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Crystallization kinetics of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy ①

WANG Huan-rong(王焕荣)[1], SHI Zhi-qiang(石志强)[1], WANG Yan(王 艳)[1],
TENG Xin-ying(滕新营)[1], YE Yi-fu(叶以富)[2,1], MIN Guang-hui(闵光辉)[1], ZHANG Jun-yan(张均艳)[1]
(1. Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University, Ji′nan 250061, China;
2. College of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China)

[Abstract] Crystallization behavior of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy under isothermal annealing condition was investigated by DSC and XRD. It is found that two exothermic peaks appear in the DSC curve of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy, indicating that the crystallization proceeds through double-stage mode. The crystallization process of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy under isothermal annealing condition is mainly controlled by nucleation and one-dimensional growth with the crystallized volume fraction smaller than 70%. With the crystallized volume fraction ranging from 70% to 90%, crystallization process is mainly dominated by the growth of three-dimensional pre-existing quench-in nuclei. And when the crystallized volume fraction reaches above 90%, transient nucleation becomes the master of the crystallization process.

[Key words] crystallization kinetics; amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy; DSC; Avrami exponent
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1 INTRODUCTION

The development of glass forming multicomponent alloy systems with very low critical cooling rates within 1～ 100K/s has offered firstly the possibility to produce metallic glass sample with maximum sample thickness almost comparable to that of oxide glasses by slow cooling from the melt, e. g. by copper mould casting or water quenching of a melt into a quartz tube[1]. As a kind of advanced materials, the thermal stability of amorphous alloys is an important factor affecting their usage, especially under certain high temperature working circumstances. Much attention has been given to the crystallization process of amorphous alloys for several years. However, their crystallization mechanisms are still unclear as yet. The investigation of crystallization kinetics is important in establishing the stability of metallic glasses.

Recently, the discoveries of a series of amorphous alloys with a large supercooled liquid region before crystallization and a high glass forming ability in Zr-Al-TM[2～5], Zr-Ti-M[6] and La-Al-TM[7～9] systems enable the crystallization studies to attract more interest. In this study, crystallization process of a ternary amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy with a wide supercooled liquid region exceeding 60K under isothermal annealing condition is investigated and the mechanisms are presented.

2 EXPERIMENTAL

An alloy ingot of composition $Zr_{65}Cu_{25}Al_{10}$ (mole fraction, %) was prepared by melting the nominal elemental constituents with an arc furnace in a water-cooled copper boat under argon atmosphere of 99.999% purity. It was remelted several times to ensure homogeneity. The amorphous ribbon for experiments was produced by a single roller melt-spinning method in a partial argon atmosphere. The diameter of the copper roller is 350mm, with the quenching temperature of 1200 ℃ and the rotate speed of 1800r/min. The ribbon is about 2～ 3mm in width and 30～ 40μm in thickness. The amorphicity of the specimen was checked by XRD and the thermal property of the melt-spun ribbon was examined by using a high-temperature Netzsch DSC404 system.

3 RESULTS AND DISCUSSION

Fig. 1 shows the DSC scan of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy at a heating rate of 20K/min. It can be seen that the glass transition temperature T_g and crystallization temperature T_x of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy are about 375 ℃ and 443 ℃, respectively, and then the supercooled liquid region between them is as large as 68K, which indicates that amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy has high glass forming ability (GFA). It should be noted that two exothermic peaks exist in the DSC trace of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy, implying that the crystallization proceeds via double-stage mode, which has not been reported in the previously published references. The first peak

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is corresponding to the precipitation and growth of Zr_2Al phase, and the second peak mainly corresponds to the growth of Zr_2Cu phase. At lower Al content (< 7.5%, mole fraction), the crystallization process is performed through a single exothermic reaction[10], which means the crystallization mode of amorphous Zr-Cu-Al alloy with the Al concentration below or above 7.5% (mole fraction) are quite different.

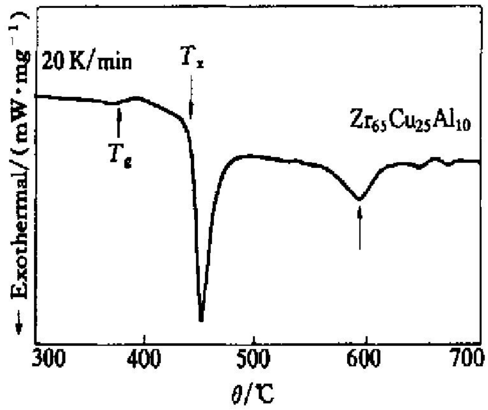

Fig. 1 DSC curve for amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy at heating rate of 20 K/min

To obtain the information on crystallization kinetics of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy, the ribbon was annealed at different temperatures T_a, ranging from 390 ℃ to 430 ℃ and the annealed curves at different temperatures are shown in Fig. 2. The average Avrami exponent n is shown as a function of annealing temperature T_a in Fig. 3. It is clear that with increasing T_a from 390 ℃ to 430 ℃, the average Avrami exponent keeps constant in the vicinity of 1.25, which suggests the crystallization process of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy is mainly controlled by nucleation and one-dimensional growth. It can be seen from Fig. 3 that the crystallization behavior of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy is independent on θ_a. In such case, there is no nucleation in the amorphous matrix during isothermal annealing process.

In order to shed more light on the crystallization

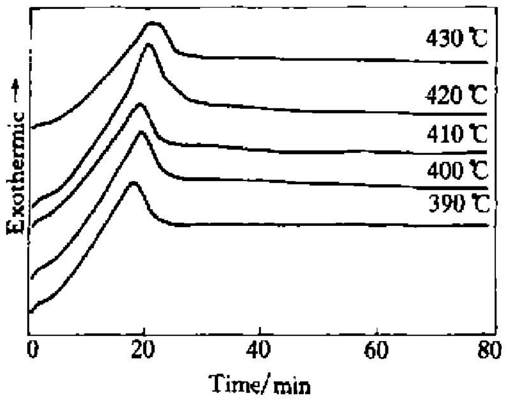

Fig. 2 Relationship between annealing temperature and annealing time

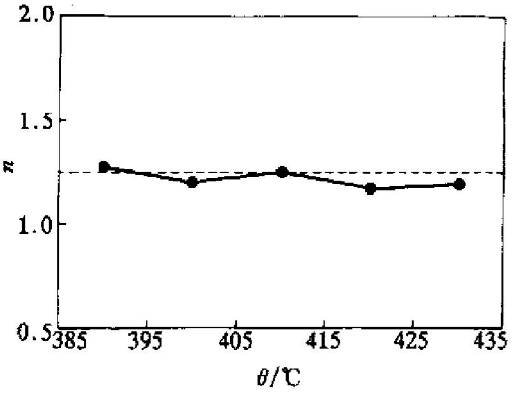

Fig. 3 Change in average Avrami exponent n with isothermal annealing temperature for amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy

kinetics of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy, local Avrami exponent, which is very successful in interpreting the crystallization process of amorphous alloys, e. g., Pd-Si, Fe-Si-B and Fe-Cr-Si-B alloys[11], is used. The definition of local Avrami exponent can be expressed as follows:

$$n(x) = \partial \ln[-\ln(1-x)]/\partial \ln[t-\tau]$$

where x is the crystallized volume fraction, τ is the incubation time and t the annealing time; $n(x)$ is the local Avrami exponent, $n(x) = 1$ for one-dimensional growth and $n(x) = 3$ for three-dimensional growth. The n values can be obtained from the plot of lnln[− (1 − x)] against ln(t − τ) at a specific temperature (As shown in Fig. 4). Theoretically, the maximum value of $n(x)$ is 3 and minimum value is 1, respectively.

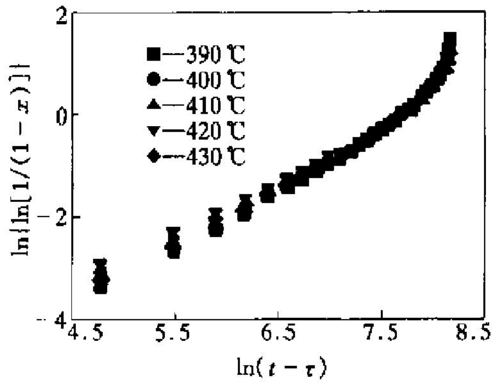

Fig. 4 Plot of ln[− ln (1 − x)] versus ln(t − τ) for amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy at different temperatures

The relationship between local Avrami exponent $n(x)$ and the crystallized volume fraction x at different annealing temperatures is given in Fig. 5. Based on the solid state phase transformation theory and the fact that below $x < 70\%$, $n(x) < 2.0$, we can conclude that the crystallization process of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy is mainly controlled by one-dimensional nucleation with a constant nucleation rate.

However, when x is larger than 70%, $n(x)$ increases from 2.0 to 3.0, indicating that nucleation and three-dimensional growth occur in the specimen. When x reaches above 90%, $n(x) > 4.0$, which means nucleation rate increases with increasing the annealing time, namely, so-called transient nucleation. These nuclei are supposed to be formed during the melt spinning. Similar trends can also be observed for amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy at other annealing temperatures. At all annealing temperatures, $n(x)$ was found to increase from 2.0 to 4.0 when x increases from 70% to 90%, suggesting that the heterogeneous distribution of quench-in nuclei. It is clear that the heterogeneous distribution of nuclei can have more influence on the value of local Avrami exponent.

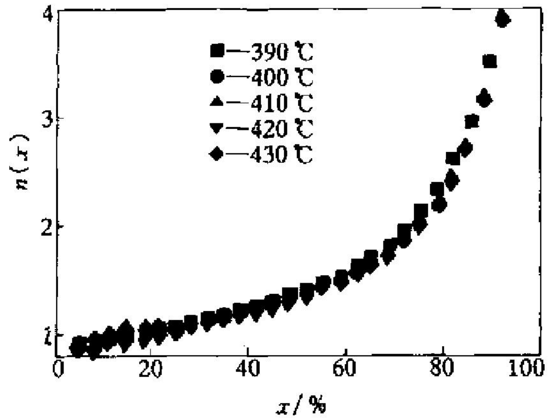

Fig. 5 Relationship between local Avrami exponent $n(x)$ and crystallized volume fraction x for amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy at different isothermal annealing temperatures

Fig. 6 is the X-ray diffraction patterns of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy annealed at 390 ℃ for different durations. It can be seen that at the initial stage, Zr_2Al phase firstly precipitates from the amorphous matrix because of the much stronger chemical affinity between Zr and Al atoms than that between Zr and Cu atoms[12]. When annealing time reaches 13 min, no Zr_2Cu particles can be observed from the XRD results, implying that the crystallization activation energy required for grain growth of Zr_2Cu is relatively larger than that of Zr_2Al. With increasing the annealing time longer than 25 min, Zr_2Cu phase begins to precipitate and grow competing with the previously formed Zr_2Al phase. Thus, the crystallized specimen is mainly consist of Zr_2Al and Zr_2Cu phases. Sequentially increasing the annealing time, no distinct change can be found from the XRD pattern.

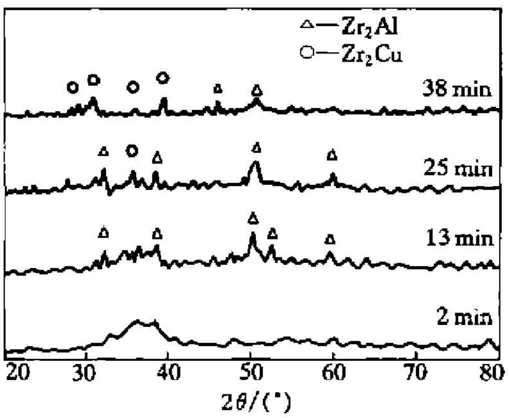

Fig. 6 XRD patterns of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy annealed at 390 ℃ for different durations

Based on the above-mentioned facts, it is presumed that the crystallization of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy under isothermal annealing condition proceeds through three stages. The first stage corresponds to the precipitation and growth of Zr_2Al phase mainly from the surface of amorphous matrix, which is one-dimensional-controlled process. The second stage is the growth of pre-existing Zr_2Cu quench-in nuclei in the matrix, which is mainly dominated by three-dimensional nuclei with a constant growth rate. The last one is a transient nucleation process, which means that new nuclei precipitate directly from the amorphous matrix. Thus, the crystallization processes under isothermal annealing condition can be briefly expressed as follows: Amorphous + Pre-existing Zr_2Cu particles $\rightarrow$ Amorphous + Pre-existing Zr_2Cu particles + Zr_2Al phase (Nucleation and one-dimensional growth) $\rightarrow$ Zr_2Al + Zr_2Cu phases (Nucleation and three-dimensional growth) $\rightarrow$ Zr_2Al + new Zr_2Cu phases (Transient nucleation).

4 CONCLUSION

The crystallization process of amorphous $Zr_{65}Cu_{25}Al_{10}$ alloy with a wide supercooled liquid region under isothermal annealing condition was investigated by using X-ray diffraction and DSC techniques. It can be concluded that when the crystallized volume fraction is below 70%, the crystallization process is mainly controlled by nucleation and one-dimensional growth. With the crystallized volume fraction ranging from 70% to 90%, it is mainly dominated by nucleation and three-dimensional growth. And the transient nucleation becomes the master of the crystallization process with crystallized volume fraction exceeding 90% at the last stage.

[REFERENCES]

[1] Gebert A, Eckert J, Schultz L. Effect of oxygen of 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: 5475-5482.

[2] Inoue A, Zhang T, Masumoto T. Zr-Al-Ni amorphous alloys with high glass transition temperature and significant supercooled liquid region [J]. Mater Trans JIM,

1990, 31: 177- 183.

[3] Zhang T, Inoue A, Masumoto T. Amorphous Zr-Al-TM (TM= Co, Ni, Cu) alloys with significant supercooled liquid region of over 100 K [J]. Mater Trans JIM, 1991, 32: 1005- 1010.

[4] Matsubara E, Tamura T, Waseda Y, et al. Structural study of $Zr_{60}Al_{15}Ni_{25}$ alloys with a wide supercooled liquid region by the anomalous X-ray scattering (AXS) method [J]. Mater Trans JIM, 1992, 33: 873- 878.

[5] Weiss M, Moske M, Samwer K. Kohlrausch exponent of amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ determined by an elastic relaxation measurements [J]. Appl Phys Lett, 1996, 69: 3200- 3202.

[6] Tanner L E, Ray R. Phase separation in Zr-Ti-Be metallic glasses [J]. Scripta Metallurgica, 1980, 14: 657- 662.

[7] Ozaki K, Haibara, Kobayashi K, et al. Effect of addition of TiB_2 powder on formation tendency of amorphous phase in $La_{55}Al_{25}Ni_{20}$ alloy [J]. Mater Trans JIM, 1995, 36: 879- 882.

[8] Inoue A, Nakamura T, Sugita T, et al. Bulkly La-Al-TM (TM = Transition Metal) amorphous alloys with high tensile strength produced by a high-pressure die casting method [J]. Mater Trans JIM, 1993, 34: 351- 358.

[9] Inoue A, Zhang T, Masumoto T. Production of amorphous cylinder and sheet of $La_{55}Al_{25}Ni_{20}$ alloy by a metallic mold casting method [J]. Mater Trans JIM, 1990, 31: 425- 428.

[10] Inoue A, Tsai A P, Zhang T, et al. Stability transformation to crystalline phases of amorphous Zr-Al-Cu alloys with significant supercooled liquid region [J]. Mater Sci Eng, 1994, A178: 255- 263.

[11] Lu K. Investigation on Crystallization and its Micromechanism for Amorphous Alloys [D]. Shenyang: The Chinese Academy of Sciences, 1989, 47- 63.

[12] Takeuchi A, Inoue A. Calculations of mixing enthalpy and mismatch entropy for ternary amorphous alloys [J]. Mater Trans JIM, 2000, 41: 1372- 1378.

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