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Understanding glass-forming ability through sluggish crystallization of atomically thin metallic glassy films

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The glass-forming ability (GFA) of an alloy, closely related to its ability to resist crystallization, is a crucial issue in condensed matter physics. So far, the studies on GFA are mostly statistical and empirical guides. Benefiting from the ultrahigh thermal stability of ultrathin metallic glassy film and high resolution spherical aberration-corrected transmission electron microscope, the crystallization of atomically thin ZrCu and its microalloyed ZrCuAl glasses with markedly different GFA was investigated at the atomic scale. We find the Zr diffusivity estimated from the density of nuclei is dramatically decreased by adding of Al, which is the major reason for the much better GFA of the ZrCuAl metallic glass. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4892448]

Since the birth of metallic glass (MG), researchers have been searching for new MGs with better glass forming ability (GFA) and made great efforts to understand the mechanism that controls the GFA.¹⁻⁷ Some alloy systems such as LaNiAl,⁸ ZrTiCuNiBe,⁹ and PdNiCuP¹⁰ with excellent GFA were successfully synthesized,¹¹ and the findings brought MG towards practical usage as engineering or functional materials.¹² However, the mechanism that controls the GFA of an alloy remains a challenge,¹³ and the seeking of MGs with excellent GFA, in practice, has always been a "hit or miss" process. In particular, it is still an unraveled mystery that a small change of composition or microalloying can dramatically change the GFA.¹¹ Therefore, it is of significance to have a deep understanding of the GFA of a material, based on which a more effective way for glassy materials searching could be found.

The GFA of an alloy is known to be closely related to its crystallization behaviors,¹⁴ and the resistance of liquid to crystallization measures the GFA of a system. The study of crystallization process of a material can provide insight on the mechanism that controls GFA.^{15,16} However, in conventional bulk MGs, the crystallization happens very fast, usually within micro seconds, when they were heated close to their crystallization of crystallization from nanoscale nuclei offers substantial experimental challenges because the conventional X-ray diffraction and transmission electron microscope are unreliable for detecting nuclei in ~1 nm scale. This limits direct observation and thorough investigation of crystallization process, especially nucleation process on a microscopic scale.

The $Zr_{50}Cu_{50}$ binary alloy has marginal GFA which can be cast in a rod with maximum diameter of ~1 mm. With minor Al addition, the GFA of $Zr_{54}Cu_{38}Al_8$ ternary alloy was drastically enhanced and the fully glassy rod with diameter of about 6 ~ 10 mm can be obtained, ^{17–19} while their glass transition temperature T_g and crystallization temperature T_x exhibit insignificant difference. Recently, it was found that, comparing with bulk glasses or thick metallic glassy films, Zr₅₀Cu₅₀ and Zr₅₄Cu₃₈Al₈ ultrathin glasses exhibit remarkably high thermal stability.²⁰ Even no signs of nuclei were observed after annealing the samples at 100 K above their crystallization temperatures in its bulk glass state for about 20 min. The thermal stability and crystallization behavior of the thin films can be tuned by controlling the thickness of the MG film. The ultrathin glassy films provide ideal system to study the crystallization behavior as well as its relation with the GFA because of their high stability and slow nucleation and growth rates compared to that of its bulk form.^{21,22}

In this Letter, we investigate the sluggish crystallization behavior of $Zr_{50}Cu_{50}$ and $Zr_{54}Cu_{38}Al_8$ ultrathin glassy films using high resolution spherical aberration-corrected transmission electron microscope (Cs-TEM) to understand the long-standing issue of GFA. It is observed that the two alloys with markedly different GFA exhibit similar crystallization behaviors but the crystal nucleation and growth rates are significantly slower for the Al additional $Zr_{54}Cu_{38}Al_8$ alloy with higher GFA. The origin of GFA and the sluggish effect of Al addition on the mobility of Zr atoms are discussed. The results might shed light on physical aspects of GFA in the alloys.

The thin-film Zr₅₀Cu₅₀ and Zr₅₄Cu₃₈Al₈ were deposited by pulsed laser deposition (PLD) onto high resolution TEM window grids (purchased from SIMPore Inc.), which is a 5 nm-thick amorphous silicon nitride film supported by monocrystalline silicon. The depositions were carried out in high vacuum $(10^{-5} Pa)$ at room temperature. The Zr₅₄Cu₃₈Al₈ and Zr₅₀Cu₅₀ bulk metallic glass were used as the target for PLD to ensure deposited thin-films have uniform composition. The thickness of the thin-films was deducted from the deposition rate (0.03 nm/pulse), which was measured by X-ray reflectivity (XRR) for thicker samples (100 pulses for a 3 nm-thick sample).²⁰ The annealing processes were carried out *in situ* right after the deposition. Annealing temperature was monitored by non-contact infrared thermometer. The as-deposited or annealed samples were quickly transferred for Cs-TEM observations. JEOL-ARM200F Cs-TEM (with cold field emission gun) was used to investigate the nucleation and growth in the samples at atomic scale.²³

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 $Zr_{50}Cu_{50}$ and its microalloyed $Zr_{54}Cu_{38}Al_8$ glassy thin films with a thickness of 0.6 nm were annealed at 873 K for 30 min, which is more than 100 K higher than T_x of their bulk glassy state. The Cs-TEM images of the annealed $Zr_{50}Cu_{50}$ [Figs. 1(a)–1(c)] and $Zr_{54}Cu_{38}Al_8$ [Figs. 1(d)–1(f)] films show both samples contain only two types of crystallized nanoparticles with significantly different sizes. Figures 1(g)–1(j) contrast the average crystalline sizes, the density of the nanoparticles in the two crystallized films. In the $Zr_{50}Cu_{50}$ film, the small particles have an average size of 3.1 nm, while it is 2.7 nm for the $Zr_{54}Cu_{38}Al_8$ film; the average big particles size is 33.9 nm in $Zr_{50}Cu_{50}$ film which is also slightly larger than 30.8 nm in $Zr_{54}Cu_{38}Al_8$ film. The similar crystallization behavior indicates that the $Zr_{50}Cu_{50}$ and $Zr_{54}Cu_{38}Al_8$ thin



FIG. 1. (a)–(c) Cs-TEM images of ZrCuAl thin film annealed at 873 K for 30 min with different magnifications. (d)–(f) Cs-TEM images of ZrCu thin film annealed at 873 K for 30 min with different magnifications. (g)–(j) Comparisons of the average density and size of small and big crystallized particles in ZrCu and ZrCuAl thin film.

films have the same nucleation and crystal growth mechanism. However, the density of the crystallized particles shows a huge difference between the two films. The density of the small particles in $Zr_{50}Cu_{50}$ is $4.9 \times 10^3 / \mu m^2$, which is much more than that of $8.5 \times 10^2 / \mu m^2$ in crystallized Zr₅₄Cu₃₈Al₈ film. This indicates that the nucleation in ZrCu thin film is strongly suppressed by the addition of Al. There is also large difference in the density of the big particles between the two samples, which is $16.2/\mu m^2$ for $Zr_{50}Cu_{50}$ and $4.95/\mu m^2$ for Zr₅₄Cu₃₈Al₈. After the 30 min annealing, the total crystallized fraction is 10.5% for Zr₅₀Cu₅₀ and only 1.7% for the Al microalloyed Zr₅₄Cu₃₈Al₈. The results also indicate that the nucleation happens on the very first stage of crystallization, and the crystallization in glassy ZrCu alloy is a growthcontrolled process at the temperature close to T_x of its bulk glassy state.⁴ The crystal growth is very sluggish in the thin films, which allows distinct comparison of nucleation rate and crystal growth rate. And the results show that the ability to form crystalline nuclei in the ZrCu film is significantly weakened by the addition of Al.

The growth process of the crystallized phase in Zr₅₄Cu₃₈Al₈ thin film was further investigated. We compared the Zr₅₄Cu₃₈Al₈ films which were annealed at 873 K for 0 and 30 min. The Cs-TEM images [Figs. 2(a) and 2(b)] show two types of crystallized nanoparticles with significant different sizes in the Zr₅₄Cu₃₈Al₈ samples annealed with different times. Figures 2(c)-2(f) contrast the average sizes and the density of the crystalline nanoparticles in the crystallized films. The size and density of small crystallized particles, which were formed in the early stage of the annealing, do not grow significantly during the annealing process [see Figs. 2(c) and 2(e)]. While the big particles had grown significantly from an average size of 13.2 nm at 0 min to 30.8 nm at 30 min as presented in Figs. 2(d) and 2(f). The crystalline phase fraction in the sample, calculated from the crystallized area in the TEM image, has increased from 1.1% at 0 min annealing to 1.7% at 30 min annealing, which confirms that the growth rate is very slow in the Al microalloyed alloy even at a temperature 100 K higher than the T_x of its bulk glassy state. The results suggest that the crystallization is a growth dominant process in the glassy thin film.

Crystallization behavior of the glassy thin films can be tuned by controlling their thickness.²⁰ The thicker Zr₅₀Cu₅₀ and Zr₅₄Cu₃₈Al₈ films (3 nm in thickness) were also deposited for further investigation. Figure 3 presents the Cs-TEM images of the as-deposited Zr50Cu50 and Zr54Cu38Al8 films 3 nm in thickness. In Fig. 3(a), the Cs-TEM image shows clear crystallized particles with an average size of about 3 nm uniformly dispersed all over the Zr₅₀Cu₅₀ film, taking up approximately 30% of the whole sample. The thicker films are much easier to crystallize comparing with the Zr₅₀Cu₅₀ film 0.6 nm in thickness which is only partially crystallized after annealing for 30 min. On the same deposition condition, no signs of crystallization can be observed in the Zr₅₄Cu₃₈Al₈ thin film 3 nm in thickness as shown in Fig. 3(b). The inset image in Fig. 3(a) shows the enlarged bright field image of the nanoparticle in Zr₅₀Cu₅₀ thin film. It is obvious that there is a much higher concentration of Zr in the crystallized particles, meaning that the formation of the particle is mainly due to the accumulation of the Zr atoms,

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FIG. 2. (a) Cs-TEM image of ZrCuAl sample annealed at 873 K for 0 min. (b) Cs-TEM image of ZrCuAl sample annealed at 873 K for 30 min. (c)–(f) Comparisons of the average density and size of small and big crystallized particles. A significant growth of big particles is obvious.

and the mobility of Zr atoms is the crucial factor for controlling crystallization, especially nucleation process. This also indicates that the mobility of Zr in ZrCu MG plays an important role in determining the GFA.

The experimental results clearly show that the nucleation and crystal growth rates of the ZrCu thin film is suppressed by the addition of Al, and clarify the role of the Al addition in the significantly enhancement of GFA of the alloy. According to the classical theory, the homogenous nucleation rate in alloys can be written as^{24,25}

$$J \propto DN^2 \exp\left[\frac{E_i}{3k_BT}\right],$$
 (1)

where *D* is the diffusion constant, *N* is the density of free atoms, E_i is the binding energy of the nuclei, and k_B is Boltzmann constant. In the same annealing temperature and time for films with different compositions, Eq. (1) can be



FIG. 3. (a) Cs-TEM image of ZrCu as-deposited thin film (3 nm in thickness). Clear crystallized particles with an average size of about 3 nm are visible. Inset: Enlarged bright field image of crystallized particles which shows a much higher Zr concentration compared to the glassy matrix. (b) Cs-TEM image of ZrCuAl sample (3 nm in thickness) showing no sign of crystallization.

rewritten as: $J \propto D$, meaning that the nucleation rate in a metallic glassy film is proportional to the diffusion coefficient. Our results show that in the annealed glassy thin film (0.6 nm in thickness), the nuclei with the same structure consist of mostly Zr atoms. The difference of nucleation rate between ZrCu and ZrCuAl reveals the difference of diffusion or mobility of Zr atoms on the substrate. And, it was estimated that the diffusion constant of Zr atoms has drop to about 1/6 of its original value after the addition of Al.

The question is then raised why Al can suppress the mobility of Zr in the thin film. We consider the mixing enthalpy between Zr and Al, which is -44 kJ/mol. The mixing enthalpy between Zr and Cu is -23 kJ/mol, and the mixing enthalpy between Cu and Al is only -1 kJ/mol.²⁶ There exists a stronger binding tendency between Zr and Al atoms, and the microalloyed Al atoms have preference to form strong bonds with Zr atoms. Such bonds could enhance the shortrange order in the system and cause a denser packing and a much slower dynamical behavior, and a lower mobility of Zr atoms in the film.²⁷ Since the mobility of Zr is the dominant factor in the crystallization process for formation of nuclei



FIG. 4. Schematic TTT diagram. The blue curve (left) represents the TTT curve of ZrCu liquid, and the other one (right) of ZrCuAl liquid, the rightward shifting of the curve, is attributed to the change in mobility of Zr atoms. The deviation of critical cooling curves shows (black) the enhanced GFA after Al addition. The insets show the difference of atomic interaction between ZrCu and ZrCuAl, and the right one emphasize the stronger bonding between Zr and Al, which causes the suppressed mobility of Zr.

and the subsequent crystalline phase growth, the crystallization rate is then dramatically slowed down. That is, the GFA is significantly enhanced by the addition of Al.

The suppression effect of Al on the mobility of Zr atoms and the crystallization or GFA can be schematically illustrated in a time-temperature-transition (TTT) diagram in Fig. 4. In general, a typical "C" shaped TTT diagram describes the competition between liquid state and crystal state in an undercooled liquid melt from a kinetic point of view, which gives abundant information on the GFA of a certain alloy system.^{28,29} The critical cooling rates, which can be obtained from the slope of cooling curves, reveal the difference of GFA between different alloy systems. The TTT curve of ZrCu is determined to be much shifted rightwards after the microalloying of Al, due to the decrease in the mobility of Zr atoms. The strongly suppressed crystallization process greatly reduces the critical cooling rate of such Zr based alloy, thus enhances its GFA.

In summary, through the comparison of the atomic scale crystallization behavior of $Zr_{50}Cu_{50}$ and $Zr_{54}Cu_{38}Al_8$ ultrathin films with markedly different GFA, the nucleation and crystal growth is found to be significantly suppressed by the addition of Al in the alloy. The Al addition can form the strong Zr-Al bonds and suppress the mobility of Zr, which is

a dominant dynamic factor for crystallization. The binding effect of Al addition reduces the diffusion constant of Zr in ZrCu alloy and enhances the GFA of ZrCu alloy. Our results might shed light on the GFA in glass-forming alloys and the mysterious microalloying effect on GFA.

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