

APPLIED PHYSICS

Ultrafast extreme rejuvenation of metallic glasses by shock compression

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Structural rejuvenation of glasses not only provides fundamental insights into their complicated dynamics but also extends their practical applications. However, it is formidably challenging to rejuvenate a glass on very short time scales. Here, we present the first experimental evidence that a specially designed shock compression technique can rapidly rejuvenate metallic glasses to extremely high-enthalpy states within a very short time scale of about 365 ± 8 ns. By controlling the shock stress amplitude, the shock-induced rejuvenation is successfully frozen at different degrees. The underlying structural disordering is quantitatively characterized by the anomalous boson heat capacity peak of glasses. A Deborah number, defined as a competition of time scales between the net structural disordering and the applied loading, is introduced to explain the observed ultrafast rejuvenation phenomena of metallic glasses.

INTRODUCTION

Time is a critical parameter for characterizing the metastable nature of glasses. The life cycle of glasses is closely associated with time. They are “born” upon cooling glass-forming liquids fast enough to avoid crystal nucleation (1) and will age with time via hierarchical dynamic relaxations (2, 3), eventually going toward “death” with full crystallization. Intriguingly, as-quenched or aged glasses can structurally rejuvenate with external energy injection. This process, the inverse of physical aging, also depends on time allowing for configurational excitations across a complex potential energy landscape (PEL). Recently, glass rejuvenation, especially the rejuvenation of metallic glasses, has captured increasing attention due to its scientific and engineering significance (4–8).

For metallic glasses, structural rejuvenation can be achieved by reheating and faster quenching (9), thermal cycling (4), elastostatic loading (10), thermomechanical creep (7, 11), heavy plastic deformation (8, 12, 13), etc. Their mechanical and physical properties have been effectively tailored through these rejuvenation strategies (6, 14), expanding their applicability. Usually, the degree of rejuvenation can be quantified by an increase in effective fictive temperature or relaxation enthalpy upon heating. In terms of PEL (1), glass rejuvenation represents dynamic hops of a system from deep “strong” basins to shallow “fragile” ones. The underlying mechanism is nonaffine atomic displacements or strains driven by applied stress (13, 15). Using high-energy x-ray diffraction (XRD), Dmowski and co-workers (5, 7, 11, 13) have revealed that atomic strains contributing to structural rejuvenation is mainly anelastic and the anelastic strain takes place via complex local rearrangements in the atomic connectivity network from atomic to nanometer length scales.

There is a natural competition between rejuvenation (disordering) and aging (ordering). This is because, in metastable glasses, aging is

spontaneous (3, 16) and sometimes can be accelerated by proper thermomechanical processing (17, 18). Once it is balanced with the aging dynamics, structural disordering will be saturated (19), and thus rejuvenation ceases to further develop (5). For deformation-induced rejuvenation, glasses are usually subjected to a long-time loading with a stress below its yielding point but beyond a threshold (7), which effectively activates anelastic atomic strain and simultaneously avoids the acceleration of aging. However, theoretical models based on the free volume (20) or shear transformation (ST) (21) concept predict that faster loadings or higher strain rates speed up the dynamic process for structural disordering (19, 22). Thus, highly rejuvenated glasses could be accessible in this situation, since there is not enough time for aging to operate. Recently, this prediction has been validated experimentally but within the quasi-static strain-rate range (5). With further increasing strain rate, higher-level structural disordering is prone to localization into shear bands with ~ 10 -nm thickness (23–25). This extreme spatial instability, in turn, reduces the extent of rejuvenation throughout the entire sample. Naturally, a question arises: Is it possible to achieve rejuvenation of glasses at very short loading time scale but without interference from shear banding? So far, there is no experimental evidence to address this challenging question.

In this work, with a specially designed self-unloading double-target technique (26), the extreme rejuvenation of a bulk metallic glass is successfully achieved in the, to date, shortest time scale of about 365 ns, while without the introduction of shear bands. The atomic mechanism for the observed ultrafast rejuvenation points to the ST-type atomic rearrangements, as revealed previously (5, 7, 11, 13). Here, using low-temperature heat capacity measurements and theoretical analysis of boson peaks (BPs), we demonstrate how nanoscale STs induce the glass rejuvenation in terms of excess relaxation enthalpy. Furthermore, from the perspective of time scales, we propose a Deborah number to explain why the ultrafast rejuvenation takes place within a very short time window. Our work provides solid evidence for the possibility of ultrafast rejuvenation of metallic glasses and also increases the understanding of atomic mechanism behind glass rejuvenation.

RESULTS

Self-unloading shock compression technique

We use a light-gas gun facility to conduct plate impact experiments with a specially designed flyer target configuration, as schematized

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in Fig. 1A. The bulk metallic glass is adopted as both flyer and target materials. The target is separated two parallel touching plates (front and back). Such a double-target technique was previously developed to study the dynamic damage of the back target (26). In this work, however, we focus on rejuvenation of the front target. Driven by a projectile, the flyer impacts the front target at an initial velocity V_0 . Further information on the experiment is available in Materials and Methods. Figure 1B is the t - X (time versus distance) diagram that illustrates how a stress wave propagates in the flyer and targets during a typical plate impact experiment. Before impact, both flyer and targets reside in a static, stress-free state (0). Upon impact, a forward compressive wave C_1 and a backward compressive wave C_2 are generated simultaneously and then propagate into the targets and the flyer, respectively. Because of the C_1 , the front and back targets successively enter a compressive stress state (2). For the front target, the duration Δt of the state (2) is determined by the release (unloading) wave R_2 that is the reflection of C_2 at the free surface of the flyer. The C_1 also reflects a release wave R_1 at the free surface of the back target. The interaction of the R_1 and R_2 brings the back target into a tensile stress state (5) where a spallation may well take place (27, 28). Such a stress wave technique allows the front target to undergo a shock compression (C_1) and sudden self-unloading (R_2). The front target, except for the region close to its free edge, resides in a one-dimensional (1D) strain and a triaxial stress state (see section S2). Therefore, the C_1 propagates approximately in 1D with a strong circumferential constraint of deformation. These strategies rule out the possibility of the shear band instability in the front target where the metallic glass is expected to deform homogeneously. According to the Hugoniot data of this glass (29), the duration Δt of the compressive wave C_1 is almost fixed to be less than 400 ns, but the stress amplitude σ_p of the C_1 depends on the particle velocity (PV) in state (2).

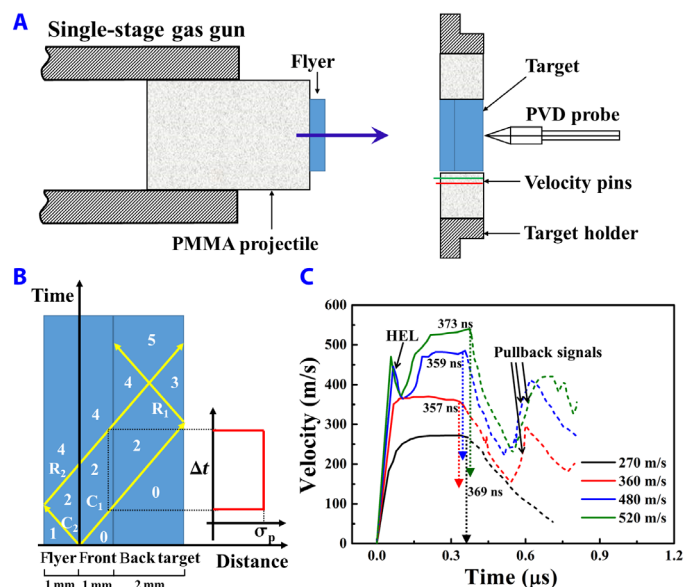


Fig. 1. Self-unloading shock compression technique. (A) Schematic of the light-gas gun-driven plate impact experimental configuration. PMMA, poly(methyl methacrylate). (B) Time versus distance diagram that illustrates the stress wave propagation in the flyer and targets. (C) FSV history of the front (solid lines) and back (solid + dashed lines) targets under different initial impact velocities of the flyer. Hugoniot elastic limit (HEL) is the dynamic yield strength of materials.

With the developed technique, four plate impact experiments were performed at initial impact velocities $V_0 = 270, 360, 480,$ and 520 m/s, respectively. The nominal strain rate correspondingly ranges from 2.7×10^5 to 5.2×10^5 s $^{-1}$. For each impact, the time evolution of PV in the targets can be obtained by measuring the free-surface velocity (FSV) of the back target, which is shown in Fig. 1C. Following the impact, the front and back targets have the same wave profile until the former rapidly separates from the latter because of the unloading effect of the release wave R_2 (Fig. 1B). Therefore, the front target only experiences a plateau-shape PV history (the solid lines), while the back target is subjected to the entire shock process (the solid and dashed lines). As designed, a sudden compression-and-unloading process is satisfactorily achieved in the front target where no PV signals of shear banding are detected. The absence of shear banding is also evidenced by the estimated shock strain with relatively small values (see table S1). The duration Δt of the compression wave C_1 is measured to be about 365 ± 8 ns, within the experimental error range. Depending on the plateau values ($\approx V_0$), the amplitudes σ_p of the C_1 are calculated to be about 4.33, 5.78, 7.71, and 8.35 GPa. With increasing V_0 or σ_p , the PV profile changes from the single-wave to the typical two-wave structure across a Hugoniot elastic limit (HEL) of about 7.16 GPa. This indicates a transition from the elastic to elastoplastic deformation of the targets, permitting one to examine the ultrafast rejuvenation of a glass across its dynamic yielding. Moreover, at $V_0 = 360, 480,$ and 520 m/s, we observed the “pullback” behaviors in the PV profiles of the back target, which is the typical signal of the spallation damage (27, 28) but beyond the focus of this study.

Ultrafast extreme rejuvenation of metallic glasses

For the front targets after shock compression, the rejuvenation extent of metallic glasses is quantified in terms of their excess relaxation enthalpy ΔH_{rel} before the glass transition. As shown in Fig. 2A, the ΔH_{rel} of 0.423 kJ/mol in the as-cast glass remarkably increases by about 68 to 212% to 0.712 to 1.321 kJ/mol in the shock-compressed ones. The higher the impact velocity V_0 or the shock stress σ_p is, the larger the ΔH_{rel} of the rejuvenated glasses (Fig. 2B). There is a more rapid increase of the ΔH_{rel} across the HEL, implying that the global dynamic yielding is more conducive to glass rejuvenation. The observed rejuvenation jump is expected to be mainly induced by anelastic deformation, where the adiabatic heating due to plasticity should play a minor role. This is evidenced by the direct correlation between the estimated shock strain and the ΔH_{rel} (see fig. S2), consistent with Fig. 2B. The highest $\Delta H_{rel} = 1.321$ kJ/mol is achieved at $V_0 = 520$ m/s or $\sigma_p = 8.35$ GPa, which is comparable to the extreme value ($\Delta H_{rel} = 1.130$ kJ/mol) recently reported by Pan *et al.* (8) in a notched Zr-based glass triaxial compressed to 40% nominal strain. An extensive comparison between this study and previous reports (4, 8, 10, 15, 30–40) (see table S2) is summarized in Fig. 3 by plotting the ΔH_{rel} of rejuvenated glasses as a function of the time scale of various rejuvenation methods. Obviously, the present shock compression technique can rejuvenate the glass into an extremely high-enthalpy state when the shock stress σ_p exceeds the HEL of glass. Note that this extreme $\Delta H_{rel} = 1.321$ kJ/mol is still below a few values reported previously (39, 40). We therefore believe that the present glasses could be further rejuvenated to higher ΔH_{rel} if the impact velocity is further increased. The extreme rejuvenation is achieved within the exceptionally short time scale of 365 ± 8 ns. This time scale is much less than those of other rejuvenation methods by about 10 orders of magnitude.

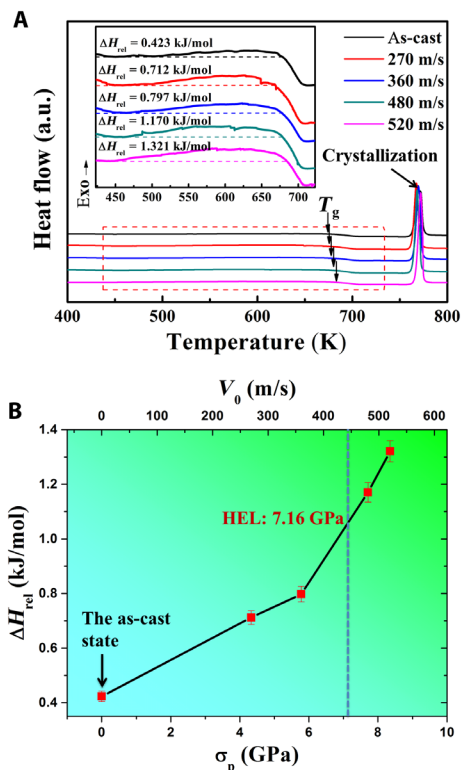


Fig. 2. Ultrafast extreme rejuvenation of metallic glasses. (A) Differential scanning calorimetry curves. Inset shows the close up of the excess enthalpy of relaxation below T_g , i.e., the region highlighted by the dashed rectangle. a.u., arbitrary units. (B) Excess relaxation enthalpy versus peak stress (bottom x axis) and initial impact velocity (top x axis) of the shock compression.

Microstructure of rejuvenated glasses

Figure 4 (A to D) presents the typical high-resolution transmission electron microscopy (HRTEM) images of the ultrafast-rejuvenated glasses at $V_0 = 270, 360, 480,$ and 520 m/s, respectively. Long-range disordered, maze-like packing of atoms is observed, which is consistent with the halo ring selected-area electron diffraction (SAED) patterns (insets). Through the quantitative analysis of these SAED patterns (see section S4) (41, 42), we obtain the diffraction intensity profiles $I_{red}(Q)$ for different rejuvenated states (see fig. S3). The first peak position Q_1 of $I_{red}(Q)$ indicates the average interatomic spacing (43, 44), which should directly link the atomic free volume in terms of the excess relaxation enthalpy ΔH_{rel} . This is confirmed by the observed inversely linear correlation between the ΔH_{rel} and the Q_1 (see fig. S4). The Fourier transform of the $I_{red}(Q)$ leads to the atomic radial distribution function (RDF) $G(r)$ in real space, as shown in Fig. 4E. This result indicates that the structural disordering behind glass rejuvenation involves complicated atomic rearrangements at length scales extending to nanometers. As compared with the as-cast state, the extremely rejuvenated glasses have a higher concentration of free volume at the atomic scale and simultaneously show larger-size structural disordering at the nanoscale. The multi-scale structural disordering can be also indicated by measuring the mechanical hardness of these rejuvenated glasses (see section S5). An inversely linear correlation between the ΔH_{rel} and the hardness is observed, as shown in fig. S5B.

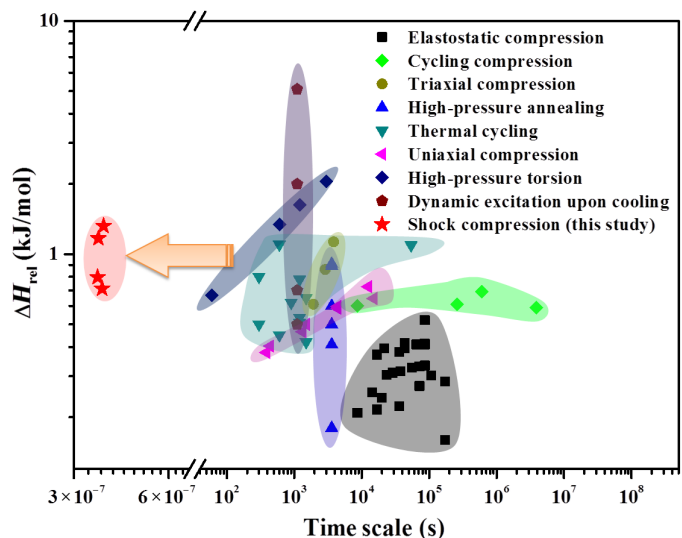


Fig. 3. Excess relaxation enthalpy of rejuvenated metallic glasses as a function of the time scale of various rejuvenation methods, including shock compression in this study, elastostatic compression (10, 15, 30–34), cycling compression (35), triaxial compression (8), high-pressure annealing (36), thermal cycling (4, 37), uniaxial compression (38), high-pressure torsion (39), and dynamic excitation upon cooling (40).

Boson heat capacity peak of rejuvenated glasses

The rejuvenated glasses are further characterized by their vibrational dynamics. At terahertz frequencies, disordered glasses universally display an excess of vibrational modes over the Debye level, forming the BP (45). These extra vibrations contribute to the enhancement of the low-temperature T specific heat capacity C_p as compared to the Debye T^3 law, and thus the BP can be visible as a maximum in the plot of C_p/T^3 versus T at temperatures of ~ 10 K. For metallic glasses, we should subtract the electronic part C_p^{ele} from the low-temperature C_p to make the BP more pronounced. The electronic $C_p^{ele} = \gamma T$, where the Sommerfeld coefficient γ can be determined by a standard procedure (see section S6 for more details) (46). Figure 5A plots $(C_p - \gamma T)/T^3$ versus T for the as-cast and shock-induced rejuvenated glasses. The BPs appear as maxima of $(C_p - \gamma T)/T^3$ at ~ 10 K, showing a positive correlation with the rejuvenation of metallic glasses. With heavier rejuvenation at higher V_0 , the BP becomes stronger. At the same time, its position T_{BP} moves to lower temperatures and shows an inversely linear correlation with the ΔH_{rel} (see Fig. 5B).

DISCUSSION

Using the ad hoc designed plate impact experiments (see Fig. 1), we successfully apply a constrained 1D self-unloading shock compression on the metallic glasses. The duration of the shock is fixed to be about 365 ± 8 ns. The shock stress amplitude ranges from 4.33 to 8.35 GPa across the HEL (7.16 GPa), i.e., the dynamic yield strength of the studied glass. The shock compression can rapidly rejuvenate the as-cast glass into extremely high-enthalpy states, which is controlled by the applied shock stress (see Fig. 2). The ultrafast rejuvenation of glasses is associated not only with the creation of atomic free volume (the increase of ΔH_{rel}) but also the structural rearrangements of atoms occurring at the nanoscale (see Fig. 4). The atomic mechanism revealed

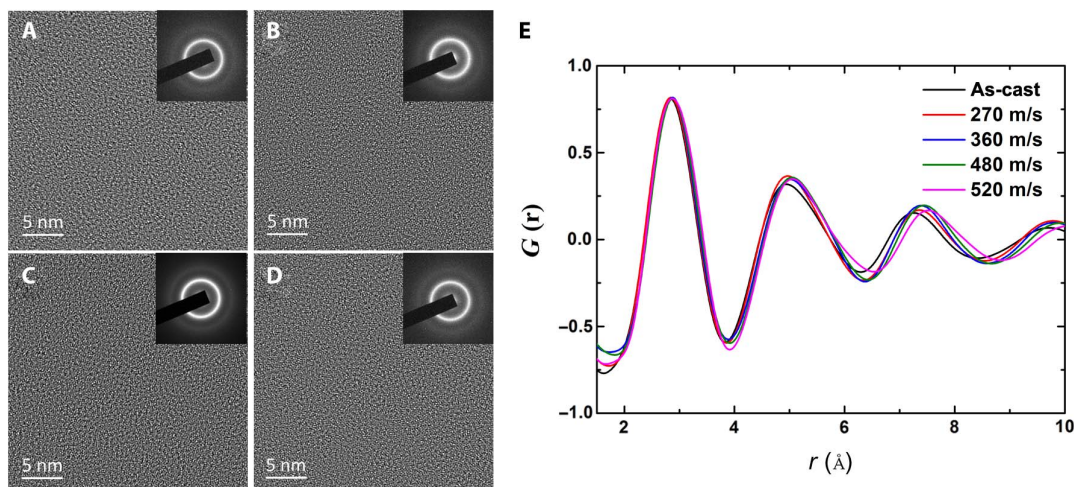


Fig. 4. Structural characterization of the rejuvenated metallic glasses. (A to D) HRTEM images of the rejuvenated states under initial impact velocities of 270, 360, 480, and 520 m/s, respectively. (E) RDFs of the as-cast and rejuvenated glasses deduced from the SAED patterns inserted in (A) to (D) and fig. S1B.

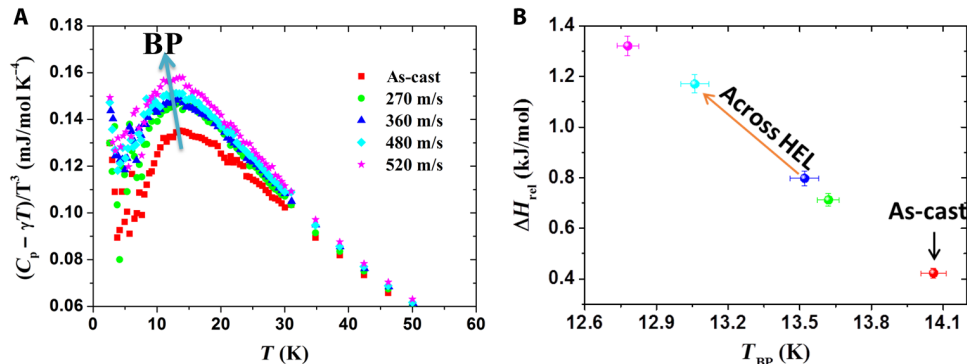


Fig. 5. BPs of the as-cast and rejuvenated metallic glasses. (A) The plot of $(C_p - \gamma T)/T^3$ versus T in the temperature interval of 2 to 50 K. (B) Correlation between the excess relaxation enthalpy and the BP temperature.

here agrees with the finding of Dmowski and co-workers (5, 7, 11, 13) that structural changes behind glass rejuvenation involve extensive atomic rearrangements beyond a simple generation of free volume at the atomic scale. The nanoscale structural rearrangements are linked to the action of STs, which can interact with the free volume dynamics (19, 22, 47).

The measured boson heat capacity peak (Fig. 5) provides a good probe of STs that underpin the glass rejuvenation, in which the frequency ω_{BP} of BPs is a key parameter. Recent studies (48, 49) have shown that the ω_{BP} coincides with the Ioffe-Regel (IR) limit of transverse phonons. At this limit, the mean free path of phonons becomes similar to their wavelength λ_{IR} , causing substantial scattering of the phonons and producing quasi-localized modes to make up the BP. The eigenvectors of BP modes tend to spatially localize in some defective regions where relaxations or STs preferentially take place (50–52). This explains the observed positive rejuvenation-BP correlation (Fig. 5). Meanwhile, the λ_{IR} measures the characteristic size of the quasi-localized modes, which can be estimated as $\lambda_{\text{IR}} \approx 2\pi c_T/\omega_{\text{BP}}$. The calculation of ω_{BP} is provided in Materials and Methods. The calculated λ_{IR} values range from 1.524 to 1.735 nm (see table S2), depending on the rejuvenation degree of glasses. These values agree well with the

characteristic sizes of STs (53, 54), which confirms the ST-related nature of the glass rejuvenation (5). Furthermore, we plot the relaxation enthalpy ΔH_{rel} as a function of the λ_{IR} , which is shown in Fig. 6A. It is seen that the ΔH_{rel} increases with λ_{IR} , indicating that larger-size STs facilitate the creation of atomic free volume during the glass rejuvenation. Such a multiscale structural disordering speeds up across the HEL (i.e., the dynamic yielding strength) of glasses. This is consistent with Fig. 2B.

Last, we introduce a dimensionless Deborah number to study the temporal possibility of the ultrafast rejuvenation of glasses. The Deborah number is defined as (24) $De = t_i/t_e$, where t_i stands for the internal structural response time under loading and t_e for the macroscopic imposed time of external loading. The magnitude of De provides a useful indication whether a material behaves in a more fluid-like or solid-like manner. In the present case of the glass rejuvenation, we consider t_i as the characteristic time scale of the underlying structural disordering and t_e as the shock pulse of about 365 ns. In shock experiments, the loading rate effect is reflected by the duration of shock stress, which is very different from the quasi-static or dynamic loading where the rising time of stress or strain is adopted. If $t_i < t_e$, i.e., $De < 1$, then the glass rejuvenation will probably

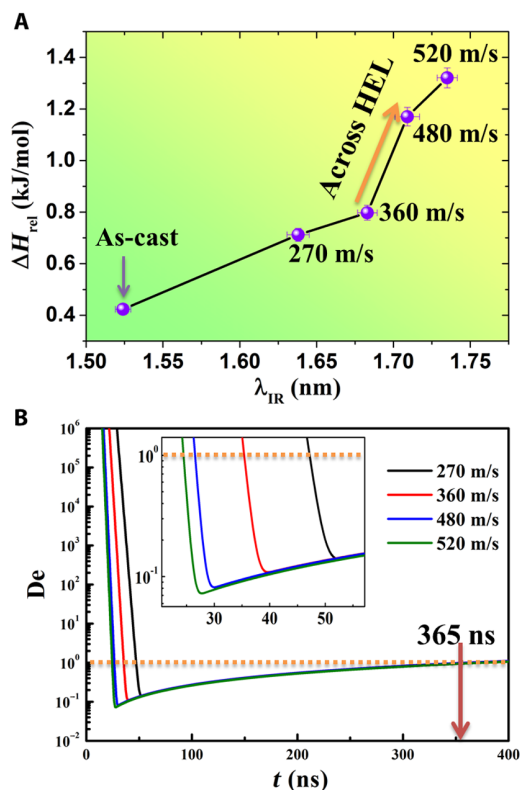


Fig. 6. Spatiotemporal mechanism for ultrafast extreme rejuvenation of metallic glasses. (A) Relaxation enthalpy ΔH_{rel} as a function of λ_{IR} . (B) Deborah number De versus loading time at different shock velocities.

take place. However, in the opposite case, i.e., $De > 1$, there is not enough time for the occurrence of structural rejuvenation. The t_i can be calculated by the Maxwell equation $t_i = \eta/G$, where η is the dynamic viscosity. Under the present high-strain rate loading, the time evolution of η is calculated on the basis of a constitutive model of amorphous plasticity developed previously by Jiang *et al.* (19). In this model, the interaction between STs and free volume dynamics is taken into account, which well captures the structural mechanism for the glass rejuvenation. Meanwhile, the decrease of G induced by the rejuvenation can be calculated on the basis of the universal evolution of boson heat capacity peaks observed in various metallic glasses (46). Figure 6B shows the variations of Deborah number De with loading time at different initial impact velocities. It is found that the De rapidly decreases from a very high value to about 0.1 within several tens of nanoseconds (see inset of Fig. 6B). Higher impact velocities lead to lower De at earlier times, indicating the possibility of faster structural rejuvenations. The underlying mechanism is that, at higher impact velocities, higher levels of stress can be reached faster, which activates STs and free volume creation more rapidly (see fig. S8). After yielding, the structural dynamics slows down, but $De < 1$ is still satisfied until the end of the shock pulse (~ 365 ns). The undershoot of De evident in Fig. 6B mirrors the well-known overshoot, which is universally seen in the stress-strain curves of glasses (19).

CONCLUSIONS

In summary, we successfully achieve the ultrafast and extreme rejuvenation of metallic glasses with a specially designed self-unloading

shock compression technique. The degree of the glass rejuvenation increases with increasing shock stress at the fixed shock pulse of ~ 365 ns, showing a surge of relaxation enthalpy across the dynamic yielding of the glass. The rejuvenated metallic glasses are extensively characterized in terms of their thermodynamics, multiscale structures, and vibrational dynamics through boson heat capacity peaks. It is revealed that the nanoscale ST-mediated free volume creation acts as the physical mechanism for the observed shock-induced rejuvenation of metallic glasses. The present results are of significance not only for the understanding of short-time glass dynamics but also for the promising application of metallic glasses in high-velocity impacts.

MATERIALS AND METHODS

Material preparation and characterizations

The bulk metallic glass, $Zr_{55}Cu_{30}Ni_5Al_{10}$ (atomic %), in this study was prepared by suction casting from master alloys ingots to a water-cooled copper mold in an arc furnace. The structure of the as-cast glass was confirmed by XRD with Cu $K\alpha$ radiation and HRTEM (JEM-2100F, JEOL, operated at 200 keV) (see fig. S1). The density ρ of glass was measured to be 6.76 g/cm³ by Archimedeian method. The longitudinal and transverse wave speeds (c_L and c_T) were determined to be 4750 and 2150 m/s, respectively, via ultrasonic pulse-echo technique. The elastic constants such as shear modulus G , Young's modulus E , and Poisson's ratio ν can be calculated on the basis of the measured density and wave speeds.

Plate impact experiment

The 101-mm bore single-stage light-gas gun was used to conduct the plate impact experiments. The schematic of the experimental configuration is shown in Fig. 1A. The flyer and the front and back targets were disk plates with the thicknesses of 1, 1, and 2 mm, respectively, along the shock direction, and their diameter was all 36 mm. A low-impedance poly(methyl methacrylate) project carrying the flyer was driven by the high-pressure nitrogen to impact the front target. The rear end of the projectile had a sealing O-ring and a Teflon key that slid in a key way inside the gun barrel to prevent any rotation of the projectile. A pair of coaxial electric probes was embedded in the epoxy holder of targets to record the initial velocity of impact. Both the flyer and the targets were carefully finished in parallel to ensure the generation of plane waves after normal impact. The stress amplitude of a shock wave can be calculated through the relation $\sigma_p = \rho c_L V_p$, where V_p is the material PV. A photonic Doppler velocimetry system was adopted to measure the FSV ($\approx 2V_p$) of the back target. All targets were soft-recovered by decelerating into several stages of cotton drags. Shear bands or cracks were not observed in the recovered front targets.

Structural and thermal characterizations

For the post-impact glasses, structural analyses were performed by HRTEM and SAED. The thermal response of glasses was investigated with differential scanning calorimetry (DSC; TA Q2000): heating the glass up to 823 K in a pure argon atmosphere at a heating rate of 20 K/min and subsequent cooling to room temperature at the same rate. The specific heat capacity was measured under high vacuum conditions with a Quantum Design physical property measurement system (PPMS), which allows cooling down to 2 K with a liquid helium system. For comparison, both DSC and PPMS measurements were also performed on the original as-cast glasses.

Calculation of the BP frequency

The total specific heat capacity C_p of the glass is expressed as

$$C_p = C_p^{ele} + n_D C_p^{Debye} + n_q C_p^{quasi} \quad (1)$$

where n_D and n_q represent the Debye and quasi-localized contributions per mole, respectively. The Debye term C_p^{Debye} is

$$C_p^{Debye} = 9R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^\xi}{(e^\xi - 1)^2} d\xi \quad (2)$$

where R is the gas constant and θ_D is the Debye temperature that can be obtained by fitting the C_p data below 8 K (see fig. S6). The quasi-localized term C_p^{quasi} can be written as

$$C_p^{quasi} = 3R \int_0^{\omega^*} \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} g_q(\omega) d\omega \quad (3)$$

where \hbar , k_B , and ω are the Planck constant, the Boltzmann constant, and the frequency, respectively. Considering the hybrid nature of quasi-localized and Debye modes (55), the upper limit ω^* of integral was reasonably chosen as the Debye frequency $\omega_D = k_B \theta_D / \hbar$. The $g_q(\omega)$ is the vibrational density of states or the frequency distribution of the quasi-localized modes, which is the key to determine the C_p^{quasi} and resultant BP. It is well accepted that the spatial heterogeneity of elastic modulus incurs the emergence of quasi-localized modes (48, 49, 56). Shear modulus and BP intensity are strongly correlated (46, 57). We therefore examined the distribution of elastic modulus in metallic glasses (58, 59) and found that the data can be well fitted by a formula analogous to the Planck's law of black-body radiation. Therefore, we assumed that the quasi-localized modes $g_q(\omega)/\omega^2$ normalized by the Debye law obeys a Planck-like distribution

$$g_q(\omega)/\omega^2 = \frac{\varphi \omega^3}{e^{\ell\omega} - 1} \quad (4)$$

where the parameter $\varphi = 5.572 \times 10^{-15}$ is determined by the high-temperature limit ($3R$) of C_p and the ℓ can be determined by the position T_{BP} of the C_p -BP. It is noticed that $\lim_{\omega \rightarrow 0} g_q(\omega) \sim \omega^4$, which is consistent with the statistic law of low-frequency quasi-localized modes revealed recently (60). Uniting Eqs. 1 to 4, both the C_p and $(C_p - \gamma T)/T^3$ data were satisfactorily fitted, and the contributions from the electronic C_p^{ele} , the Debye C_p^{Debye} , and the quasi-localized vibrational C_p^{quasi} can be calculated, respectively. The results are shown in fig. S7, and all relevant parameters are listed in table S3. According to the measured T_{BP} , the frequency ω_{BP} of BP can be determined by $\partial[g_q(\omega)/\omega^2]/\partial\omega|_{\omega_{BP}} = 0$.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/8/eaaw6249/DC1>

Section S1. Structural characterizations of the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass
 Section S2. Stress and strain state analysis for the front target
 Section S3. Experimental data about rejuvenation of metallic glasses from literature
 Section S4. Diffraction profile analysis of SAED patterns

Section S5. Nanoindentation measurements and analyses
 Section S6. Determination of the electronic C_p contribution
 Section S7. Theoretical fitting of low-temperature heat capacity data
 Section S8. Calculations of the constitutive behaviors of metallic glasses
 Table S1. The triaxial stress and the 1D strain state in the front target under different impact velocities.
 Table S2. Relaxation enthalpy of metallic glasses by various rejuvenation methods.
 Table S3. All parameters related to the BP analyses.
 Fig. S1. Structural characterizations of the as-cast $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass.
 Fig. S2. Correlation between excess relaxation enthalpy and calculated shock strain.
 Fig. S3. Diffraction profiles of SAED patterns.
 Fig. S4. Correlation between excess relaxation enthalpy and first peak position of reduced diffraction profile.
 Fig. S5. Nanoindentation measurements on the as-cast and rejuvenated glasses.
 Fig. S6. Determination of the electronic contribution to low-temperature specific heat capacity.
 Fig. S7. Theoretical fitting of low-temperature heat capacity data.
 Fig. S8. Constitutive responses of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass under the present high-strain rate loading.

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