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Nonmonotonous atomic motions in metallic glasses

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Abstract

Peculiar temporal intermittent microscopic dynamics has been recently reported during structural relaxation in metallic glasses, while its origin is poorly understood. By using x-ray photon correlation spectroscopy, we have investigated the atomic motions in a model system of metallic glass with distinct stability and *in-situ* stress states. We find that the microscopic dynamics can be tuned from dramatically nonmonotonous to monotonous. The intermittent dynamics is always accompanied by the activation of a secondary relaxation process, as indicated by the drop of the initial nonergodic plateau of the intensity-intensity correlation function. Both phenomena depend on the material state and can be suppressed by simultaneously lowering the fictive temperature and external loading, leading the glass in a stationary metastable state which appears independent on the thermal history of the system.

Keywords: metallic glass; physical aging; relaxation; intermittent dynamics; XPCS

I. INTRODUCTION

Glasses are usually formed by rapid cooling high-temperature liquids. This process brings the materials in a non-equilibrium state, from where they spontaneously relax toward the corresponding equilibrium liquid. Knowledge of the relaxation dynamics in glasses and its evolution due to physical aging is crucial for understanding their mechanical response and controlling the long-time evolution of their properties during applications [1-3]. Two main microscopic relaxation processes have been identified in glasses, the locally initiated β -relaxation and the large-scale α process [4-7]. The first process can be associated with microscopic islands of mobility in the material, while the second one corresponds to collective motions of the whole system. Both processes contribute to the glass formation and physical aging, but their role and interplay are not yet fully understood [7].

Recent enthalpy recovery and stress relaxation studies in hard and soft glasses have shown the existence of a surprising multi-steps relaxation process for long annealing, which contrasts with the usual steady evolution of the dynamics during physical aging [8-10]. Distinct aging regimes have been reported also during the evolution of the microscopic structural relaxation process in metallic glasses (MGs) at the atomic scale [11] and in complex soft materials [12-14], and are likely related to internal stresses [15,16]. In the case of MGs, abrupt intermittent fluctuations of the microscopic structural relaxation time have also been reported [17], suggesting an avalanche-like particle motion [18,19]. This anomalous intermittent dynamics of MGs at atomic scale has been observed under annealing protocols [20] and *in-situ* application of external stresses at ambient temperature [21]. In this latter case, the effect has been attributed to microplastic events occurring in the material. Despite these two excellent studies, the origin

of this anomalous intermittent dynamics is still elusive. In particular, it is not clear yet what are the physical parameters triggering these abrupt dynamical events, and why the intermittent dynamics has been reported only in very few cases.

In order to shed some light on the nature of the microscopic intermittent dynamics of MGs, we use the x-ray photon correlation spectroscopy (XPCS) technique to explore the atomic motions in a $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ (vit1b) MG with distinct fictive temperatures (T_f) obtained by pre-annealing the samples below the glass transition temperature (T_g), and as a function of external stresses induced in the material. In the XPCS measurements, incoming coherent hard x-rays are scattered when going through the material, leading to an interference pattern whose intensity is related to the exact spatial arrangements of the scatters in the material. Information on the dynamics can be obtained by the temporal correlation of the fluctuations of the scattered intensity [22]. Additional differential scanning calorimetry (DSC), high-resolution transmission electron microscopy (HRTEM), high-energy synchrotron x-ray diffraction (XRD), and mechanical stress relaxation measurements were performed to determine the fictive temperature, the microstructure and the macroscopic relaxation behavior of the samples. Our results show that the intermittent atomic motion is related to the activation of a fast secondary relaxation and can be tuned at wish by changing the applied thermal and mechanical protocols to the sample. Although the microscopic intermittent dynamics seems contrasting with the macroscopic steady relaxation of glass properties, our results indicate that an underlying correlation between the two exists.

II. EXPERIMENTAL TECHNIQUES

A. Materials

$\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ (at.%) master alloys were prepared by arc-melting elements with purities above 99.99% in a Ti-getter high-purity (99.9995%) argon atmosphere. MG ribbons 20 μm in thickness were produced by melt-spinning technic. Bulk MG plates were prepared by copper-mold-casting. The pre-annealing was conducted at 559 K in a muffle furnace with temperature stability of ± 1 K, with the samples sealed in quartz tubes with high-purity argon gas to prevent oxidation.

The DSC measurements were performed on a Perkin-Elmer DSC 8000 to examine the thermodynamic properties of the samples at a heating rate of 20 K min^{-1} with 20 mL min^{-1} flowing high-purity argon gas to prevent possible surface oxidation. The instrument was calibrated according to the melting transitions of indium and zinc. The mass of DSC samples was ~ 20 mg to achieve good data accuracy. The stress relaxation experiments were conducted on a dynamic mechanical analyzer (DMA, TA Q800). As the temperature was stabilized at the planned temperature, a 0.3% tensile strain was applied on the MG ribbon and the stress evolution was simultaneously detected.

The microstructure of the samples was characterized by HRTEM and high-energy synchrotron XRD. The TEM samples were carefully prepared by ion milling with 2 keV argon ions at the liquid nitrogen temperature. HRTEM observations were conducted using a JEOL-2100 plus TEM. The high-energy XRD was performed at beamline 11-IDC at Advanced Photon Source, Argonne National Laboratory, U.S.A. The x-ray energy is 105.1 keV and the beam size is ~ 0.5 mm $\times$ 0.5 mm. The experiment was carried out at room temperature in transmission geometry for bulk MGs ~ 0.4 mm in thickness with exposure time of 20 s. Assuming independent atomic contributions to the scattering, the static structure factor, $S(q)$ is

calculated as:

$$S(q) = \frac{\alpha I_s(q) - I_C(q)}{Z_{\text{tot}}^2(q) f_{\text{eff}}^2(q)},$$

where Z_{tot} is the sum, weighted by the atomic concentrations, of the atomic numbers Z of the atoms, I_C is the Compton scattering calculated as the sum of the individual atomic components and f_{eff} the effective electronic form factor, calculated as the weighted sum of the atomic scattering factors, divided by Z_{tot} . I_s is the sample scattering after subtraction of the background signal and α a density dependent normalization factor, which is found following the iterative procedure reported in Ref. [23].

B. X-ray photon correlation spectroscopy measurements and data processing

XPCS measurements were performed at beamline ID10 at the ESRF in Grenoble, France. Coherent x-rays were used with an energy of 8.1 keV ($\lambda = 1.53 \text{ \AA}$) and a coherent flux of $\sim 10^{11}$ photons per second per 200 mA, and a size of $10 \text{ \mu m} \times 10 \text{ \mu m}$. Series of speckles patterns were collected in transmission geometry by a charge-coupled-device from Andor technology ($13 \text{ \mu m} \times 13 \text{ \mu m}$ pixel size) placed $\sim 70 \text{ cm}$ downstream the sample at an angle $\sim 38^\circ$ corresponding to the maximum of the first sharp diffraction peak of our samples. The detector was mounted on a diffractometer which could rotate around the sample in order to measure the corresponding static structure factor $S(q)$ as well. More details about the experimental set-up can be found in Refs [24,25]. The samples were mounted in a furnace providing a temperature stability of 0.1 K and heated at 12 K min^{-1} from 300 K to the isothermal temperature of 539 K. The measurements were conducted in a way that after collecting every 3000 or 4000 frames (i.e. about 3 or 4 h each) the $S(q)$ was measured to ascertain that the sample remains amorphous, which leads to gaps of about 10 min in the data. The raw data were treated as in Ref. [26].

The time evolution of the microscopic dynamics is directly captured in XPCS by the intensity two-time correlation function (TTCF) $C(t_1, t_2)$, which is defined as

$$C(q, t_1, t_2) = \frac{\langle I(q, t_1)I(q, t_2) \rangle_p}{\langle I(q, t_1) \rangle_p \langle I(q, t_2) \rangle_p},$$

where $\langle \dots \rangle_p$ denotes an ensemble averaging performed on all pixels of the detector corresponding to the same wave vector q [22]. The time-averaged dynamics are extracted from the TTCF as a function of the waiting time, $t_w = t_0 + (t_f - t_i)/2$ where t_0 is the delay time between sample temperature equilibration and the first measurement point, and t_f and t_i are the final and starting times, respectively. This is accomplished through a temporal averaging of the TTCF within a fixed time interval $\delta t = t_f - t_i$ over all possible starting times t_i and expressed as a one-time intensity correlation function $g_2(q, t) = \langle C(q, t_i, \delta t) \rangle$. The $g_2(q, t)$ was calculated from the TTCF within a time range defined by a certain number of frames. In order to calculate the dependence of $g_2(q, t)$ on t_w , a certain frame step was chosen and $g_2(q, t)$ was calculated as a function of successive frame steps over the given frame range. Depending on the observed behavior of the TTCF, frame range of about 1000 images were chosen to give sufficient measurement statistics and evaluate correctly the different parameters, while taking care not to average out any interesting dynamical features of the TTCF. The values of $\tau(t_w)$, $c \cdot f_q^2(t_w)$ and $\beta(t_w)$ shown in Fig. 4, Fig. 5 and Fig. 7 were taken from the Kohlrausch-Williams-Watts (KWW) fits of the $g_2(q, t)$ functions. $\tau(t_w)$ was obtained using a continuous binning of 200 images as in Ref. [20] and around the intermittent events, where the dynamics is too slow to see substantial decay in the correlation functions, it was calculated from binning of larger groups of images, while for $c \cdot f_q^2(t_w)$ and $\beta(t_w)$ we used around 1000 frames like those plotted in Fig. 2. This different approach is due to the fact that while $\tau(t_w)$ is a more robust parameter

unaffected by the usage of 200 or 1000 images, $c \cdot f_q^2(t_w)$ and $\beta(t_w)$ are better evaluated with more statistics.

III. RESULTS

A. Fictive temperature

Figure 1a shows the DSC profiles of the as-cast MG and samples pre-annealed at 559 K for 3 h and 192 h. Compared to the annealed samples, the as-cast glass is highly unstable and exhibits a broad sub- T_g exothermic peak, indicative of the abundant excess enthalpy trapped in the glass with a structure far away from equilibrium. Upon annealing, the excess enthalpy is sequentially released, followed by an increase in the endothermic peak above T_g associated to enthalpy recovery. The inset shows the enthalpy of the samples obtained by integrating the heat flow profiles. The T_f is determined from the intersection between the extrapolated enthalpies of glass and supercooled liquid [27]. Annealing induces a remarkable reduction in enthalpy and T_f , implying an increased stability of the glass [6]. The as-cast MG has a $T_g = 621$ K and exhibits the highest enthalpy with $T_f = 752$ K, $\approx 1.2T_g$, consistent with previous reports [28]. When the sample is annealed for 3 h, T_f decreases to 603 K, while the 192 h annealed glass shows much lower enthalpy with $T_f = 565$ K, almost 200 K lower than that of the as-cast glass.

B. Microscopic structure

As is visible in Fig. 1b and c, both the as-cast and the 192 h pre-annealed samples show a homogeneous maze-like pattern in the HRTEM images, indicative of a fully amorphous structure. The diffuse halos in the electron diffraction patterns (see the insets in Fig. 1b and c) further corroborate the amorphous nature of the samples. Figure 1d shows the static structure factor $S(q)$ obtained at room temperature for the as-cast and the 192 h pre-annealed samples

obtained from high-energy synchrotron XRD measurements. The inset in Fig. 1d is a close-up view of the first peaks of $S(q)$, which show smooth curves without any indication of crystallization even for the longest 192 h annealed sample. Moreover, a slight shift of the peak position towards larger q values can be observed for the 192 h pre-annealed sample, indicating an increment of the density typical of physical aging [29].

C. Atomic-scale dynamics by XPCS

The microscopic structural relaxation process and its temporal evolution was studied with XPCS by performing long isotherms at 539 K, thus below the T_f of all samples, and for a unique wave vector $q_0 = 2.67 \text{ \AA}^{-1}$ corresponding to the first maximum of $S(q)$ (Fig. 1d). In this configuration, we are directly probing the atomic motions on a characteristic inter-particle length scale $2\pi/q_0 = 2.35 \text{ \AA}$. We performed a systematic study of the atomic motions in three representative samples, the as-cast, the 3 h pre-annealed, and the 192 h pre-annealed, with and without *in-situ* mechanical stresses. The free samples were directly mounted in the furnace, thus without external stress during the XPCS measurements. To induce external stress in the samples, we designed an *ad-hoc* clamp as illustrated in Fig. 1e to restrict the MG ribbon around a mandrel with a diameter $\Phi = 4.0 \text{ mm}$. For a bent ribbon, the strain on the outer surface is tensile and that on the inner surface is compressive, the neutral surface has no strain. The MG ribbons have smooth surfaces and a uniform thickness of $d = 20 \text{ \mu m}$. The largest strain on the surfaces is $\varepsilon = d/(\Phi+d) = 0.5\%$. The Young's modulus E and the yield strength σ_y of the studied MG is $96 \pm 1 \text{ GPa}$ and $1900 \pm 100 \text{ MPa}$, respectively [30]. Therefore, the stress induced on the surfaces is $480 \text{ MPa} \approx 0.25\sigma_y$. The increase of E for the longest annealed MG would be $\approx 10\%$ [31,32], which means a variation of just $0.025\sigma_y$ for the applied stress. As such, well-defined

in-situ elastic strain/stress was induced during the XPCS measurements.

Figure 2a shows the typical intensity-intensity correlation functions, $g_2(q_0, t)$, measured for the stressed as-cast sample. The decay of the curves provides information on the atomic motions, being $g_2(q, t)$ related to the density fluctuations, thus to the intermediate scattering function, $f(q, t)$, through the Siegert relation $g_2(q, t) = 1 + c|f(q, t)|^2$, where c is a set-up dependent contrast related to the coherent degree of the x-rays, the scattering angle, and the thickness of the samples [33]. The data can be modeled with the KWW function $g_2(q_0, t) = 1 + c \cdot f_q^2(t_w) \exp[-2(t/\tau(t_w))^{\beta(t_w)}]$ where all parameters depend on the waiting time, t_w , elapsed since the beginning of the isotherm at 539 K: $\tau(t_w)$ is the decay time of the relaxation process, $\beta(t_w)$ the shape parameter, and $f_q(t_w)$ is the nonergodic plateau associated to the trapping of the particles in the nearest neighbors cage before their escape during the structural relaxation [34]. With increasing t_w , $g_2(q_0, t)$ experiences firstly a continuous shift towards longer decays, signaling that the dynamics becomes spontaneously slower, and then a backward shift to faster decays. Such a behavior strongly contrasts with the steady slowing-down of relaxation dynamics reported in macroscopic studies, revealing a spontaneous intermittent aging process. Intriguingly, we found that this nonmonotonous evolution of the dynamics is accompanied by a surprising abrupt drop of the initial plateau value of $g_2(q_0, t)$. This effect is better appreciated in Fig. 2b where the same data are scaled along the x-axis and reported as a function of the reduced time $t/\tau(t_w)$.

In the macroscopic limit of $q \rightarrow 0$, the short-time plateau of $g_2(q_0, t) - 1$, $c \cdot f_q^2(t_w)$, is related to the elastic properties of the material through the nonergodicity parameter, and it usually increases steadily with time due to the growth in elasticity as reported in gels and colloidal suspensions [13,35-37]. Although the elasticity of MG also increases during isotherms

[31,32,38,39], here $c \cdot f_q^2(t_w)$ decreases by almost 20% with t_w (Fig. 2b). Furthermore, our measurements are performed at the maximum of the $S(q)$, where the nonergodicity factor is expected to be close to unity [40]. Hence, we cannot attribute the observed phenomenology to changes in the elastic response of the material. From the technical point of view, beamline instabilities may affect XPCS measurements leading to a drop in contrast in different ways: 1) Beam jumps. Sudden changes in beam position (e.g. induce by the electron beam instabilities in the synchrotron radiation storage ring) will decorrelate the data breaking the continuity of the TTCFs. We never observed such events and it is clearly not the case as the contrast drop is observed at the slowest dynamics (i.e. any fast sudden instability will kill immediately the data). 2) Contrast decreasing because of the degradation of the beamline optical alignment. For XPCS, the stability of the optical alignment of the beamline is critical for the optimum contrast, since any (transient) misalignment will produce a degradation of the contrast. This is usually the result either of a drift of the optics (monochromator, focusing optics) or by the progressive degradation of a beamline component due to heat load. We point out that these effects cannot be solved spontaneously, i.e. they need the human intervention either to restore the optimum alignment or to adjust the damaged component. Furthermore, the induced degradation is usually progressive, i.e. beamline contrast is degrading progressively with time. We never observed such slow contrast degradation trends in our measurements and we didn't need to realign systematically beamline optics beyond standard fast daily beam checks, in particular not during the intermittent events or between the gap of XPCS data sets due to the necessity to check the $S(q)$. During our experiment, the data jump from high to low contrast, depending on the sample and waiting time. The measured initial contrast of about 2.2% is thus restored several times during the whole beamtime, guaranteeing the reproducibility of the value. Following these observations, we think that the only possible explanation for the contrast variation observed along a smooth and slow dynamics is to activate an additional internal fast process prior to the primary structural rearrangements. This process results in an additional step decay in the correlation functions at times too short to be directly captured in the temporal window of the current XPCS, and with a strength corresponding to the missing value of $c \cdot f_q^2(t_w)$.

A drop in $c \cdot f_q^2(t_w)$ has been reported also in $\text{Pd}_{77}\text{Si}_{16.5}\text{Cu}_{6.5}$ MG [41]. Differently from our

case, this phenomenon was therein triggered by temperature changes and it has been ascribed to a thermally activated secondary relaxation process associated to the onset of crystallization, but without any fluctuation in the relaxation time τ [41]. In our experiments, it has been corroborated by both high energy synchrotron XRD and HRTEM that our samples, including the longest 192 h pre-annealed one, keep fully amorphous without any indication of nanocrystallization (Fig. 1b-d). Furthermore, the structure has been checked *in-situ* after collecting every 4000 frames during the XPCS measurements. Figure 3 shows the XRD pattern for the 192 h pre-annealed sample after the collection of all XPCS data at 539 K, the sample keeps fully amorphous. These observations exclude the possibility that our results were related to crystallization. Previous studies reported that Be-containing ZrCu-based MGs are prone to chemical phase separation subjected to annealing near or above the glass transition [42,43], while it has been demonstrated in $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ MG that no phase separation occurs prior to crystallization [44]. We have also carefully verified with both dark field and bright field HRTEM at different length scales that no phase separation occurs in all our samples. Therefore, we conclude that the intermittent microscopic dynamics observed also in other MGs [11,20] is an intrinsic property of glass relaxation, rather than a result of nanocrystallization or chemical decomposition.

The connection between the intermittent dynamics and the secondary relaxation process can be more appreciated by looking at the temporal evolution of the relaxation time $\tau(t_w)$ and $c:f_q^2(t_w)$ as shown in Fig. 4a. The as-cast MGs show highly heterogeneous dynamics. In the stressed sample, for $t_w < 1.7 \times 10^4$ s, $\tau(t_w)$ increases rapidly to 1.2×10^4 s. It subsequently decreases dramatically, and finally becomes stationary with $\tau(t_w) \approx 3 \times 10^3$ s. This intermittent

event leading to the peak in $\tau(t_w)$ spans approximately 1.3×10^4 s with a fluctuation of $\Delta\tau(t_w) \approx 8.8 \times 10^3$ s. As marked by the red hatched area in Fig. 4a, this dynamical fluctuation is accompanied by an abrupt drop of $c \cdot f_q^2(t_w)$ (bottom panel), indicating the strong connection between these two features. In the free as-cast glass, we observe also a sharp intermittent event at much earlier stage of the isotherm and a simultaneous rapid drop of $c \cdot f_q^2(t_w)$ (see the olive hatched area in Fig. 4a). Although the fluctuation of $\tau(t_w)$ is not as large as in the stressed MG, it is equally sharp, with an increase of $\Delta\tau(t_w) \approx 800$ s spanning 1.6×10^3 s, and the drop in $c \cdot f_q^2(t_w)$ is of equal amount to that of the stressed sample. Despite the missing data for the free as-cast MG at larger times due to beam lost in the synchrotron, the present data clearly show that both samples exhibit intermittent dynamics accompanied by a secondary relaxation process.

The temporal evolution of the intermittent microscopic dynamics can be better visualized by looking at the TTCF $C(t_1, t_2)$, which represents the instantaneous correlation between averaged configurations measured at times t_1 and t_2 . Figure 4b and c show the TTCFs corresponding to the data for the as-cast sample with stress. The diagonal from the bottom left to the top right corner indicates the evolution with t_w , while the width of the yellow-red ridge along the diagonal is proportional to $\tau(t_w)$. Thus, Fig. 4b and c illustrate visibly the fast slowing-down and the subsequent abrupt speeding-up of the structural relaxation process.

Interestingly, we found that the intermittent dynamics is strongly suppressed by the concomitant use of stress and pre-annealing. Figure 5a plots $\tau(t_w)$ and $c \cdot f_q^2(t_w)$ for the 3 h pre-annealed glass. The free sample shows distinct regimes of atomic motions: i) An abrupt increase in $\tau(t_w)$ up to $t_w \approx 1.1 \times 10^4$ s, ii) a stationary regime where $\tau(t_w)$ remains basically constant at 4×10^3 s, and iii) a rapid acceleration to another stationary regime with $\tau(t_w) \approx 1 \times 10^3$

s. As marked by the olive hatched area, also in this case the intermittent event is accompanied by a substantial reduction in $c \cdot f_q^2(t_w)$, but in a slower way than in as-cast sample. In stark contrast, the sample under stress shows a monotonous slowing-down of the dynamics with only tiny fluctuations in $\tau(t_w)$ and a slight decrease in $c \cdot f_q^2(t_w)$. Notwithstanding, the relaxation times of both samples (i.e. with and without stresses) do overlap at long waiting times, indicating that the presence of external stress affects only the appearance of the intermittent event.

Figure 5b provides a comprehensive comparison between the dynamics in all as-cast and pre-annealed samples. The decreased T_f induced by thermal pre-annealing leads to: i) a delay in the intermittency, from $t_w \approx 3.3 \times 10^3$ s for the as-cast sample to $t_w \approx 2.1 \times 10^4$ s in the 192 h pre-annealed one, ii) a change in the shape of the intermittent event, from a sharp peak in $\tau(t_w)$ in the as-cast glass, to a blunt one with a stationary regime between the rapid increase and the decrease in $\tau(t_w)$ in the 3h pre-annealed glass. A similar event occurs also for the 192 h pre-annealed MG, while due to its much longer delay we do not have the full event depicted. When stress is applied, the intermittent event is observed but only in the as-cast sample and it occurs at later times than in the free glass, whereas both pre-annealed MGs display only a monotonous temporal slowing-down of the dynamics. Surprisingly, the $\tau(t_w)$ of the 3 h and 192 h pre-annealed MGs under stress coincides, contrasting with their macroscopic relaxation behaviors which show a difference in timescale by over one order of magnitude (Fig. 6). By looking at the $\tau(t_w)$ of the 3 h and the 192 h pre-annealed MGs in Fig. 5, it is clear that when the intermittent events terminate or become well suppressed by the simultaneous use of stress and pre-annealing, the microscopic relaxations exhibit consistent dynamics with the same $\tau(t_w)$, independently on the T_f of the glass. These observations suggest two mechanisms responsible

for the aging process at the microscopic scale: i) the intermittent dynamical event that is sensitive to the variation of the sample's T_f and external loading, and ii) the steady slowing-down of the dynamics which is independent of the material state.

IV. DISCUSSION

Nonmonotonous relaxations have been reported also in an excellent work of Mauro and colleagues following the evolution of fluctuations in density and enthalpy in distinct glasses [45]. Studying glasses equilibrated at distinct T_f and then quenched at a given temperature, they show that both enthalpy and density fluctuations initially overshoot the equilibrium value and then relax from the other side. Furthermore, the magnitude of the overshoot increases with the increasing distance between the measured temperature and the initial T_f of the glass. In this picture, the intermittent events in the density fluctuations observed by XPCS here and in other MGs [20], can be viewed as similar nonmonotonous relaxations of the characteristic time of collective atomic motions due to density fluctuations during isotherms at temperatures lower than T_f . It is important to stress that in our case the final state is metastable although persistent for long times. The system is still in the glassy state and the relaxation time is far from the corresponding equilibrium liquid value.

Our data show that the abrupt intermittent relaxations are accompanied by the spontaneous activation of a fast secondary relaxation process as signaled by $c \cdot f_q^2(t_w)$. The sharper the event in $\tau(t_w)$, the larger is the strength of the process and thus the drop in $c \cdot f_q^2(t_w)$. The presence of a secondary relaxation process suggests that the abrupt fluctuations in the structural relaxation time come from the activation of the motion of fast components in the amorphous matrix, that persist even after the event as confirmed by the persistent low value of $c \cdot f_q^2(t_w)$. In other words,

the applied stress (and/or temperature) activates a secondary relaxation process which - at the first stage - perturbs the main structural relaxation process leading to strong fluctuations in the relaxation time. Pre-annealing leads to a much smaller and slower drop in $c \cdot f_q^2(t_w)$, partially suppressing the secondary process. This decrease of the process with annealing is typical for secondary relaxation processes and has been reported also for the β -relaxation in mechanical studies [46-48]. Unfortunately, due to technical constraints, we are not able to quantify the timescale associated to the secondary relaxation process related to the intermittent dynamics and compare it with other known processes. The current advent of 4th generation synchrotrons [49], will help elucidating the nature of this microscopic secondary process.

Interestingly, we find a constant compressed (i.e. $\beta(t_w) > 1$) value of the shape of the $g_2(q_0, t)$ for all samples (see Fig. 7), in agreement with previous works [11,17,20,25,41,50]. No discernable dependence of $\beta(t_w)$ on the sample age or the stress state is observed, while we do observe a minimum in correspondence of the peak maximum of the sharp intermittent dynamical events (denoted by the arrows in Fig. 7), consistent with the previous observation in Ref. [20]. The fact that the shape parameter does not display any particular trend, means that its nature is basically not affected by external stress and thermal history, at least in the studied composition, being more a property of the glassy state. The initial increase of $\beta(t_w)$ is likely to be an artefact induced by the limited points at short times and requires further studies. The anomalous compressed shape of the relaxation process is often considered a signature of out of equilibrium dynamics in many complex systems [25,51-53]. Recent numerical simulations in MGs associate this behavior to an increasing number of icosahedral clusters during the vitrification which generate additional frustration in the material [16]. In this regard, the

compressed decay appears more as an intrinsic property of the out-of-equilibrium frozen structure as suggested also by studies in ultrastable MGs [50].

XPCS measurements have been previously performed in different MGs [17], while intermittent dynamics has only been observed during isothermal studies in $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ MG [20] and in a smoother way in $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ MG [11]. Here, we report the presence of much stronger intermittent effects in $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ MG. This is likely due to the applied protocol that is, a combination of rapid heating, relatively low measuring temperature and long observation time. Strong intermittent dynamics has also been reported in a Zr-based MG under mechanical stresses at room temperature and attributed to microplastic events occurring in the material [21]. In contrast to our work and Ref. [20], the intermittency is there driven only by the stress, and no events have been observed in its absence. This apparent discrepancy is likely a consequence of the fact that those measurements were performed at room temperature ($0.44T_g$), while in our work and in Ref. [20], the dynamics is mainly triggered by temperature changes (the rapid heating to $0.87T_g$ in our case). This observation is in agreement also with numerical simulations which have shown the occurrence of similar thermally-activated or stress-activated avalanche-like atomic motion in MGs [18,54].

Finally, it is important to highlight that the increased uniformity of the dynamics under the small applied stress in our work is in agreement with previous studies in glassy systems [55,56]. Molecular dynamics (MD) simulations [56-58] have shown that depending on the strength of the applied strain (or stress) it is possible to drive the glass through deeper or higher minima in the potential energy landscape, corresponding thus to new states overaged or rejuvenated with respect to the initial one. In particular, small strain (or stress) is found to drive the glass in

metastable state with lower energy minima and thus more stable, in agreement with the results reported in our work, being the strain induced in our sample less than 0.5%, i.e., well below the yielding strain of metallic glasses at our experimental temperature [59]. Following the results of MD simulations, thus the fact that small strain leads to overaging [57], it is then normal to expect a delayed intermittent event in the as-cast sample under stress (Fig. 4a). Such a delay is a signature of the increased stability as indeed it occurs also with the pre-annealing (and without stresses, Fig. 5b). In this scenario, the almost stationary dynamics in pre-annealed samples measured under stress, indicates that the combination of temperature and stress suppress the occurrence of intermittent event in agreement with MD results showing the occurrence of localized, non-diffusive dynamics for small stress [58,60].

V. CONCLUSION

We have performed a systematic study of the relaxation dynamics of a series of $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ MGs with distinct stability and *in-situ* stress, with the aim at shedding some light on the recently discovered intermittent microscopic dynamics [20,21]. We show that the nonmonotoneous temporal evolution of $\tau(t_w)$ results from the thermal activation of the motion of fast components in the amorphous matrix as signaled by the simultaneous appearance of a secondary relaxation process. The events in $\tau(t_w)$ and the secondary process are strongly affected by the stability of the glass. Large intermittent dynamical events are indeed more frequently observed in the most unstable (i.e., the as-cast) MG. As T_f decreases upon pre-annealing, the dynamic intermittency gets delayed. The simultaneous use of stress and pre-annealing, allows tuning the glass in a stationary metastable state which appears independent on the details of the system.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure 1. (a) Thermodynamic characterization of the MGs with different thermal histories: as-cast and pre-annealed at 559 K for 3 h and 192 h. The heating rate is 20 K min⁻¹. Inset: Corresponding enthalpy obtained by integrating the heat flow curves. The intersection between the extrapolated enthalpies of glass and supercooled liquid (dashed curves) defines T_f . (b,c) HRTEM images of (b) as-cast and (c) 192 h pre-annealed MGs. The insets show the electron diffraction patterns. (d) Static structure factor $S(q)$ measured with high-energy synchrotron XRD at room temperature for as-cast and 192 h pre-annealed MGs. Inset: a close-up view of the first peaks. (e) Schematics of XPCS measurement for the stressed MG ribbons.

Figure 2. (a) Waiting time dependent $g_2(q_0, t)$ functions measured with XPCS for the as-cast sample under stress during isotherm at 539 K. Lines are fits obtained by the KWW model. The arrows indicate the nonmonotonous evolution of the $g_2(q_0, t)$ with t_w . (b) The same data reported as a function of $t/\tau(t_w)$. The arrow emphasizes the sudden drop of the initial plateau.

Figure 3. X-ray diffraction in the vicinity of the first diffraction maximum measured *in-situ* using XPCS after isotherm of $t_w \approx 4 \times 10^4$ s for the 192 h pre-annealed MG under stress.

Figure 4. (a) $\tau(t_w)$ (upper panel) and $c \cdot f_q^2(t_w)$ (lower panel) for the as-cast sample during isotherm at 539 K without (free) and with mechanical *in-situ* stress. $\tau(t_w = 0 \text{ s}) \approx 100 \text{ s}$ at the beginning of the isotherm. The hatched areas mark the range of the intermittent events. (b) TTCF for the as-cast MG under stress. The small red square at the beginning is the acquisition at 300 K, after which the temperature is raised at 12 K min^{-1} where the diagonal is blue. At $t_1 = 0 \text{ s}$, T attains 539 K and then stays constant. (c) Continuation of the TTCF in (b).

Figure 5. (a) $\tau(t_w)$ (upper panel) and $c \cdot f_q^2(t_w)$ (lower panel) for the 3 h pre-annealed MG measured at 539 K. The hatched areas mark the range of the intermittent event. (b) Comparisons between the $\tau(t_w)$ of the as-cast, 3 h and 192 h pre-annealed MGs measured at 539 K at free (upper panel) and stressed (lower panel) states.

Figure 6. Stress relaxation at 539 K for as-cast and pre-annealed MGs. The stress $\sigma(t)$ is normalized by the initial value $\sigma(0)$ at $t = 0$. Solid lines are fits of a double KWW equation as in Ref. [10]. Inset: fitted relaxation time of the initial faster process τ_1 (square) and the later primary process τ_2 (circle) as a function of the pre-annealing time t_a , the solid symbols represent as-cast sample. Continuous increase of the timescale of the primary decay process τ_2 with the pre-annealing time is well visible.

Figure 7. Waiting time dependent shape parameters of different samples. The arrows emphasize the minimum of $\beta(t_w)$ in the as-cast samples which occurs in concomitance with the maximum of the relaxation time.