**Supplementary Material**

**Liquid like Nucleation in Free-standing Nanoscale Films**

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The supplementary material covers the following aspects related to the manuscript on "Liquid like nucleation in Nanoscale Thin Films": (i) details of the theoretical/computational and experimental methodology (Section-1) and (ii) additional results, which may be of interest to a perspicacious reader (Section-2).

1. **Methodology**

The details of the methods used in the main manuscript are described in this section. The experimental details included are: (i) synthesis of samples, (ii) heat treatment, (iii) X-ray diffraction (XRD), (iv) differential scanning calorimetry (DSC), (v) transmission electron microscopy (TEM) and (vi) electron energy loss spectroscopy (EELS).

1.1 **Experimental details**

Starting with pure elements (Cu, Al & Zr (Crystal bar) of 99.9 wt.% purity) arc melting was used for the preparation of the CuZrAl alloy. The alloy was Suction cast in copper mold to obtain a high cooling rate and hence to form an amorphous structure. During melting, in order to avoid oxidation of the sample Ti was used as a getter. The sample was re-melted in the arc furnace four times to obtain a homogeneous sample. X-ray diffraction (XRD) (using Cu Ka radiation Pananalytical) was used to ascertain the amorphous nature of suction cast sample. Differential scanning calorimetry (DSC, SDT Q600) was performed under a flow of pure argon to determine the glass transition temperature. The heating rate in DSC was 10 K/s.

The Annealing (Heat treatment) of the alloy was performed using two kinds of samples: (i) bulk samples (aged at 200°C for 4hrs) and (ii) thin samples (aged at 200°C, 10 mins). The annealing temperature was decided based on the results obtained using DSC and the fact that there will be a melting point depression with size in thin nanoscale samples¹. The preparation of thin samples ((ii) above) is described next and these samples served as the free-standing thin films.
The thin samples (with thickness in the range of tens of nanometers) were prepared by the standard techniques used for obtaining electron transparent material for transmission electron microscopy\(^2\). The final stage of the preparation of the thin foil is twin jet electropolishing, which minimizes artifacts related to damage in the sample (as compared to a technique like ion milling). Electropolishing was carried out using a solution of 20 vol.% HNO\(_3\) and 80 vol.% CH\(_3\)OH as an electrolyte, at a temperature of -30°C and at an operating D.C. potential of 20V. Annealing of the samples is carried out in an evacuated quartz tube sealed in with titanium, which serves as a getter to minimize oxidation of the samples. Zeiss Libra 200FE (a FEG gun instrument with a resolution of 0.9Å, operating at 200 kV and equipped with an in-column EELS Filter) was used for high-resolution lattice fringe imaging (HRLFI) and Electron Energy loss Spectroscopy (EELS).

A gold standard was used for the calibration of the scale bar of the TEM and crystal size was determined by counting the number of lattice fringes. In the EELS technique, the local thickness of the sample (t) is determined using the standard log-ratio formula \(t = \lambda \ln(I_T/I_0)\)\(^3\), where \(I_0\) & \(I_T\) are the areas under the zero loss peak and the entire spectrum (total) in the EELS plot respectively and '\(\lambda\)' is the inelastic mean free path. The values of the mean free paths used in the computation of 't' are\(^4,5\): \(\lambda_{\text{matrix}} = 62.35\ \text{nm}\) and \(\lambda_{\text{crystallite}} = 62.47\ \text{nm}\) (computed using \(\lambda_{\text{Cu}} = 65.66\ \text{nm}, \lambda_{\text{Zr}} = 59.36\ \text{nm}\) & \(\lambda_{\text{Al}} = 84.52\ \text{nm}\)). The composition of the amorphous matrix is \((\text{Cu}_{64}\text{Zr}_{36})_{96}\text{Al}_4\) and that of the crystallite is \(\text{Cu}_{10}\text{Zr}_7\). This composition \((\text{Cu}_{64}\text{Zr}_{36})_{96}\text{Al}_4\) has good glass forming ability with a critical cooling rate of 40 K/s and critical diameter of 7 mm\(^6\). It is to be noted that the EELS method is gives thickness values only within an accuracy of about 20%\(^2\). The HRLFI technique is also associated with a measurement 'error bar' of at least one digital pixel (~0.032nm). Additionally, the crystallite size was measured using the distance from a bright fringe to another bright fringe. This implies that if two dark fringes are present at the ends of the 'representative integration line', there will be a error of about one fringe spacing. In small particles this could be a source of additional error.

One of the parameters used in the computation of strain energy using the finite element model is the linear misfit \(f_m\). The linear misfit can be calculated using the volume/density mismatch between the glass and the crystal. The density of the glass has been measured using the standard Archimedes principle/method\(^7\).
1.2 Theoretical and Computational Methods

1.2.1 Nucleation and Growth Rates

Crystallization of the BMG samples was carried out at 200°C. It is important to know the relative rates of nucleation and growth at this temperature. These rates can be computed using the classical nucleation theory.\(^8\) The nucleation (\(I_v\)) and growth rate (\(u\)) are as given below\(^9\).

\[
I_v = \frac{A_v}{\eta(T)} \exp \left[ \frac{-16 \pi \gamma^3}{3 \, K_b \, T \, \Delta G(T)} \right]
\]

(1)

where, \(A_v\) is a constant, \(\eta\) is viscosity, \(\Delta G\) is the difference in the Gibbs free energy difference between the glass and the crystal (per unit volume), \(K_b\) is the Boltzmann constant and \(\gamma\) is the interfacial energy.

\[
u = \frac{K_b \, T}{3 \, \pi \, l^2 \, \eta(T)} \left[ 1 - \exp \left( \frac{-n \, \Delta G(T)}{K_b \, T} \right) \right]
\]

(2)

where, \(\eta(T) = A \exp \left( \frac{B}{T - T_0} \right)\), \(l\) is the average atomic diameter and \(n\) is the atomic volume \((l = 2.668 \text{ Å} \text{ and } n = 5.549 \text{ Å}^3 \text{ for CuZrAl system})\). The Stoke-Einstein equation has been used in Eq.(2) to relate diffusivity and viscosity, for temperatures above glass transition temperature\(^8,10\).

The plot of nucleation and growth rates calculated using equations (1,2) are shown in Fig.1. It is seen from the figure that at 200°C, the rate of growth is negligible and we are in the 'nucleation dominated regime'.
An alternate method to ascertain the relative nucleation and growth rates at the heat treatment temperature, is to utilize the Johnson-Mehl-Avrami-Kolmogrov (JMAK) theory and compute the Avrami exponent using the formula:

\[
\left(\frac{dx}{dt}\right)_p = 0.37 \left(n_{\text{Avrami}}\right) \left(\frac{Q}{RT_p}\right)
\]

(3)

where, Q, T_p, E, R, \(d(x / dT)_p\) and n_{\text{Avrami}} are the heating rate (K/min), the peak temperature (K), the activation energy (J), the ideal gas constant (J/mole/K), the maximum crystallization rate and the Avrami exponent, respectively. At the heat annealing temperature of 200°C the value of the exponent (n_{\text{Avrami}}) is 4.7, thus indicating that we are in the nucleation dominated regime and hence we can be reasonably certain that the crystallites observed in the TEM are 'critical nuclei' (i.e. have not undergone any significant growth).

It should be noted that, the JMAK model used is strictly applicable only in the macroscale, wherein 'random homogeneous nucleation and isotropic growth' conditions exist. Modifications to the model for finite size samples have been presented in literature. The dimensionality of the transformation has been emphasized in some of these articles. The experimental evidence presented in the current work strongly suggest that the growth mode is not dominant (as crystallites larger than \(r_{\text{bulk}}^*\) have not been observed, with the size of most
crystallites being smaller than this value). As described in the main manuscript, thin samples were heat treated for 10 min. Before the choice of this time period for heat treatment, few samples were heat treated for a time less than 10 min and no nuclei were observed in these samples. This implies that observable nucleation commences around the 10 min mark and very little growth could have occurred in the sample heat treated for 10 min. This is consistent with literature,\textsuperscript{15,16} wherein it has been stated that the growth rate is initially slow for newly formed nuclei.

1.2.2 Surface Energy (Molecular Dynamics)

Molecular Dynamics (MD) simulations have been employed to compute the surface energy of Cu\textsubscript{10}Zr\textsubscript{7} crystal (along (100), (010) and (001) surfaces) and (Cu\textsubscript{64}Zr\textsubscript{36})\textsubscript{96}Al\textsubscript{4} bulk metallic glass (BMG). As mentioned in the main manuscript, these attempts are preliminary and a detailed study is required to understand the phenomenon of surface nucleation and the issues involved therein. Some of these issues are as follows. (i) The crystallography of the surface. (ii) Surface faceting (including breakup of the surface into ledges and kinks) and reconstructions (if any). (iii) Shape of the nuclei. (iv) Surface contamination or oxide formation, (v) Surface relief (if any) on nucleation. It may also be necessary to improve on the accuracy of the MD simulations via improvements to the model used. Depending on the specific surface under consideration, the sign of $\gamma_{\text{crystal}} - \gamma_{\text{amorphous}}$ may also change.

The MD simulations have been performed using the LAMMPS\textsuperscript{17,18} code. A vacuum of layer of 14 Å (greater than twice of the cut-off of the potential (6.5 Å)) has been created in the direction normal to the surface (i.e. [100], [010] and [001] directions), to accommodate the 'free-surface condition', maintaining compliance with the periodic boundary condition. A simulation box of 12x6x6, 6x12x6 and 6x6x12 supercells (containing 29376 atoms) of Cu\textsubscript{10}Zr\textsubscript{7} unit cell has been used to calculate the surface energy of the (100), (010) and (001) surfaces, respectively. To achieve the desired composition ((Cu\textsubscript{64}Zr\textsubscript{36})\textsubscript{96}Al\textsubscript{4}) BMG a two step process is followed: (i) Zr atoms are substituted by Cu atoms (to achieve the desired ratio of Cu to Zr, viz., 64:36) and (ii) Al atoms substituted in Cu and Zr sites of Cu\textsubscript{10}Zr\textsubscript{7} crystal. In step (ii) the process is carried out randomly, but maintaining the ratio of Cu to Zr. The final simulation box contains 18046 Cu atoms, 10155 Zr atoms and 1175 Al atoms.

The NPT (constant number of particles, pressure and temperature) ensemble within the framework of LAMMPS. To obtain (Cu\textsubscript{64}Zr\textsubscript{36})\textsubscript{96}Al\textsubscript{4} BMG, the system is heated to 2000 K followed by equilibration at that temperature for 100 picoseconds (ps). The liquid state thus
obtained is quenched to $T = 10$ K at a quenching rate 20 K/ps. The radial distribution function (RDF) of BMG has been plotted in Fig. 2. The non-crystalline nature of the 'sample' can be deduced from the RDF plot. The configuration of the atoms obtained from the MD simulations for the Cu$_{10}$Zr$_7$ crystal ([001] projection) and (Cu$_{64}$Zr$_{36}$)$_{96}$Al$_4$ BMG is shown in Fig. 3. A comparison of Fig. 3a and b parts clearly reveals the amorphous nature of the sample in Fig. 3b.

The interaction potential between atoms was treated using EAM potential as developed by Sheng et al.$^{19}$ The surface energies have been calculated using$^{20}$:

$$\gamma_s = \frac{E_{\text{slab}} - (E_{\text{coh}} \times N_{\text{atoms}})}{2A}$$

(4)

where, $\gamma_s$, $E_{\text{slab}}$, $E_{\text{coh}}$, $N_{\text{atoms}}$ and $A$ are the surface energy, total energy of the system containing two surfaces, bulk cohesive energy per atom of the system, number of atoms in the slab and area of the surface of the slab, respectively. The results of the computation of surface energy are listed in Table 1. The order of the surface energies for the three surfaces of the crystalline Cu$_{10}$Zr$_7$ phase is: (100) > (010) > (001). The average surface energy (obtained by averaging energy values obtained from the three numerical quenching experiments is also listed in the table. A point to be noted is that though the results are listed to three decimal places, the true accuracy is a function of many parameters including that of the interatomic potential used (i.e. the accuracy of the model may have to be improved in the future).

In the current work a limited number of MD simulations were carried out to illustrate the importance of surface energy of the crystal and amorphous structure in the surface nucleation process. A detailed study needs to be carried out assemble the 'full picture', which forms the scope for future work.
Fig. 2 Radial distribution function of \((\text{Cu}_{64}\text{Zr}_{36})_{96}\text{Al}_4\) after quenching (at a rate of 20 K/ps), indicating the formation of an amorphous structure.

Fig. 3 The configuration of the atoms obtained from the MD simulations: (a) [001] projection of \(\text{Cu}_{10}\text{Zr}_7\) crystal and (b) \((\text{Cu}_{64}\text{Zr}_{36})_{96}\text{Al}_4\) BMG. The amorphous nature of the 'sample' in (b) is to be noted.

Table 1. Surface energy of the crystalline \(\text{Cu}_{10}\text{Zr}_7\) phase along (100), (010) and (001) directions at 473 K. The values within parentheses are the surface energy values of crystalline \(\text{Cu}_{10}\text{Zr}_7\) at 0 K. The value obtained for the amorphous \((\text{Cu}_{64}\text{Zr}_{36})_{96}\text{Al}_4\) alloy is also listed for reference.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Surface energy at 473K (0K) ([\text{J/m}^2])</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}_{10}\text{Zr}_7)</td>
<td>1.322 (1.337) 1.230 (1.239) 1.169 (1.177)</td>
<td>1.240 (1.251)</td>
</tr>
<tr>
<td>((\text{Cu}<em>{64}\text{Zr}</em>{36})_{96}\text{Al}_4)</td>
<td>Average value obtained from the 'numerical quenching experiments' (\rightarrow)</td>
<td>1.335</td>
</tr>
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</table>
2. Results and Discussions

2.1 Experimental

Fig. 4 shows the XRD pattern obtained from suction cast (Cu_{64}Zr_{36})_{96}Al_{4} alloy. The broad peak indicates the formation of an amorphous structure. The non-existence of crystalline phases is confirmed by selected area diffraction (SAD) and high resolution transmission electron microscopy (Fig. 5). The absence of lattice fringes (Fig. 5b) and the presence of diffuse rings (only) in the SAD pattern (Fig. 5a) confirms the formation of a fully amorphous sample.

Fig. 4 XRD pattern showing the formation of amorphous structure in the suction cast (Cu_{64}Zr_{36})_{96}Al_{4} alloy.

Fig. 5. (a) (Inset) SAD pattern obtained from the suction cast (Cu_{64}Zr_{36})_{96}Al_{4} alloy showing diffuse rings. This proves the existence of the amorphous phase. (b) High resolution transmission electron microscopy micrograph showing 'salt & pepper' contrast, which is typical of the amorphous phase. The absence of lattice fringes is to be noted.
Fig. 6 shows the DSC plot obtained at a heating rate of 10 K/s, wherein the glass transition temperature ($T_g$) and the crystallization temperature ($T_x$) are marked. It is to be noted that the DSC was performed on bulk samples and in nanoscale samples the phase transformations, including melting, will occur at lower temperatures\(^1\). Annealing in both sample (bulk and thin film) were performed below the glass transition temperature marked in Fig. 6.

\[
\begin{align*}
T_g &\approx 427 ^\circ C \\
T_x &\approx 491 ^\circ C
\end{align*}
\]

Fig. 6 DSC plot used for the determination of the glass transition temperature ($T_g$).

2.2 Computational

2.2.1 Finite Element Method

It was noted in the main manuscript that two effects lead to a reduced strain energy of the system due to crystallization in thin films: (i) reduced volume of strained material and (ii) domain deformations. Domain deformations are prominent under two circumstances: (i) the crystallite is positioned closed to a free surface (as shown in Fig. 7a) or (ii) the diameter of the crystallite is large fraction of the thickness of the film (as shown in Fig. 7b).
Fig. 7 The effect of formation of a crystal on thin free-standing films: (a) near the free surface 
(r = 0.5 nm, t = 8 nm, h = 0.6 nm) and (b) at the centre of a thin domain (r = 0.7 nm, t = 1.6 nm) The 
free-surface deformations due to crystallization are to be noted.


