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Relaxation dynamics of Pd-Ni-P metallic glass: Decoupling of anelastic and viscous processes.

Daniel Soriano^a, Hongbo Zhou^b, Sven Hilke^b, Eloi Pineda^{c,*}, Beatrice Ruta^d, Gerhard Wilde^b

^a *Escola d'Enginyeria de Barcelona Est, Universitat Politècnica Catalunya - BarcelonaTech, 08019-Barcelona, Spain. E-mail: dsoriano.ds@upc.edu*

^b *Institute of Materials Physics, University of Muenster, Wilhelm-Klemm Strasse 10, 48149 Muenster, Germany. H.Zhou Email: h_zhou04@uni-muenster.de*

^c *Departament de Física, Centre de Recerca en Ciència i Enginyeria Multiescala de Barcelona, Institut de Tècniques Energètiques, Universitat Politècnica de Catalunya - BarcelonaTech, 08019-Barcelona, Spain. E-mail: eloi.pineda@upc.edu*

^d *Institut Lumière Matière, UMR5306 Université Claude Bernard Lyon 1 - CNRS, 69622 Villeurbanne, France. E-mail: beatrice.ruta@univ-lyon1.fr*

*Corresponding author:

Eloi Pineda

EEBE, Av. Eduard Maristany 16 - Edifici C

08019 Barcelona, Catalonia - Spain

Tel. +34935521141

E-mail: eloi.pineda@upc.edu

Abstract

The stress relaxation dynamics of metallic glass Pd₄₀Ni₄₀P₂₀ was studied in both supercooled liquid and glassy states. Time-temperature superposition was found in the metastable liquid, implying an invariant shape of the distribution of times involved in the relaxation. Once in the glass state, the distribution of relaxation times broadens as temperature and fictive temperature decrease, eventually leading to a decoupling of the relaxation in two processes. While the slow one keeps a viscous behavior, the fast one shows an anelastic nature and a time scale similar to that of the collective atomic motion measured by X-ray Photon Correlation Spectroscopy (XPCS). These results suggest that the atomic dynamics of metallic glasses, as determined by XPCS at low temperatures in the glass state, can be related to the rearrangements of particles responsible of the macroscopically reversible anelastic behavior.

Keywords: Stress relaxation, Relaxation dynamics, XPCS, Metallic glasses, Mechanical properties.

1. Introduction

The relaxation dynamics of metallic glasses and liquids is intrinsically linked to their mechanical properties, such as the viscous and plastic behaviors [1], and to the rejuvenation and aging processes [2]. Above the glass transition temperature (T_g) the supercooled liquid (SCL) is a metastable equilibrium phase which is characterized, among other properties, by a density and a structural relaxation time that change with temperature. The structural relaxation time, τ , determines how fast the structure returns to the equilibrium configuration after a change of the external conditions, pressure or temperature, or the application of an external stimulus. Therefore, it controls the viscosity of the SCL as well as the relaxation towards the new equilibrium configuration after a sudden change of temperature. This process, so called α -relaxation, is characterized by a stretched exponential shape of the time-dependent relaxation curves, often attributed to the presence of a distribution of relaxation times whose average value follows a super-Arrhenius temperature dependence, usually well described by a Vogel-Fulcher-Tammann behavior [3].

During a cooling process from the SCL phase, the super-Arrhenius behavior of τ makes that at a given temperature the change of temperature becomes too fast for the system to reach the equilibrium configuration, and the system becomes arrested in a glass state. The specific state of a glass is therefore an out-of-equilibrium configuration which is inherently prone to changes towards the metastable equilibrium by means of structural relaxation, this process is known as physical aging. The relaxation dynamics of the glass are therefore responsible of two processes: the response of the system under the application of external forces and the physical aging, and they become usually mingled in most mechanical experiments below T_g . Furthermore, the application of high stresses and deformation rates may also induce rejuvenation of the glass [4], and subsequent intensification of aging during the experiments [5].

If the glass is well aged and the applied stresses are low enough to do not induce rejuvenation, the relaxation dynamics of isoconfigurational glass states may be tested by mechanical experiments. In the seminal works of Taub and Spaepen [6][7], creep experiments of metallic glass ribbons showed the presence of anelastic and viscous contributions to the relaxation of isoconfigurational states. The viscous relaxation was found to produce a constant deformation rate proportional to the applied stress, with absolute values of viscosity changing for

different isoconfigurational states but with Arrhenius temperature dependences with similar activation energies. In addition to the subjacent slow viscous flow, the anelastic relaxation was found to dominate the first hours, or even days, of the creep experiments. The intensity of the anelastic relaxation was found to be linear with the applied stress and totally recoverable after unloading, thus showing its total anelastic nature.

Concerning the physical aging of glasses, the relaxation processes involved are a matter of intense debate. The distribution of relaxation times responsible for the structural relaxation in the SCL state is expected to stem from spatial and dynamical heterogeneities, involving microscopic particle movements with various correlation lengths and diverse degrees of cooperativity. Once the system is arrested in a given glass configuration, some of these processes may become too slow to contribute to a detectable physical aging while others remain active. The evolution of the distribution of relaxation times as a function of temperature and aging dictates which processes can be observable in a particular experiment. The progressive separation of the characteristic times of the relaxation processes in glasses is manifested by the presence of double step aging [8][9] and the observation of multiple secondary relaxations in mechanical experiments [10][11]. Despite the important advances in the field done in the last years, the nature of the relaxation processes involved in deep glassy states is still far from being understood due to the difficulty to probe the microscopic details of the systems with both experiments and numerical simulations, and the concomitant lack of a direct connection between atomic scale processes and macroscopic relaxations [2].

Here, we present a detailed characterization of the relaxation dynamics of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ metallic glass at both macroscopic and microscopic scale. The macroscopic relaxation was characterized by mechanical stress-relaxation experiments in the SCL and in glasses with different degrees of aging. The evolution of the distribution of relaxation times was analyzed by means of fitting the experimental curve to single and double stretched exponential decays. The microscopic features of the different relaxation processes were investigated by X-ray Photon Correlation Spectroscopy (XPCS). The experimental conditions used in the stress relaxation tests and the control of the aging state allowed us to characterize a wide temperature-time region, in both the glass and the SCL states, showing a clear differentiation between stress-driven, anelastic processes and viscous-like relaxation.

2. Methods

$\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ master alloys were first prepared by melting Pd plates and Ni_2P granules in a silica crucible under a Ti-gettered argon atmosphere. The samples in ribbon shape for stress relaxation tests were re-melted and ejected onto a Cu wheel rotating at a surface velocity of 40 m s^{-1} . The samples for XPCS measurements were re-melted and cast in a copper mold obtaining 5 mm diameter rods. Disk-shape slices of the rod were grinded until obtaining a thickness of $20 \text{ }\mu\text{m}$ used in the XPCS experiment.

The stress relaxation and mechanical spectroscopy experiments were performed in a DMA Q800 TA Instruments apparatus using ribbon-shape samples of 2 mm width and $30 \text{ }\mu\text{m}$ thickness. In both, mechanical spectroscopy and stress relaxation tests, a first annealing at 523 K ($250 \text{ }^\circ\text{C}$) while applying a tensile stress of 0.7 N was performed in order to reduce the as-cast bending of the ribbons. The mechanical spectroscopy tests were performed applying a single frequency and an amplitude of oscillation of $\varepsilon=0.01\%$ (approximately $1 \text{ }\mu\text{m}$) while heating at a constant rate of 1 K min^{-1} . Stress relaxation measurements were performed isothermally. During the heating or cooling protocols before reaching the desired temperatures, as well as during temperature stabilization, a static force of 0.01 N was constantly applied in order to maintain the straight shape of the samples. After reaching each temperature, the samples were stabilized during 30 minutes, which is required as it was checked that at least during the first 15 minutes the dimensions of the whole system (clamps and sample) were changing, thus inducing artefacts in the stress measurement. After the temperature stabilization step, a constant deformation of $\varepsilon=0.05\%$, 0.1% or 0.2% was applied; most tests were performed at $\varepsilon=0.1\%$ and only some selected cases were performed with the other strain values with the aim of determining if there was any significant effect of the applied initial stress. The length of the samples was approximately 10 mm, which means that for $\varepsilon=0.1\%$ the constant deformation was of the order of $10 \text{ }\mu\text{m}$, the exact absolute value depending on each sample. The static force needed to maintain the applied deformation was monitored as a function of time thus obtaining the stress relaxation curves.

The mechanical measurements were performed under a nitrogen-rich atmosphere. X-ray diffraction of samples collected after the relaxation experiments did not show detectable traces of oxide or crystalline phases. In addition, the following procedure was made: After long experiments the samples were reheated above T_g and

tested in order to check if the response was again in agreement with the equilibrated SCL behavior, thus discarding a change of the mechanical response because of the formation of oxide surface layers or crystallization.

XPCS measurements were performed at beamline ID10 at ESRF (France). The sample was placed under vacuum inside a furnace with kapton foil windows and illuminated with a coherent X-ray beam of $10 \times 8 \mu\text{m}$ ($H \times V$) size with an intensity of about 10^{11} photons per second per 200mA at a photon energy of 8 keV. The diffracted speckle patterns were acquired every 5 second by a CCD detector (Andor Ikon-M, 1024×1024 pixels, $13 \mu\text{m}$ pixel size) in transmission geometry. The detector was placed at a distance of 70 cm from the sample at an angle corresponding to a momentum transfer of $q_0 = 2.87 \text{ \AA}^{-1}$, which is the maximum of the structure factor $S(q)$ in this material. The measurements were performed isothermally at different temperature steps as detailed below, the heating and cooling rates between isothermal steps were 6 K min^{-1} . After each isothermal measurement, an angular scan of the diffracted intensity was realized in order to detect any sign of crystallization in the $S(q)$.

3. Results

3.1 Stress relaxation of the supercooled liquid

The stress relaxation curves were measured in different temperature regions. A first series of measurements were performed at temperatures from 560 K to 585 K in the SCL metastable equilibrium. The glass transition temperature of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ is detected around 580 K in calorimetric measurements at a heating rate of 20 K min^{-1} [12]. Considering the liquid fragility of this material, $m=41$, the estimation of the onset of the glass transition at a heating rate of 0.1 K min^{-1} would be at 560 K [13]. From equilibrium viscosity measurements, defining the glass transition at $\eta=10^{12} \text{ Pa s}$, T_g was determined at 561 K [14]. Therefore, the stress relaxation experiments presented in this work, which were performed isothermally, are considered to probe the SCL state when performed above 560 K. In this temperature range the shape of the stress relaxation curves is well described by a stretched exponential function

$$\sigma(t) = \sigma_0 \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right]. \quad (1)$$

The fitting of Eq. 1 to the stress relaxation curves gave relaxation times from 70 s at 563 K to 2 s at 583 K. The stress relaxation curves at some selected temperatures are shown in Figure 1-a, the experimental data is shown by purple circles and Eq. 1 by purple solid lines. Figure 1-b shows the loss modulus obtained from mechanical spectroscopy applying oscillation frequencies of 1 Hz and 0.1 Hz at a constant heating rate. The values of the β exponent and the relaxation times τ obtained from the fitting of the stress relaxation curves in the SCL region are plotted with purple circles in Figures 1-c and 1-d, respectively. As shown in Figure 1-c, the shape of the relaxation function in the SCL region is constant with temperature, with a stretched value of the β exponent around 0.5 and without a neat tendency to increase or decrease with temperature. The temperature dependence of τ in the SCL state (Figure 1-d) is in good agreement with previous works reporting viscosity [15] and mechanical spectroscopy measurements [16][17][18]. Both the free-volume model of Cohen and Grest [19], with the parameters obtained from viscosity fits in ref. [15], and the Vogel-Fulcher-Tammann (VFT) equation, with parameters $B=5381$ K and $T_0=419$ K from mechanical spectroscopy measurements in ref. [18], can describe reasonably well the temperature dependence of the SCL stress relaxation times measured in this work. The VFT function is shown by a dashed blue line in Figure 1-d.

Figure 1. a) Stress relaxation curves obtained above $T_g=561$ K (purple symbols) and from 523 K to T_g (red symbols), solid lines are the KWW functions of Eq. 1. b) Loss modulus obtained at 1 Hz (blue) and 0.1 Hz (orange) at a heating rate of 1 K min^{-1} . c) Stretching exponents of Eq. 1 obtained by fitting the experimental curves above T_g (purple symbols), and below T_g by cooling at 10 (red), 5 (orange), 1 (yellow), 0.1 (green) and 0.05 (blue) K min^{-1} . At the lowest temperature, 523 K, and the slowest cooling rates of 0.1 (green) and 0.05 K min^{-1} (blue), Eq. 2 was used for the fitting, values of β and β_2 are shown with triangle and diamond symbols respectively. d) Relaxation times obtained by fitting the stress relaxation curves (same symbols as in Figure 1-c). Star symbols correspond to the relaxation times obtained

from mechanical spectroscopy measurements of the loss modulus. The VFT (dashed blue line) and the relaxation times expected for the secondary relaxation (dashed green line) are calculated with the parameters taken from Ref. [18].

The relaxation times obtained from the maximum of the loss modulus peak are shown with star symbols in Figure 1-d. Here it is pertinent to recall the relationships between the relaxation times obtained from different types of measurements. In this work, all τ values will refer to the relaxation time of the Kohlrausch-Williams-Watts (KWW) function (Eq. 1), which is related to the average relaxation time by $\langle \tau \rangle = \tau \beta^{-1} \Gamma(\beta^{-1})$. The α -peak of the loss modulus corresponds to the transformation of the KWW function into the frequency domain. For a KWW exponent of $\beta \approx 0.5$, this transformation can be well described by a Havriliak-Negami (HN) function, $[1 + (i\omega\tau_{HN})^\alpha]^{-\gamma}$, with exponents $\alpha=0.809$ and $\gamma=0.510$, and a relationship between the HN and the KWW times given by $\tau_{HN} = 2.92\tau_{KWW}$ [20], with $\tau_{KWW} = \tau$ in this work. The loss modulus peak corresponds to the imaginary part of the HN function, with a maximum found at $\omega\tau_{HN} = \left[\tan\left(\frac{\pi}{2(\gamma+1)}\right) \right]^{1/\alpha}$. Therefore, for $\beta \approx 0.5$, the time corresponding to the inverse frequency at the maximum of the loss peak is related to the KWW time by $\tau_{max} = \omega_{max}^{-1} = \tau_{HN}/1.93 = 2.92\tau/1.93 \approx 1.5\tau$. This relationship is used here for calculating the values of the relaxation times τ from the maximum of the loss peak at temperatures $T_{0.1Hz}=581$ K and $T_{1Hz}=596$ K. Figure 1-d shows that the relaxation times from the stress relaxation curves follow the same VFT line than the ones obtained from mechanical spectroscopy, the latter in agreement with the data reported in other works [16][18].

The fact that in the SCL state the stress relaxation curves all have the same KWW exponent implies that the time-temperature-superposition (TTS) principle is valid for this metallic glass-forming melt. Figure 2-a shows how all the SCL measurements converge to the same master curve when the time is normalized by the corresponding τ at each temperature, the shape of the relaxation being well described by Eq. 1 with $\beta \approx 0.5$ (black solid line). This is in agreement with previous works in mechanical spectroscopy, where it was found that almost all metallic glass-forming systems can be well described by a loss modulus peak corresponding to the frequency domain transformation of a KWW relaxation with $\beta \approx 0.5$ [21][22][23].

Figure 2. a) Stress relaxation measurements above 560 K plotted as function of t/τ (symbols) and Eq. 1 with $\beta=0.5$ (black solid line). b) Stress relaxation at 553 K and 523 K after cooling from the SCL state at 0.05 K min^{-1} (blue symbols). Eq. 1 with $\beta=0.5$ (solid black line for 553 K and dashed line for 523 K). Double relaxation fitting of Eq. 2 for the 523 K measurement (red line).

3.2 Stress relaxation in the glass state, cooling from above T_g

Figure 1 and Figure 2 also show the results obtained by a series of stress relaxation measurements in the glass within the temperature region from 523 K to $T_g=561 \text{ K}$. In order to control the glass state, this series of experiments were performed with the following thermal protocol. Firstly, the material was heated above T_g , in the SCL state, performing a stress relaxation measurement at this temperature and checking that the response was in agreement with the expected VFT behavior and $\beta \approx 0.5$ as discussed above. Secondly, the temperature was decreased following a fixed cooling rate until reaching the desired temperature. Subsequently, a 30 min thermal stabilization step followed by an isothermal stress relaxation measurement was performed. Therefore, the measurements were always performed in samples coming directly from the SCL state at a known cooling rate, in this way the degree of physical aging leading to different glassy configurations was only due to the difference in cooling rates, minimizing the inherent complexity of physical aging induced by the thermal history and the application of temperature steps once the system is below T_g .

Figure 1-a shows the stress relaxation curves (red circles), and the corresponding fits with Eq. 1 (red solid lines), obtained at 523 K, 533 K, 543 K and 553 K for the case of a cooling rate of 10 K min⁻¹. Figures 1-c and 1-d show the KWW exponents and the relaxation times obtained for different cooling rates: 0.05, 0.1, 1, 5 and 10 K min⁻¹. In the case of the slowest cooling rate, 0.05 K min⁻¹, only the tests at the two extreme temperatures (523 K and 553 K) were realized. In the glass region, Figure 1-d shows how the relaxation time increases for slower cooling rates, at 523 K varying more than one order of magnitude between the fastest and the slowest cooling rates. The corresponding KWW exponents (Figure 1-c) are not constant anymore and show a definite tendency towards lower values as temperature decreases. The change of the relaxation shape is exemplified in Figure 2-b. At 553 K, the fitting gives a β value consistently below 0.5 in all the tests but the relaxation can still be fitted well by Eq. 1 with $\beta=0.5$ (solid black line). On the contrary, at 523 K, a value of $\beta=0.5$ (dashed black line) is not able to fit the experimental data. The decrease of the KWW exponent of structural relaxation below T_g is predicted in theoretical constructions of the glass state, like the random first-order transition [24]. The stretching of the stress decay observed here may be due to the presence of in-situ aging during the relaxation tests, this producing that the average relaxation time increases along the test. However, as shown in the Discussion section below, the main contribution explaining the decrease of the KWW exponent is due to a widening of the underlying relaxation times distribution as the system goes deep into the glass state.

At this point, it is worth to describe in more detail the results obtained for the lowest temperature (523 K) and the slowest cooling rates (0.05 and 0.1 K min⁻¹). For all the other temperatures and cooling rates, a good fitting could be performed with Eq. 1 obtaining KWW exponents decreasing progressively as the temperature goes down below T_g . However, for these two slowest cooling rates, the initial shape of the stress decay starts to show a slight bump (see Figure 2b and Figure S1 in supplementary materials). Here, the fitting with Eq. 1 is not any more appropriate and a double relaxation function

$$\frac{\sigma(t)}{\sigma_0} = A \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] + (1 - A) \exp \left[- \left(\frac{t}{\tau_2} \right)^{\beta_2} \right] \quad (2)$$

gives a perfect fit to the initial steps of the relaxation process. In Figure 2-b, the red line shows the fitting with a double relaxation function with $\tau=34800$ s, $\beta = 0.402$, $\tau_2 = 59$ s, $\beta_2=0.65$ and $A=0.89$. In this case, the single

relaxation fit would give $\tau=24200$ s and $\beta = 0.323$. For these two conditions (523 K after cooling at 0.1 K min^{-1} and 523 K after cooling at 0.05 K min^{-1}) Figure 1-c and Figure 1-d show the relaxation times and KWW exponents obtained using Eq. 2 instead of Eq. 1. Differently from the other temperatures, the evident decoupling observed for the samples cooled with the slowest rates leads to a slight increase of the β parameter obtained for the slow process (green and blue triangles in Figure 1-c), due to a less wide relaxation time distribution of the slow process once the contribution of the fast τ_2 process is subtracted.

3.3 Stress relaxation in the glass state, heating from room temperature

In this series of relaxation experiments the samples were heated consecutively in isothermal steps starting at room temperature. At each isothermal step a stabilization of 30 min followed by a stress relaxation experiment was performed. Two types of pre-annealing protocols were applied to the samples, the first protocol (protocol A) consisted in heating to 523 K and immediately cooling down at a heating/cooling rate of 2 K min^{-1} . At 523 K the structural relaxation of the as-quenched $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ ribbons is already active and with this protocol the ribbons released part of the residual stresses and lost the bended shape acquired during the quenching process. The second protocol (protocol B) consisted in pre-annealing at 523 K during 6h. This protocol resulted in a more aged state and a similar protocol was applied also on the disk-shaped samples used in the XPCS experiments.

Figure 3-a shows the initial part of the stress decay curves of samples pre-annealed with protocol A at some selected temperatures (373, 423, 473 and 553 K), the complete curves are shown in Figure S2 in the supplementary materials. The signature of a double relaxation with a short relaxation time, τ_2 , and a long one, τ_1 , is observed at the lowest temperatures, as well as the progressive change towards a single relaxation as temperature increases. At the lowest temperatures (373 and 423 K) only the stress relaxation due to the fast process is observable within the test time (2 h); at these temperatures the curves can be well fitted by a partial decay, i.e. with Eq. 2 with $\tau \rightarrow \infty$, as the relaxation time of the slow process is too long to be determined. From 473 to 523 K the stress decays were fitted by a double relaxation function and above 523 K by a single relaxation. Table S2 lists the fitted parameters at the different temperatures.

Figure 3. Stress relaxation curves (a) and recovery of the strain after the stress relaxation experiments (b) at 373 K (skyblue), 423 K (greyblue), 473 K (blue) and 553 K (purple) of a sample pre-annealed following protocol A. Solid lines in a) are fits to Eq. 2 (373, 423, 473 K) or Eq. 1 (553 K). KWW exponents (c) and relaxation times (d) obtained from the fits. Green symbols: β_2 and τ_2 (diamonds) and β and τ (triangles) for samples pre-annealed with protocol A. Pink symbols: β_2 and τ_2 (diamonds) and β and τ (triangles) for samples pre-annealed with protocol B. Yellow circles are β and τ from XPCS experiments done similarly to protocol B, while the blue circles are XPCS β and τ measured upon

cooling from above T_g at 6 K min^{-1} . Purple dots are the stress relaxation measurements in the SCL region already shown in Figure 1. In (d) dashed blue line is the VFT curve expected for the SCL behavior, dash-dotted blue and red lines are the trends obtained for the glasses cooled with the slowest (more aged) and highest (less aged) cooling rates shown in Figure 1, dashed green line is the behavior expected for the secondary relaxation taken from ref. [18].

Figure 3-b shows the recovery steps after the stress relaxation measurements. In such recovery steps the load on the sample was released and the evolution of the sample length recorded. The figure shows the results at the selected temperatures of 373, 423, 473 K and 553 K. The first three temperatures correspond to stress relaxation experiments that were able to record basically only the stress decay due to the fast relaxation process, and it is observed that the strain is totally recovered after the test. This indicates a completely anelastic nature of the fast relaxation. On the contrary, at 553 K the stress relaxation is completed during the experiment and the deformation becomes permanent, which indicates the viscous nature of the relaxation process at this temperature.

Light green diamonds in Figures 3-c and 3-d show the values of β_2 and τ_2 , corresponding to the fast process, obtained for the samples pre-annealed following protocol A. The intensity of the relaxation associated to the fast process ($1-A$ in Eq. 2) is very small at 373 K, inducing only around a 3% of the stress decay (see Figure S2 and Table S2 in supplementary materials). This makes the determination of the relaxation times and exponents difficult as shown by the dispersion of the results in figure 3-d at this temperature. At temperatures from 423 K to 498 K the results of the fits to Eq. 2 are very reproducible and they show a clear temperature dependence of τ_2 . If fitted to an Arrhenius behavior the activation energy would be about $\sim 50 \text{ kJ mol}^{-1}$, which is less than 1/3 of the activation energy of the beta-relaxation determined by Zhao et al. [18] by means of mechanical spectroscopy (green dashed line in panel d).

From 473 K on and above, the presence of the slow viscous process is clearly observed in the stress relaxation experiments of samples pre-annealed with protocol A, green triangles show the corresponding values of β and τ in Figures 3-c and 3-d. At 473, 498 and 523 K the relaxation times τ are slightly shorter than those obtained by cooling at 10 K min^{-1} from the SCL state (red dashed line taken from Figure 1). This indicates that the glass is less aged than the one attained by cooling from the SCL. Above 523 K, the isothermal steps induce aging and

τ becomes comparable and even larger than those obtained by controlled cooling. The green solid line shows the path of τ as function of temperature showing a slight kink at 523 K due to aging. Finally, above 561 K the data merge with the values found in the SCL state.

The contribution of the fast anelastic process to the total relaxation is found to increase from around 3% at 373 K to a maximum of 15% at 473 and 498 K, and starts decreasing at 523 K when the relaxation time of the viscous process becomes shorter and the two processes overlap in the stress decay curves. At temperatures higher than 523 K it is not possible to separate the two processes anymore (see Figure S2 in supplementary materials). Concerning the shape of the relaxation curves, the values of β_2 for samples annealed following protocol A (green diamonds in Figure 3-c) are found lower than 1 at all temperatures. As for the shape of the slow relaxation, the values of β (green triangles in Figure 3-c) are found to follow the same tendency as observed in the glasses obtained by controlled cooling; β is near 0.5 at T_g and it decreases with temperature until 523 K where the fast relaxation can be fitted and, therefore, its contribution is not taken into account anymore when analyzing the shape of the slow relaxation. This observation again indicates that the change in the distribution of relaxation times in the glassy state is mainly due to the progressive separation between the fast and the slow processes as temperature decreases, the former with a much smaller activation energy than the latter.

Figures 3-c and 3-d also show the results of relaxation times and stretching exponents obtained from the samples pre-annealed according to protocol B (6 h at 523 K). Pink diamonds correspond to β_2 and τ_2 while pink triangles to β and τ . A comparison of the stress relaxation curves between glasses pre-annealed following protocols A or B is shown in Figure S3 in the supplementary materials. It is observed that the long pre-annealing at 523 K induced a more aged state in which the contribution of the fast process is reduced and the relaxation time of the slow process becomes longer. The reduction of the contribution of the fast process made it impossible to determine it at temperatures below 423 K. The main effect of the change of the pre-annealing treatments is therefore the increase of τ in the samples with a higher degree of aging, while τ_2 shows similar values for the two protocols. The presence of two relaxation processes with different sensitivity to aging has been observed previously in other out-of-equilibrium materials [25], and it has been reported recently also in metallic glasses [11][26]. In this work, the absence of appreciable aging of the fast process is evident by looking at the data

measured at 523 K. While τ (pink triangles in Figure 3-d) ages approaching the value obtained by cooling the samples from SCL at 0.05 K min⁻¹ (blue dash-dotted line), τ_2 keeps constant independently on the applied protocol. Compared to previous works [11][26], in which the detected secondary process showed a constant relaxation time of about 10 min, insensitive to either temperature or aging, here the secondary process shows a relaxation time changing with temperature, although with a relatively small activation energy as discussed above.

3.4 Microscopic dynamics

The microscopic relaxation dynamics of Pd₄₀Ni₄₀P₂₀ were investigated by means of multi-speckle XPCS, from the evaluation of the autocorrelation of the intensity fluctuations, $g_2(q, t)$, as specified in ref. [27][28]. This quantity is related to the density fluctuations, and thus the dynamics, through the Siegert's relation $g_2(q, t) = 1 + b(q) f(q, t)^2$, with $b(q)$ a set-up dependent parameter and $f(q, t)$ the intermediate scattering function [29]. XPCS measurements were performed following a temperature program similar to protocol B, with a pre-annealing of 6h at 533 K followed by a series of consecutive isothermal steps 373, 423, 473 and 523 K heating from room temperature. After the last isotherms at 523 K the system was heated to 573 K, above the glass transition, and cooled back down to 543 K and a last isothermal measurement was performed. The experimental thermal protocol, i.e. the time spent in each isothermal step, was also the same as applied in the stress relaxation experiments. In the same experiment, samples previously subjected to mechanical rejuvenation were also probed, the comparison between aged and rejuvenated samples is described elsewhere [30].

The detector was placed at the maximum of the structure factor $q_0 = 2.87 \text{ \AA}^{-1}$, thus probing the dynamics at the atomic length scale. Considering a KWW decay of the intermediate scattering function $f(q, t) = f_q(T) \exp[-(t/\tau)^\beta]$, with $f_q(T)$ the non-ergodicity factor, the experimental autocorrelation functions were fitted to

$$g_2(q, t) = 1 + a(q, T) \exp[-2(t/\tau)^\beta] \quad (3)$$

in order to obtain the relaxation time τ and the exponent β . Figure S4 shows the two-time correlation functions at the different isothermal steps, the width of the diagonal color bands is proportional to the relaxation time and the diagonal direction is the experiment time line. At 423 and 473 K a slight increase of the width is evident, and it implies an increase of the relaxation time due to in-situ aging during the measurements. Figure S4 shows the average autocorrelation functions obtained at each isothermal step and the corresponding fitting functions using Eq. 3. It is observed that the relaxation time τ becomes shorter as temperature increases from 373 to 473 K, while at 523 K the relaxation becomes slower and noticeably more stretched. A similar behavior was observed in other metallic glasses in previous studies and it has been associated to the onset of the equilibration in the glass transition region [31]. Figures 3-c and 3-d display the KWW exponents and relaxation times obtained from the XPCS experiment as yellow circles for the heating steps and a blue circle in the case of the measurement performed after cooling from above T_g . The relaxation times at 373, 423 and 473 K overlap with the ones obtained for the fast process in the stress relaxation experiments, while at 523 K the microscopic relaxation time is comparable to those obtained for the slow process. The shape of the relaxation functions is characterized by a high, compressed exponent ($\beta > 1.5$) for the lowest temperatures, which progressively decreases with temperature and becomes stretched ($\beta < 1$) at 543 K in the glass cooled down from the SCL state. Compressed exponents are the hallmark of the out-of-equilibrium dynamics of many systems like metallic glasses [2][32], polymer gels and colloidal systems [33] and they have been attributed to internal stress driven dynamics [34].

4. Discussion

4.1 Relaxation of the supercooled liquid, $T > 561$ K

The stress relaxation of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ in the SCL state has been found to be well described by a KWW function with a relaxation time following a VFT temperature dependence and a constant stretching exponent. The time resolution of the static stress relaxation experiments in our equipment is around 0.5 s. At temperatures above T_g , where the relaxation time scale is of the order of few seconds, this implies that the first part of the stretched decay is not visible. This fact requires a careful procedure in order to analyze the shape and estimate the

parameters of the curve. In this work, the constant value of β is inferred from the superposition of the stress relaxation results in a master curve as shown in Figure 2.

In previous works on stress relaxation of metallic glass-forming melts, the KWW exponents determined in the SCL region near T_g were found to increase rapidly with temperature, from values around $\beta=0.5$ at T_g to values approaching $\beta=1$ at temperatures just 10-20 K above [35]. This increase was in contradiction with mechanical spectroscopy results, where the main α -peak of the loss modulus has been consistently found with an invariant shape, in most systems corresponding to the frequency domain transformation of a KWW time decay with an exponent $\beta \approx 0.5$ [21][22]. It should be taken into account that mechanical spectroscopy is usually performed at frequencies ν ranging from 0.01 to 100 Hz, corresponding to characteristic times $(1/2\pi\nu)$ ranging from 15 s to 1.5 ms, meaning that the α -relaxation peak is always characterized in the SCL state. The time scaling of the relaxation of various physical properties is observed in different classes of glass-forming liquids [36], and the scaling of the density-density autocorrelation function has been found in metallic SCLs near the glass transition [31][37]. If the constant relaxation shape (i.e. the validity of the TTS principle in the SCL region) is a peculiarity of some systems or if it is common in metallic glasses, and how far above T_g it extends, are interesting points to check by performing accurate stress relaxation measurements in the SCL state of metallic glass-forming systems.

4.2 Relaxation of the glass state

In Figure 1-d, the stress relaxation curves of the glasses quenched with controlled cooling rates show the expected increase of τ as the degree of aging is increased [5]; the samples cooled down with slower rates being more aged. In addition, the shape of the relaxation is progressively stretched with aging (see Figure 1-c). The decrease of the parameter β in the glass state can be attributed to two effects; the presence of in-situ aging during the relaxation experiments and the evolution of the relaxation times distribution through aging. Of course, both processes may occur simultaneously under some conditions. In the case of the first effect, the stretching of the stress relaxation function is associated to a $\tau=\tau(t)$ changing significantly between the beginning and the end of the experiment. Many phenomenological models have been proposed to describe the evolution of $\tau(t)$, the one

proposed by Lunkenheimer et al. [38], which was able to reproduce the glassy aging dynamics in dielectric experiments of non-metallic glass formers, introduces an aging controlled by the relaxation time itself

$$\tau^{-1}(t) = [\tau_0^{-1} - \tau_{VFT}^{-1}] \exp \left[- \left(\frac{t}{\tau(t)} \right)^\beta \right] + \tau_{VFT}^{-1} , \quad (3)$$

with $\tau(t)$ going from an initial value $\tau_0 = \tau(t=0)$ towards the equilibrium $\tau_{VFT} = \tau(t \rightarrow \infty)$. This equation can be solved numerically and introduced in the KWW function, $\phi(t) = \exp \left[- (t/\tau(t))^\beta \right]$, to model the effects of in-situ aging on the stress decay. Figure S5 in supplementary materials shows the relaxation curve obtained by Eq. 3 considering different initial values of the relaxation time τ_0 and the corresponding apparent β parameters obtained by fitting the result to Eq. 1. As expected, the system with the higher effect due to in-situ aging is the one with a τ_0 more distant to τ_{VFT} , as it involves faster aging and, therefore, a larger change of $\tau(t)$ throughout the stress relaxation. This result will be qualitatively similar if another aging model was used instead of Eq. 3.

The results obtained for the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass with different degrees of aging show a decrease of the KWW exponent as the system goes deeper in the glassy landscape of states and τ_0 becomes longer, which is exactly the contrary behavior as the one shown in Figure S5 if the effects of in-situ aging were significant. Therefore, the change in the shape of the relaxation decay as a function of the cooling rate of the quenching process cannot be attributed to in-situ aging but to the changes of the underlying relaxation time distributions $D(\tau)$ of different glassy states, in agreement also with some theoretical work [39]. Figure 4 shows the relaxation curves obtained considering different $D(\tau)$ s calculated as

$$\phi(t) = \int_0^\infty D(\tau) \exp[-t/\tau] d\tau . \quad (4)$$

Figure 4-left shows, qualitatively, the situation in the equilibrium SCL state. The shape of the distribution is invariant and only the average value of τ changes with temperature. Consequently, the corresponding relaxation curves are also invariant in shape, the fitting to Eq. 1 providing the same value of the KWW exponent. The plots in Figure 4-right are meant to show a conceivable picture of what happens once the system is in the glassy state.

As previously noted when discussing Figure 1, the stress decay curves reflect a wider distribution of times involved in the relaxation both when reducing temperature and increasing aging. In other words, the lower the fictive and real temperatures the lower the value of the KWW exponent. Eventually, the distribution of relaxation times becomes decoupled between the fast and the slow processes, which have different temperature dependences and apparent activation energies. In Figure 4-right, this effect is qualitatively represented by shifting the $D(\tau)$ with different activation energies between the fast and the slow contributions. In the case of the Figure 4 a ratio of $E_{fast} / E_{slow} = 0.5$ has been chosen. It is shown how the fitting to Eq. 1 provides a stretching exponent of the relaxation function which is progressively reduced and, finally, how the decoupling between the fast and the slow parts of the distribution becomes evident.

Figure 4. Relaxation time distributions (Top plots) and corresponding decay functions (Symbols in the bottom plots) with the value of β obtained by fitting Eq. 1 (lines in the bottom plots). Left: Invariant shift of the relaxation time distribution. Right: Shift of the relaxation function applying different activation energies for the fast and the slow processes, the plots correspond to $E_{fast}/E_{slow} = 0.5$.

Therefore, the non-invariant widening of $D(\tau)$ with the reduction of temperature and the degree of aging explains qualitatively the effects observed in the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass. The change of $D(\tau)$ with temperature can be

explained by the presence of a distribution of activation energies [40], with relatively lower activation energies for the relaxation mechanisms with shorter characteristic times. Relaxation processes with different activation energies are indeed observed by mechanical spectroscopy in various metallic glasses [10], designated as secondary relaxations. Here, it is interesting to note that the fast process described in this work shows an activation energy different from the secondary relaxation as determined by mechanical spectroscopy [18] (green dashed line in Figures 1-d and 3-d). However, around 450 K, where the fast relaxation is more clearly observable in the stress relaxation tests, it shows a similar characteristic time. Contrary to the α -relaxation at temperatures near and above T_g , the connection between the mechanical response in the frequency and the time domains is not clear in the time-temperature region corresponding to the secondary relaxations and would be worth to be investigated in future experiments. It is worth noting that in this qualitative picture we have not considered the changes of the amplitude ratio between the fast and slow parts of the distribution (see values of the 1- A parameter in Tables S2 and S3). This parameter shows a progressive diminution of the relative intensity of the fast contribution as temperature decreases, and it would introduce a further change of the shape of $D(\tau)$, which is not taken into account in the current discussion.

Concerning the effect of aging, the change of $D(\tau)$ indicates that aging seems to affect very differently the diverse relaxation times contributing to the stress relaxation, showing a progressive differentiation of $D(\tau)$ from the one observed in the equilibrium SCL state. This means that while aging increases the average τ , making it more close to the equilibrium τ_{VFT} value, it differentiates the shape of the τ distribution. The latter effect was not anticipated as aging was expected to reduce the spatial and dynamic heterogeneity of the glass. The observed decoupling between the fast and slow relaxations with aging may be due to a different nature, anelastic/stress-driven vs viscous/diffusive, of the processes involved. It could also be conceivable that this effect is associated to a certain stage of the aging process, as the values of τ in the glass states tested in this work are all far from the expected equilibrium values indicated by the VFT line in Figures 1-d and 3-d.

The presence of decoupling and different aging sensitivities between the fast and slow processes has been reported in other kinds of disordered systems [25]. As in those cases, while the slow, α -process keeps evolving with aging, the fast relaxation seems independent on the applied protocol. This is in agreement with recently

published results in which the microscopic relaxation time was found not dependent on the fictive temperature of the glass [41]. On the other hand, a recently published work [30] shows that the dynamics of the stress-driven relaxation process is accelerated by rejuvenation induced by severe plastic deformation, although the activation energy of the relaxation was not found significantly altered. Therefore, the low temperature stress-driven dynamics, here identified with the fast relaxation process, are actually affected by the aged/rejuvenated state of the glass but with much lower sensitivity than the observed for the viscous-like relaxation. Further investigation of the change of the spatial and dynamical heterogeneities through aging is needed to clarify the origin of the observed macroscopic behavior.

Recently, the higher mobility of the atoms in the surface of metallic glasses [42] has also been identified as a source of dynamic decoupling [43]. Structural heterogeneity due to surface effects is expected within a layer of the order of 10 nm, and it has been proven to originate fast relaxation processes that affect the dynamics of ultrathin samples [43]. In our work, the samples were 30 μm thick and it is not expected that the structural heterogeneity due to surface effects can modify significantly the intrinsic bulk heterogeneity. The contribution of the fast relaxation process discussed above reaches more than 10% of the total stress decay in some of the test conditions (see Tables S2 and S3), while the total fraction of volume sample affected by surface heterogeneity would be less than 0.1 %. The mechanical spectroscopy results, applying oscillating strain and shown in Figure 1-b, do not show any significant difference with the behavior obtained for thicker samples in single-cantilever mode [18], indicating that the mechanical response is not affected by a surface effect.

Finally, it is interesting to discuss the coincidences and differences of time scales and shapes between the microscopic relaxation measured by XPCS and the macroscopic stress decay. At the lower isothermal steps (373, 423 and 473 K), the decorrelation of the intensity fluctuations shows the same time scale as the first relaxation process observed in the stress decay curves. This may indicate that the origin of the two observations is the same, and the dynamics observed by XPCS experiments is related to the same movements of the glass structure that lead to a macroscopically anelastic response. The microscopic mechanisms originating such behavior are not clear. The anelastic relaxation times of metallic glasses are long [6], many orders of magnitude away from any time scale attainable in simulations, thus making a theoretical microscopic description difficult. At these lower temperatures, the shape of the microscopic relaxation function is compressed with $\beta > 1$ (Yellow

circles in Figure 3-c), such high compressed exponents indicate that this relaxation process is not of diffusive nature and may be due to collective dynamics driven by the presence of stress fields [2][33][34][44][45].

In spite of the coincidence in time scales, the values of the macroscopic shape parameter β_2 of the fast relaxation (Diamonds in Figure 3-c) are clearly lower than that of the microscopic exponents. Therefore, in this region of temperatures (373, 423 and 473 K), although the time scale of the microscopic dynamics coincides with the decoupled, faster part of the stress relaxation process, the shape of the relaxation is not at all coincident. The origin of the compressed exponent and the difference between the macroscopic and microscopic shape parameters, which is observed in many systems, is still controversial and remains an open question and a matter of intense research [45][46][47][48][49][50]. The XPCS measurements showed in this work were performed at the maximum of the structure factor, thus probing the decorrelation of atomic scale configurations. The coincidence of time scales suggests that the atomic scale dynamics control the relaxation process, but the macroscopic response may have contributions of time scales associated to other length scales.

At 523 K, the XPCS results show an increase of the decorrelation time (Circles in Figure 3-d), orders of magnitude longer than in the previous isothermal step, and a decrease of the stretching exponent (see also Figure S4). Hence, above this temperature the decorrelation of the intensity fluctuations seems to start showing the contribution of the slow diffusion-like process. This diffusive-like mechanism may be active at lower temperatures, but much slower than the stress-driven dynamics that dominate the microscopic XPCS observations in such a temperature region. As seen in Figure 3, increasing the temperature towards the glass transition causes the microscopic dynamics to change from compressed to stretched, while showing a time scale more similar to the overall stress relaxation. At temperatures near and above T_g , the macroscopic and microscopic dynamics of metallic glasses have been found coincident in other experiments [31][51][37].

The results of this work indicate that going down in temperature through the glass transition, the macroscopic stress relaxation progressively stretches, changing from a constant shape (TTS) behavior towards a decoupling between fast and slow parts of the relaxation time distribution. This coincides with the emergence of compressed dynamics in the intermediate scattering function observable by XPCS, suggesting that the movements responsible of the anelastic part of the relaxation in glass are microscopically very different from the diffusion-

like hopping mechanism in supercooled liquids [52][53], which is characterized by stretched microscopic dynamics with exponents $\beta < 1$.

This picture has many similarities with a recent model [45]. This model proposes that above T_g the activation of a local relaxation event increases the rigidity of the neighboring relaxation zones, thus leading to a stretched relaxation. On the contrary, below T_g , the local relaxation changes to avalanche-like events. In the latter case, the relaxation event softens the surroundings accelerating the dynamics and leading to a compressed behavior. The results of our work, however, point to a low temperature relaxation mechanism which is reversible, as the fast part of the stress relaxation does not introduce a permanent deformation in the sample, and this seems not compatible to an avalanche-like mechanism. The microscopic origin of the anelastic relaxation could be also explained by other models. For instance, it may be similar to the one observed in bead packs, see for instance [54]. In this picture the relaxation is driven by movements along stress chains or stress fields formed in the amorphous structure, without necessity of local rearrangements implying change of neighbors or breaking of bonds. A collective motion driven by a stress field may generate a compressed exponent similar to the dynamics observed under flow [55]. Further studies, with controlled stress conditions could unveil the nature of this glass relaxation mechanism.

Detailed knowledge of the relaxation behavior is an important technological aspect for low temperature forming processes of metallic glasses [56]. In this sense, XPCS is a unique technique to access the microscopic out-of-equilibrium dynamics. For instance, the time scales of the relaxation processes dealt with in this work are many orders of magnitude longer than the ones accessible by molecular dynamics simulations. While in the supercooled liquid state mechanical and XPCS results show an overall agreement in time scale and relaxation shape, the interpretation of XPCS experiments is complicated in the glassy state, where the inherent out-of-equilibrium effects like aging can be merged with the relaxation of internal stress fluctuations or external stress fields. This work presents a first evidence of coincidence between the time scales of the microscopic dynamics in the glass and a macroscopic effect, which will pave the way to further studies.

5. Conclusion

In summary, the results of stress relaxation experiments have shown that the stress relaxation of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ is controlled by a relaxation time distribution with invariant shape above T_g , producing a corresponding constant KWW exponent. Below this temperature, the distribution broadens progressively, which indicates different temperature dependences of the microscopic processes involved in the distribution. The decrease of the KWW exponent is also observed as a function of aging, which implies that the different time scales in the relaxation distribution have different aging sensitivity and the dynamic heterogeneity increases. When temperature decreases far from T_g and the system ages enough, the distribution of times decouples between fast processes with recoverable, anelastic behavior and slow, irreversible, viscous-like relaxations. While the main slow process evidently ages with time, the fast one is found independent on the specific applied protocol as in some soft glasses [25]. The coincidence between the macroscopic stress relaxation behavior and the microscopic dynamics suggests that, at the lower temperatures, the microscopic dynamics measured by XPCS show only the effects of the fast process, i.e. the anelastic-like relaxation of the system under the presence of stress fields. This connection would explain the peculiar compressed shape of the intermediate scattering function of metallic glasses at the atomic scale and deserves further studies.

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