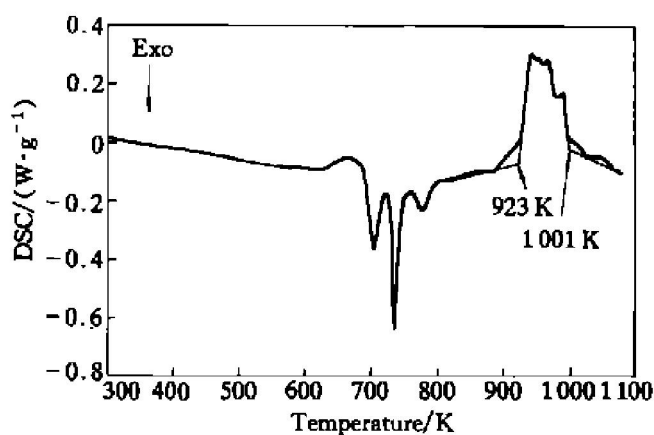(a) —Crystalline; (b) —Amorphous

Fig. 6　Molten range of bulk amorphous $Zr_{41}Ti_{14}Cu_{12.5}Be_{22.5}$ alloy measured by DSC

point of copper, the one with the lowest melting temperature among these elements, is 1 357 K of zirconium; another one with the highest melting temperature is 2 138 K.

4　DISCUSSION

From the data of RDF, r_{max} and N_c, it can be obviously seen that the solid structure is almost directly kept from liquid, especially from supercooled liquid (643 K). In the transition of the amorphous alloy from solid to liquid, the r_{max} and N_c respectively go through the path from large (0.312 nm, 11.23) to small (0.301 nm, 10.932) and to large (0.305 nm, 11.296) again. This fact shows that the amorphous alloy has some tendency for crystallization in supercooled liquid. This is confirmed by X-ray diffraction analysis at just starting crystallization in the amorphous alloy sample.

The crystal structure of this alloy is consisted of several phases; they are intermetallic compounds, such as (Cu, Ni)Zr_2, Be_2Zr, etc. The melting temperature of the mixture of the intermetallic compounds is largely lower than that of any element in

the amorphous alloy.

The X-ray diffraction peaks (Fig. 5(a) of the alloy in crystal state are covered under the first peak and second peak (Fig. 5(b)) of this bulk amorphous alloy. This fact indicates that there is a relationship between the structure of the short-range order of bulk amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy and that of this alloy in crystal state.

From the above mentioned it can be derived that the structure of the intermetallic compounds is the stable phase of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. Then the crystallizing process of the bulk amorphous alloy is that the atoms rearrange to form intermetallic compounds. Because the structure of intermetallic compounds is more complex than that of single atoms, and the crystalline phase of this alloy is consisted of several intermetallic compounds. Then the resistance to forming several intermetallic compounds by atoms' rearranging is largely greater than that to forming simple metal crystalline. In a short time, it is too difficult to form the structures of long-range order of several types of intermetallic compound by atoms' rearranging. In this case, the glass is formed.

5   CONCLUSIONS

1) The amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy is of almost the same structure in solid, supercooled liquid and liquid states. But in supercooled liquid region, it has some tendency to crystallization.

2) The crystal structure of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy is consisted of several intermetallic compounds, such as $(Cu, Ni)Zr_2$, Be_2Zr, etc.

3) The structures of this alloy in amorphous state and crystal state are almost the same. But in amorphous state, the structure is only short-range order.

4) For this alloy, it is difficult for atoms to rearrange and form several intermetallic compounds over a long distance, which is the reason of glass formation.

[REFERENCES]

[1]   Inoue A. High strength bulk amorphous alloys with low critical cooling rates (overview) [J]. Mater Trans JIM, 1995, 36(7): 866– 875.

[2]   Inoue A, Kato A, Zhang T, et al. Mg-Cu-Y amorphous alloys with high mechanical strengths produced by a metallic mold casting method [J]. Mater Trans JIM, 1991, 32(7): 609– 616.

[3]   Peker A, Johnson W L. A highly processable metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ [J]. Appl Phys Lett, 1993, 63(17): 2342– 2344.

[4]   WANG Wei-hua, WANG Wei-kui. The discovery and development of new multicomponent bulk amorphous alloy materials [J]. Physics, (in Chinese), 1998, 27(7): 398– 403.

[5]   Xing L Q, Ochin P, Faudot F, et al. Cast bulk Zr-Ti-Al-Cu-Ni amorphous alloy [J]. Mater Sci & Eng, 1996, A220: 155– 161.

[6]   HE Guo, BIAN Zhan, CHEN Guo-liang. Kinetic study on formation of bulk glass state $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy [J]. Trans Nonferrous Met Soc China, 1999, 9(2): 273– 277.

[7]   Inoue A, Zhang T, Masumoto T. Glass-forming ability of alloys [J]. J Non-Cryst Sol, 1993, 156– 158: 473.

[8]   Nishiyama N, Inoue A. Glass-forming ability of bulk $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloy [J]. Mater Trans JIM, 1996, 37(10): 1531– 1539.

[9]   Jiang H G, Baram J. Estimation of the glass transition temperature in metallic glasses [J]. Mater Sci & Eng, 1996, A208: 232– 238.

[10]   Wang Wei-hua, Wei Q, Friedrich S. Microstructure, decomposition, and crystallization in $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass [J]. Phys Rev B, 1998, 57(14): 8211– 8217.

[11]   Gebert A, Eckert J, Schultz J. Effect of oxygen on phase formation and thermal stability of slowly cooled $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ metallic glass [J]. Acta Mater, 1998; 46(15): 5475– 5482.

[12]   Inoue A, Negishi T, Kimura H M. High packing density of Zr- and Pd-based bulk amorphous alloys [J]. Mater Trans JIM, 1998, 39(2): 318– 321.

[13]   He G, Bian Z, Cheng G L. Investigation of phases on a Zr-based bulk glass alloy [J]. Mater Sci Eng, 2000, A279: 237– 243.

[14]   Waseda Y. The Structure of Non-Crystalline Materials-Liquids and Amorphous Solids [M]. New York: Mc-GRAW-HILL International Book Company, 1980.

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