Significantly enhanced memory effect in metallic glass by multistep training

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The state of metastable equilibrium glass can carry an imprint of the past and exhibit memory effect. As a hallmark of glassy dynamics, memory effect can affect glassy behavior as it evolves further upon time. Even though the physical picture of the memory effect has been well studied, it is unclear whether a glass can recall as many pieces of information as possible, and if so, how the glass will accordingly behave. We report that by fractionizing temperature interval, inserting multistep aging protocols, and optimizing the time of each temperature step, i.e., by imposing a multistep “training” on a prototypical Pd40Ni10Cu30P20 metallic glass, the memory of the trained glass can be significantly strengthened, marked by a pronounced augment in potential energy. These findings provide a new guide for regulating the energy state of glass by enhancing the nonequilibrium behaviors of the memory effect and offer an opportunity to develop a clearer physical picture of glassy dynamics.

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I. INTRODUCTION

The metastable glass undergoes a continuous structural relaxation (also called physical aging) to states of lower energy and enthalpy at finite temperatures below glass transition temperature, \( T_g \). In contrast to physical aging, memory effect \([1,2]\) breaks the monotonic decrease in enthalpy or volume during structural relaxation and creates an increase to a maximal value in enthalpy or volume with time followed by a subsequent decrease toward the lower energy state. As illustrated in Fig. 1, if the glass is first preannealed at \( T_0 \) for time \( t_0 \) and then annealed at \( T_1 \) for time \( t_1 \). Instead of following the monotonic aging path (see the blue curve), at \( T_1 \), the glass preannealed at \( T_0 \) first neglects its “future” but recalls its past (see the red curve). This phenomenon reflects that a glass can remember its previous high-energy state.

Memory effect has been noticed for decades and appears to be a common feature of many out-of-equilibrium systems such as various glasses \([3–5]\), granular materials \([6]\), and even disordered mechanical system \([7,8]\). The memory is associated with heterogeneous local dynamics and connected to a very broad range of relaxation units which carry individually the information during relaxation. This ubiquity, reflecting their history-dependent behaviors, suggests that there exists a unified principle that governs the dynamics. Exploring memory effect not only yields insights into the internal structure of glassy materials and their dynamics but also is of technological importance for MGs because their thermodynamic \([9]\), mechanical \([10,11]\), and physical properties \([12,13]\) all shift accordingly as they evolve with time. Recent investigation \([14–16]\) suggests that memory effect of MGs originates from the mismatch of thermal expansion coefficient between neighboring local regions because they achieve different degrees of relaxation during preannealing. Upon change of annealing temperature, this mismatch creates internal stresses that can result in reactivation of previously relaxed local atomic structures accompanied with increase of internal energy. This motivates us to consider whether this reactivation can be memorized by a glass through memory effect and, if so, how will the glass behave with such reactivation. In other words, whether a metallic glass (MG) can recall as many pieces of information as possible and how to enhance its memory capability through appropriate thermal treatment.

In this work, we demonstrate that by fractionizing the temperature interval and imposing a multistep aging protocol, memory effect of a MG can be significantly enhanced by appropriate “training.” As a consequence, the tendency to approach equilibrium upon aging can be reversed in the MG, and the enhancement of energy manifested by memory effect can be retained. Furthermore, the enhanced memory effect enables us to modulate the energy states of the MG in a broad range from far away to close to equilibrium. These findings provide an opportunity to develop a clear physical picture and in-depth understanding of dynamics in nonequilibrium systems.

II. EXPERIMENTAL

Pd40Ni10Cu30P20MG rods of diameter of 2 mm and length of 40 mm were fabricated by arc-melting the master alloy followed by suction cast into a copper mold. The amorphous nature of the rods was confirmed by x-ray diffraction. Disks of 30 mg in mass for thermal analysis were cut from the glass rods. A Perkin-Elmer differential scanning calorimeter DSC 8000 was used for aging experiments and thermal analysis. To ensure the glass samples have comparable and reproducible initial thermal state before any further tests, the as-prepared disks were first heated at 40 K/min from room temperature (RT) to 608 K into the equilibrium liquid state where they were held for 3 min, followed by a rapid cooling back to RT at a rate of 80 K/min within DSC. An up-scan from RT to 608 K at 40 K/min was then performed to obtain the heat flow curve for the initialized glass state. \( T_g \) of the initialized Pd40Ni10Cu30P20MG is 578 K determined by the extrapolated onset of the heat capacity curve, as indicated in Fig. 2(a).
Preannealing was conducted within DSC by cooling the initialized glass from 608 K to \(T_0 = 543\) K at rate of 80 K/min for 30 min right after the initialization scan. Then, the sample was heated at a rate of 40 K/min to various aging temperatures (558, 559, 560, 561, 562, and 563 K) for the different aging times \(t\), followed by cooling the sample back to RT at 80 K/min. A final up-scan at a rate of 40 K/min was carried out to obtain the heat flow curve for the aged sample. More technical details about the MG multistep training procedures can be seen in the Supplemental Material [17]. XRD measurements confirmed that the aged samples remained fully amorphous [17].

### III. RESULTS AND DISCUSSIONS

Figure 2(a) shows heat flow curves of the MGs aged for different times at 558 K after preannealing at \(T_0 = 543\) K. These curves were determined by DSC upon an up-scan from RT to 608 K at 40 K/min. In comparison with the initialized state, obvious endothermic peaks can be seen in all the curves of aged glasses due to enthalpy recovery, which is ascribed to the creation of excess volume necessary for glass-to-liquid transition [18]. However, the change in peak height is not monotonic, i.e., the peak height first decreases and then increases with aging time \(t\). To better reveal the tendency, we present in Fig. 2(b) the enthalpy change relative to equilibrium \(\Delta H\) plotted against different aging time \(t\). The time reaching the maximum \(\Delta H\) is \(t_p = 6.4\) min. The green solid line is drawn as a guide for the eyes.

The fact that glass behavior is dependent on thermal history [21,22], together with the apparent increase in enthalpy shown in Fig. 2(b) suggests that further enhancement of energy state can be achieved if aging is ceased before memory effect diminishes. To “memorize” the enthalpy increase to a larger extent for the glass, we next raise aging temperature from 558 K to 563 K after annealing for \(t_p = 6.4\) min where the change of enthalpy reach the peak value. Figure 3(a) displays the evolution of \(\Delta H\) with aging time at 563 K. For comparison, the \(\Delta H\) versus \(t\) curve at 558 K is replotted in Fig. 3(a). As can be seen, instead of decrease in enthalpy with the prolonged aging time at constant temperature [see the black line in Fig. 3(a)], \(\Delta H\) remains to evolve in a nonmonotonic fashion and the raise at the annealing temperature results in another peak manifested by the memory effect. To “memorize” the enthalpy increase to a larger extent for the glass, we next raise aging temperature from 558 K to 563 K after annealing for \(t_p = 6.4\) min where the change of enthalpy reach the peak value. Figure 3(a) displays the evolution of \(\Delta H\) with aging time at 563 K. For comparison, the \(\Delta H\) versus \(t\) curve at 558 K is replotted in Fig. 3(a). As can be seen, instead of decrease in enthalpy with the prolonged aging time at constant temperature [see the black line in Fig. 3(a)], \(\Delta H\) remains to evolve in a nonmonotonic fashion and the raise at the annealing temperature results in another peak manifested by the memory effect. Relative to the well-aged state, the peak \(\Delta H\) value is remarkably higher, and an increase \(\sim 25\%\) is obtained, which is more than twice that without additional temperature raise. The results shown in Fig. 3(b) not only indicate that tailoring thermal history of
a MG followed by aging at a higher temperature can prevent further aging of the glass, but also that enhanced memory effect can be gained. Furthermore, the results shown in Fig. 3(a) imply that the occurrence of peak on $\Delta H$ versus $t$ curve is independent of specific annealing temperature raised to, but whether the glass undergoes a temperature change while aging. These inspire us to consider that by annealing the glass in a stepwise fashion, the peak arising from memory effect of a glass might be pushed upwards further, and a maximal enhancement can be achieved if the temperature jump is designed at the aging times when $\Delta H$ peaks appear.

To verify the hypothesis, we keep the temperature range unchanged, in which annealing is carried out, i.e., from 558 to 563 K, but take a stepwise pattern of temperature jumps. For example, once $\Delta H$ reaches the peak at 558 K, we insert an additional aging process at 560 K, and then raise the temperature to 563 K when enthalpy peak is identified at 560 K. The evolution of $\Delta H$ against time for the final 563 K aging is displayed in Fig. 3(b). Again, apparent nonmonotonic fashion of $\Delta H$ evolvement can be seen. More importantly, with this additional aging, the peak value of $\Delta H$ increases, and the obtained increase in enthalpy is 30% compared with the well-aged state and more than that by a single temperature jump. The results clearly demonstrate how the training can enhance the memory effect and influence the thermodynamic energy states of a glass. The enthalpy recovery curves are shown in Fig. 4(a). We can regard the protocol of enthalpy recovery through memory effect as the training of MG. If we define that one temperature jump corresponds to one time of training, as the times of training increase, a monotonical decrease in the height of enthalpy recovery peak can be observed. This indicates that there is more energy stored in the glass $[19,23]$. By integrating heat capacity, the enthalpy of the glasses can be obtained $[24]$, as displayed in Fig. 4(b). For clarity, we only present the enthalpy for the glasses that reach the peaks on the $\Delta H$ versus $t$ curves for each 563 K aging. Up-shift of the enthalpy curves is evident when the glass is trained for more times in the temperature range from 558 to 563 K. This is a strong indication that the enhanced memory effect can push a glass to higher levels in potential energy landscape. To more directly evaluate the energy state for each glass, we used TNM model to calculate fictive temperature $T_f$ $[25,26]$. The inset of Fig. 4(b) displays the $T_f$ as a function of training times, along with that for the well-aged (0 training time) and initialized glass. As can be seen, the six-times-trained glass exhibits considerably larger $T_f$. This unambiguously demonstrates that the glass is at much higher-energy state relative to the well-aged glass. In addition, this increase in energy after six times training is comparable to that by cryogenic cycling $[27]$. As indicated in inset of Fig. 4(b), the tendency of $T_f$ evolves toward the initialized glass, suggesting
that even higher energy state can be reached by further training the MG. Our results show that modulation of energy states can be achieved either by expanding the temperature range or by involving more training steps within a certain range of aging temperature, because both of them promote the glass to remember more of its previous thermal history. In the present study, we only presented temperature jumps at the peaks of memory effect to maximize the enhancement. It is predicted that the enhanced memory effect can lead a glass to reside at any energy levels between initialized and equilibrium states in the potential energy landscape.

The broad distribution of relaxation times arising from inhomogeneous glass structure [28,29] is believed to account for the nonmonotonic aging reflected by memory effect. A number of theoretical and experimental investigations have demonstrated that MG structures are composed of subensembles [30,31], such as loosely packed regions embedded in densely packed matrix [32–37]. The loosely packed regions have shorter relaxation times and vice versa. The differences between adjacent regions can lead to variation of thermal expansion coefficient from one location to another on microscopic level. Although preannealing partially homogenize the overall structure by annihilation of fast-relaxing flow units [16,38], the regions that have longer relaxation times remain intimate. Upon a quick temperature jump, all the flow units are required to recoordinate themselves so that they can follow their own relaxation path corresponding to the new temperature [3]. Because of the mismatched thermal expansion coefficient between adjacent regions, internal stresses can build up and induce local disordering that result in transient augmentation of inhomogeneity before the glass is able to completely follow the aging path at the new temperature. In our training process by multiple stepwise aging protocols, each temperature jump was implemented at the peak of memory effect. In this case, the augmented inhomogeneity results in even larger mismatch in thermal expansion coefficient, so that new internal stresses leading to new local disordering are created upon the temperature jumps. As a consequence, the memory effect is dramatically enhanced associated with rejuvenation [27,39], and the degree of inhomogeneity of the glass gradually approaches that of the initialized state, consistent with the current understanding that a metallic glass at higher energy state quantified by a larger $T_f$ exhibits more inhomogeneous structure [40,41].

It is known that a number of phenomenological interpretation of memory effect have been proposed, and TNM model [2], KAHR model [42] and Ngai’s coupling model [43] can capture many of the experimental observations associated with the glass transition and structural recovery. However, the parameters used in these models vary with thermal history, and are difficult to explain how enthalpy recovery of a glass occurs at $T < T_g$. Through our multistep thermal treatment, we found that the glassy systems not only undergo nonmonotonic behavior in relaxation, but also can reserve the energy during continuous temperature jump. This phenomenon is hard to be described by simple fitting with existing models. Therefore, models of parameters that can capture the dynamics associated with memory effects and the enhanced memory effect remain to be established. The enhanced memory effect can also be utilized to tailor properties of the glass. For an example, we find that, by using the multistep protocols, the plasticity can gradually increase with increasing training times possibly owing to the enhanced heterogeneity during training (not show here).

IV. CONCLUSIONS

In summary, even though the prolonged aging leads a glass to lower energy state, appropriate design of annealing protocol can modulate the energy states of MGs. We used multistep annealing to train the glass so that the glass system can recall multiple pieces of information gain increase in enthalpy caused by memory effect. It is expected that further enhancement of memory effect can be obtained by involving more temperature jumps in a certain range of aging temperature, which can train the glass to remember more of its previous history. The results provide a new guide for regulating the energy of glasses and offer an opportunity to develop a clearer physical picture of the memory effect and in-depth understanding of glass dynamics.

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