Ultrastable metallic glass by room temperature aging

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Glasses have markedly different stability around their glass transition temperature (T_g), and metallic glasses (MGs) are conventionally regarded as metastable compared to other glasses such as silicate glass or amber. Here, we show an aging experiment on a Ce-based MG around its T_g (~0.85T_m) for more than 17 years. We find that the MG with strong fragility could transform into kinetic and thermodynamic hyperstable state after the long-term room temperature aging and exhibits strong resistance against crystallization. The achieved hyperstable state is closer to the ideal glass state compared with that of other MGs and similar to that of the million-year-aged amber, which is attributed to its strong fragility and strong resistance against nucleation. It is also observed through the asymmetrical aging approach experiment that the hyperaged Ce-based MG can reach equilibrium liquid state below T_g without crystallization, which supports the idea that nucleation only occurs after the completion of enthalpy relaxation.

RESULTS

Structural characterization

As-cast Ce70Al10Cu30 MG was naturally stored under ambient condition for a period of ~17.7 years (6443 days). The RT aging is equivalent to aging at 0.85T_g for the Ce-based MG as shown in Fig. 1A and is only about aging at 0.45T_g for Zr-based MG. Obviously, the RT aging effect on Ce-based MG is much stronger than that of other MGs with higher T_g (see table S1). To our knowledge, such a long-time aging investigation close to its T_g of MG has never been reported before. The phase structure of the aged MG at RT was reexamined by x-ray diffraction (XRD). The XRD patterns for the rejuvenated and 17.7-year-aged Ce70Al10Cu30 MGs are given in Fig. 1B, where both exhibit a broad diffraction peak, indicating an amorphous structure.

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It is found that the heat capacity curves of the rejuvenated and 1-day-aged samples are nearly the same. To further check the short-time aging effect, the heat capacity curve of a 300-s-aged sample is also measured and presented in fig. S1 for a clear display. It is shown that the heat capacity curve of the 300-s-aged sample is almost identical to those of the rejuvenated and 1-day-aged samples. For the 10-day-aged sample, its heat capacity curve in the glass transition region starts to change compared with that of the 1-day-aged sample, and a more pronounced endothermic peak is observed. These results suggest that within the short aging time of around 1 day, the relaxation process of the present sample is still not substantially activated by RT aging. While the aging time increases to more than 1 day, the onset temperature of glass transition in the heating process rises gradually, and the endothermic peaks during the glass transition become more and more pronounced. A distinct increase of onset temperature \( \Delta T \sim 27 \text{K} \) between the rejuvenated and 6443-day-aged samples could be observed in Fig. 2A, suggesting a significantly enhanced kinetic stability. In addition, there are no perceptible distinctions of crystallization temperature \( (T_x) \) and crystallization enthalpy \( (\Delta H_x) \) of these samples for different aged states (see fig. S1), ruling out the possibility of nanocrystal precipitation during the prolonged aging process.

To further quantify the thermodynamic stability of the hyperaged Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\) MG, \( T_g \) from the cooling process and the fictive temperature \( (T_f) \) have been determined. \( T_g \) is theoretically regarded as a measure of the temperature range where vitrification occurs on cooling from the liquid state, and it is defined as the intersection of the extrapolated glass and liquid lines made on cooling (19). However, because of the supercooling issue (crystallization under nonthermodynamic equilibrium conditions) in differential scanning calorimetry (DSC) measurements, it is difficult to obtain the correct \( T_g \) value from the cooling process. Simon and co-workers have shown that the value of \( T_g \) is approximately equal to that of \( T_f \) (20). Therefore, one can directly take \( T_f \) from heating as \( T_g \) on cooling (20). The concept of \( T_f \) was first introduced by Tool (21) and was defined as “the temperature at which the glass would find itself in equilibrium if suddenly brought to it from its given state.” It is an important parameter to describe thermal history and a measure of the average level of its corresponding liquid on the PEL. Here, \( T_f \) is obtained from the intersection between the extrapolated glass and liquid lines shown in Fig. 2B, and its accuracy has been confirmed by Moynihan area matching method (see the Supplementary Materials). As the value of \( T_g \) is almost the same as that of \( T_f \), the aging time–dependent \( T_g \) for Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\) MGs is obtained (fig. S2). It is found that \( T_g \) has no change in the initial aging time below about 1 day, then starts to decrease, and lastly approaches the aging temperature \( T_t \) with increasing aging time. Obviously, the 6443-day-aged Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\) MG has a much lower \( T_g \) (\( \Delta T_g \sim 46 \text{K} \)) than those of its rejuvenated sample, demonstrating the higher thermodynamic stability.

Figure 2C shows the aging time \( t_a \)–dependent recovered enthalpy \( \Delta H_{rec} (T_{\infty}, t_a) \). When \( t_a \) extends to infinity, it can be expected that \( \Delta H_{rec} \) will reach a saturation value; eventually, the sample stays at an equilibrium glassy state, and the density of flow units (FU) would be exhausted (22). The exhaustion process of FU can be approached as \( 1/t_{\alpha} \) term, and then, the recovered enthalpy can be well depicted as \( \Delta H_{rec} (T_{\infty}, t_a) = \Delta H_{eq} [1 + (t/\beta t_{\alpha})^\beta] \), where \( \Delta H_{eq} \) is the saturation value at \( t_a \rightarrow \infty \), \( \tau \) is the characteristic relaxation time, and \( \beta \) is a fitting parameter. Considering that the aging process has not been activated initially in the short-time region below about 1 day, only the recovery

Inset in Fig. 1B displays the appearance of a hyperaged sample with a light blue oxide layer on its surface. When the oxide layer is removed by sandpaper, the surface is as bright as that of the as-cast one (18). Typical high-resolution electron microscopy image and the corresponding selected area electron diffraction pattern shown in Fig. 1C further confirm its glassy state without nanocrystals.

**Kinetic and thermodynamic stability**

Heat capacity curves for the fully rejuvenated and 1-, 10-, 49-, 79-, 325-, 1043-, 4597-, 5215-, and 6443-day-aged Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\) MGs are given in Fig. 2A, which mainly focus on the glass transition region.
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ideal glass state in the PEL. In contrast, after conventional aging at 0.95\(T_g\) for about 1 year, the \(\theta\) values for IMC (28) and PS (25) polymer glasses eventually decrease to 0.79 and 0.89, respectively, and the decrease rates of \(\theta\) upon aging time for the polymer glasses are much smaller than that of Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\) MG. The 20-million-year-old amber (4) exhibits a \(\theta\) value of 0.39 that is slightly higher than that of the hyperaged CeAlCu MG. The short-time annealing can also enhance the thermodynamic and kinetic stability of MGs (8, 31, 32). For example, the Au\(_{49}\)Cu\(_{26.9}\)Ag\(_{5.5}\)Pd\(_{2.3}\)Si\(_{16.3}\) MG annealed at 0.89\(T_g\) for 1\( \times \)10\(^5\) s can increase onset temperature by about 28 K with an enthalpy decrease of about 8.7 J/g (31), and 1 week of annealing at 0.94\(T_g\) can increase onset temperature by about 13 K with an enthalpy decrease of about 5.5 J/g for Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) (32). However, the \(\theta\) values for Au\(_{49}\)Cu\(_{26.9}\)Ag\(_{5.5}\)Pd\(_{2.3}\)Si\(_{16.3}\) (31) and Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) (32) are estimated to be 0.44 and 0.53, respectively, which are much higher than 0.32 of the hyperaged Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\). Among MGs, which have poor glass-forming ability and stability among glassy materials, our aged Ce-based bulk MG is, so far, closest to the bottom of the PEL and superstable.

**DISCUSSION**

It is known that the metastable MGs cannot be annealed for a long time near \(T_g\); otherwise, it would precipitate nanocrystals and gradually crystallize (2, 6). As shown in Fig. 4, MGs usually have poor resistance against crystallization at high temperature around \(T_g\) and short-time annealing near \(T_g\) of Zr-, Cu-, Pd-, and Al-based MGs easily leads to the precipitation of nanocrystals and crystallization. On the other hand, for long-term aging on MGs, such as CuZr MG aged for years at RT (about 0.44\(T_g\)) far below \(T_g\), the micron-scale Cu crystal precipitates, showing poor ability against crystallization (10). However, the present Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\) MG maintains a fully amorphous state after aging at relatively high temperature (~0.85\(T_g\)) for more than 17 years, showing an extremely strong resistance against crystallization. The hyperaged Ce-based MG not only is in a thermodynamic low energy state in the PEL but also has an exceptionally strong resistance against crystallization, which makes it similar to amber (see Fig. 4) (3, 4). To our knowledge, such an amber-like state is not observed for other MGs.

![Graph showing the parameter \(\theta = (T_f - T_0)/(T_g - T_k)\) used to describe how far away the glassy system is from the ideal glass state in the PEL. Aging time log \(t\) versus \(\theta\) for the vapor-deposited IMC (11), TNB (11), TL (30), ethylbenzene (EB) (47, 48), PS (26), and Teflon (13, 27) and conventionally aged Ce\(_{70}\)Al\(_{10}\)Cu\(_{20}\), Au\(_{49}\)Cu\(_{26.9}\)Ag\(_{5.5}\)Pd\(_{2.3}\)P\(_{16.3}\) (31), Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) (32), amber (3), IMC (28), and PS (25). Solid line is the best fitting result through a linear function for PS, IMC, and CeAlCu. The aging time for the vapor-deposited samples was estimated by the time taken to prepare a film of 1 nm in thickness.](image1)

![Graph showing the resistance against crystallization for MGs and amber when they are annealed at different temperature ranges for different periods of time. When the Zr-, Cu-, Pd-, and Al-based MGs are annealed near \(T_g\) for a short time (\(T_a\) is annealing temperature), nanocrystals are likely to precipitate and gradually crystallize. The Cu\(_{50}\)Zr\(_{50}\) MG crystallized after aging at RT (about 0.44\(T_g\)) for years (10). The 20-million-year-old amber shows super thermal stability against crystallization (4). The present CeAlCu MG maintains a fully amorphous state even after RT (about 0.85\(T_g\)) aging for more than 17 years and exhibits a kind of amber-like stability. For the specific data, refer to table S5.](image2)
strong resistance against crystallization has never been reported in known MGs.

Another issue of current interest is why Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG can achieve a deeper basin than most glassy materials under aging and how it accomplishes this process. It is known that glasses can be classified as either strong or fragile liquids according to the extent of viscosity that deviates from Arrhenius behavior around \( T_g \). In general, strong glasses have almost constant activation energy to relaxation and display strong landscapes consisting of a single megabasin, whereas fragile glasses exhibit variable activation energy and a diversity of well-separated megabasins (33, 34). The fragility of Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG was measured to be \(~28\) (17), which is much stronger than that of organic IMC \([-82.8 (16)]\) and PS \([-116 (16)]\). Although IMC (28) and PS (25) were aged at higher temperature around \( 0.95 T_g \), the decline rates of \( \theta \) along the aging time for fragile IMC and PS are much smaller than that of strong Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG (see Fig. 3). The relaxation rate of a glass can also be simply evaluated by its activation energy (35). According to the heating rate–dependent \( T_g \) shown in fig. S7, the activation energy of Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG is calculated to be 210.8 kJ/mol. The \( T_g \) values of PS (373 K) and IMC (314 K) are similar to that of Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG. However, the activation energies of PS and IMC were measured to be 774 and 340 kJ/mol (36, 37), respectively, which are much higher than that of Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG. Thus, the relaxation rate of Ce\textsubscript{70}Al\textsubscript{10}Cu\textsubscript{20} MG is expected to be higher than those of PS and IMC. The above scenario can be understood by the schematic diagram in Fig. 5. Upon aging or deposition, fragile glass is easily trapped in a megabasin with local minimum energy. Conversely, the structural relaxation for strong glass can be realized by continuous basin hopping until it infinitely approaches the ideal glass state. Thus, strong glass is able to keep going down to a lower energy state as long as there is sufficient aging time. The small value of \( m \approx 28 \) demonstrates that Ce-based liquids belong to the strong glass formers, and the structural origin of strong liquid behavior is closely related to the existence of partial covalent bonding formed by Ce-4f electron delocalization (38). The higher the interaction potential among the particles constituting the system, the stronger is the fragility (39). The strong covalent bonding in Ce-based MG makes it one of the strongest glass formers.

As discussed above, the strong fragility provides chances for MGs to be annealed effectively toward the ideal state. However, the crystal nucleation still could intervene the long-term aging and transform the glass to crystal. We then also consider the resistance against crystallization of the Ce-based MG. We estimate the homogeneous nucleation frequency \( I \) based on the classical nucleation theory (40, 41) and the relation between viscosity and fragility (42). The resulted homogeneous nucleation frequency \( I \) can be expressed as

\[
I = k_m \left( \eta_0 \exp \left( \frac{2 \ln 10}{3} m^2 T_{rg} \right) \right) \exp \left( -b \left( \frac{T}{T_g} \right)^{1/3} \right) T_r \left( 1 - \frac{T_r}{T_g} \right)^{-1} \tag{1}
\]

where \( k_m \), \( b \), and \( \eta_0 \) are constants; \( \alpha \) and \( \beta \) are dimensionless parameters; \( T_r = T/T_g \) is reduced temperature; and \( m_{min} \) is the minimum value of fragility. Therefore, \( I \) can be described as a function of fragility \( m \) and \( T_{rg} \) parameter, and the detailed calculation procedure of \( I \) is given in the Supplementary Materials. Figure 6 shows the nucleation frequency differences between CeAlCu and other MGs with poor stability as seen in Fig. 4. It is obvious that the nucleation frequency of CeAlCu over a wide range of temperature is much lower than that of other MGs with poor stability, demonstrating the excellent stability of CeAlCu MG against nucleation. According to Eq. 1, the variation of nucleation frequency \( I \) is mainly determined by fragility \( m \) and \( T_{rg} \) parameter. We have further analyzed the contribution of \( m \) and \( T_{rg} \) to nucleation frequency \( I \) in the Supplementary

![Fig. 5. Schematic diagram of the PEL for strong and fragile glassy system.](image)

- **A** Strong glass with a single megabasin can relax to approach the ideal glass by continuous basin hopping.
- **B** Fragile glass with diverse megabasins is easily trapped in a local megabasin.

![Fig. 6. Homogeneous nucleation frequency was calculated to evaluate the resistance of MGs to nucleation.](image)

- Reduced temperature \( (T_r = T/T_g) \)–dependent logarithm of homogeneous nucleation frequency of CeAlCu and other MGs with poor stability shown in Fig. 4. The open symbols represent the values of nucleation frequency at \( T_g \) point.
Materials, and we show that $m$ plays a dominant role in determining $I$ compared to $T_{rg}$, especially when $m$ is less than 35. Therefore, the low nucleation frequency of CeAlCu MG benefits mainly from its extremely strong fragility, whose structural origin is closely related to the existence of partial covalent bonding formed by Ce-4f electron delocalization (38).

Few experiments in polymer and selenium glasses (43, 44) have found that nucleation occurs only after the completion of the enthalpy relaxation. However, it is controversial whether the metastable solid MGs can reach equilibrium liquid state before nucleation, because the enthalpy reduction of MG is usually so small in the short-time annealing process that it is hard to measure using a conventional DSC. The present CeAlCu MG with long-aging history is suitable for studying this controversy through the signatures of the glassy kinetics developed by Kovacs (45). The first one is the isothermal aging of CeAlCu MG at RT below $T_g$ for a long enough time. As presented in Fig. 7A, if CeAlCu MG ages for a long enough time, then it can eventually reach equilibrium liquid state (yellow solid dot), where $T_f$ is equal to aging temperature $T_a$. The current 17.7-year aging has driven the rejuvenated sample to a very deep position (green solid dot), which is close to the equilibrium liquid state but not yet reached. The heat capacity curves in fig. S1 show that the exothermic crystallization enthalpy and onset temperature of crystallization are almost invariable with the aging time, demonstrating that there is no crystal growing into nanocrystals during the aging process toward equilibrium liquid state.

It has been reported that the glassy kinetics can also be observed by the asymmetrical approaching experiment developed by Kovacs (45). It is expected that the asymmetrical approaching experiment (partial aging at a low temperature and jumping to a higher temperature) can result in a crossover event where the enthalpy of the sample first rises across that of the equilibrium liquid and then falls back to that of the equilibrium liquid state due to the memory effect. Thus, an endothermic peak of enthalpy recovery followed by an exothermic peak of overshoot could be observed from the corresponding time-dependent heat flow curve. As presented in Fig. 7A, the enthalpy differences between the 6443-day-old sample and its equilibrium liquid at 348 and 353 K are 4.39 and 4.85 J/g, respectively. Here, the enthalpy curves of the rejuvenated and 6443-day-old CeAlCu MGs are taken from Fig. 2B. The 6443-day-old CeAlCu MG was heated rapidly from RT to higher temperatures of 348 and 353 K and then kept their isothermal states, as indicated by the violet and magenta dotted lines in Fig. 7A, respectively. As shown in Fig. 7B, endothermic peaks with enthalpy of 4.65 and 5.13 J/g are observed for the isothermal annealing at 348 and 353 K, respectively. These values are obviously higher than the above enthalpy differences between the 6443-day-old sample and its equilibrium liquid, indicating that the enthalpy of the sample has already crossed above that of the equilibrium liquid during the asymmetrical approaching experiments. Unfortunately, we did not observe an exothermic peak representing a decrease in enthalpy as it retreats toward the equilibrium liquid. This is probably because the overshoot enthalpy is so small that it is difficult to observe the exothermic peak by a traditional DSC instrument.

The above asymmetrical approaching experiments have demonstrated that the hyperaged CeAlCu sample has reached the equilibrium liquid state during the asymmetrical approaching experiments at temperatures of 348 and 353 K. In fig. S9, we checked their DSC curves after the annealing experiments and found that their crystallization temperature and enthalpy of crystallization had almost no change compared with the rejuvenated and hyperaged samples. Therefore, for the present CeAlCu MG, we have confirmed that no crystallization occurs during the aging process to equilibrium liquid state, which is consistent with the idea that nucleation only occurs after the completion of enthalpy relaxation.
In summary, we show the Ce$_{70}$Al$_{10}$Cu$_{20}$ MG can reach ultrastable state by aging around its glass transition temperature even for more than 17 years, which is similar to amber. The obtained hyperstable MG state has highly kinetic stability to resist crystallization and exceptional thermodynamic stability that tend toward the ideal glass state. The hyperaged CeAlCu MG can reach the equilibrium liquid state without crystallization. The ultrastability is attributed to its relatively simple energy landscape and strong resistance against nucleation.

**MATERIALS AND METHODS**

**MG preparation**

Master alloy ingots with nominal atomic percent composition of Ce$_{70}$Al$_{10}$Cu$_{20}$ was prepared by arc melting of the individual elemental components (Ce: 99.5 weight %; Al: 99.99%; and Cu: 99.99%) in a Ti-gettered ultrahigh-purity Ar atmosphere. The ingot was remelted for more than four times and suction-cast into a Cu mold to prepare bulk glassy rods of 2 mm in diameter.

**Aging and rejuvenation processes**

As-cast Ce$_{70}$Al$_{10}$Cu$_{20}$ MG was produced in 2004 (18) and stored in a zippered plastic box under ambient condition for 12.6 years (4597 days), 14.3 years (5215 days), and 17.7 years (6443 days), respectively, to reach a hyperaged state. For comparison, rejuvenated Ce$_{70}$Al$_{10}$Cu$_{20}$ MG was obtained by heating the hyperaged sample to the temperature higher than the end of glass transition temperature by 5 K at 20 K/min, holding for 60 s, and then cooling down to RT at 20 K/min under a purified nitrogen atmosphere, thus erasing the thermal history of the hyperaged sample. Rejuvenated samples were naturally aged at RT for 300 s and 1, 10, 49, 79, 325, and 1043 days, respectively.

**Amorphous structure characterization**

The amorphous structure of hyperaged and rejuvenated samples was confirmed by a D/MAzet2500V x-ray diffractrometer using 40 kV, Cu Kα radiation (λ = 1.5405 Å) at a scanning rate of 4°/min, and in the range of 10° to 90° (2θ). Specimens for transmission electron microscopy (TEM) characterization were carefully prepared by ion milling with 3-keV Ar ions at the liquid nitrogen temperature. The high-resolution TEM images were captured using a JEM-2100F instrument operated at 200 kV.

**DSC measurements**

The PerkinElmer DSC 8000 was used to perform and examine the kinetics and thermodynamics of the samples at a heating rate of 10 K/min under flowing pure argon gas at 20 ml/min to prevent possible surface oxidation. To ensure the reliability of the data, temperature and enthalpy were calibrated with an indium and a zinc standard specimen, giving an accuracy of ±0.2 K and ±0.02 mW, respectively. Heat capacity ($C_p$) of Ce$_{70}$Al$_{10}$Cu$_{20}$ MGs was obtained by comparing with that of a sapphire standard sample. Identical measurement procedures were performed on the empty pan as a baseline to be subtracted from the sample and the sapphire. The specific heat capacity of the sample can be determined by

$$C_p(T)_{sample} = \frac{Q_{sample}}{m_{sample}} - \frac{Q_{sample}}{m_{sample}} \cdot \frac{m_{sample}}{C_p(T)_{sapphire}}$$

where $m_{sample}$ is the mass of sample and sapphire; $Q_{sample}$ is the heat flow of the empty pan, sample, and sapphire; and $C_p(T)_{sapphire}$ is the heat capacity of the standard sapphire. The asymmetrical approaching experiment was performed by quickly heating the hyperaged samples from RT at 100 K/min to 348 and 353 K and then keeping the temperature there for more than 10 hours.

**Physical property measurements**

The density $\rho$ was determined using Archimedes’ principle in distilled water, and the measuring uncertainties are within 0.2%. The acoustic longitudinal ($v_l$) and transverse ($v_t$) velocities of the rejuvenated and hyperaged CeAlCu MGs were measured at RT using a pulse echo overlap method (24). The travel time of ultrasonic waves propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. The carrying frequency of the ultrasonic is 10 MHz. The Young’s modulus $E$, shear modulus $G$, bulk modulus $K$, and Poisson’s ratio $\sigma$ were derived from the acoustic velocities and density as follows:

$$G = \frac{\rho v_l^2}{2(\rho v_t^2 - 4/3\rho v_s^2)}; \quad K = \rho(v_l^2 - 4v_t^2)/(2v_l^2 - v_t^2); \quad E = 2G(1 + \sigma)$$

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abn3623

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