XPCS on metallic glasses

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It is only in recent years that the study of the microscopic dynamics of metallic glasses (MGs) has become possible thanks to the advance in X-ray photon correlation spectroscopy (XPCS). This is precisely the technique we used for the analysis of a $La_{60}Ni_{15}Al_{25}$ Lanthanum-based glass (LaMG) and a high-entropy $LaCeYNiAl$ glass (LaHEMG). We are particularly interested in two parameters that describe their dynamics: the relaxation time τ_α and the shape parameter β , which describe the relaxation process at different temperatures. In this article we experimentally obtained these parameters from the characterisation of the intermediate scattering function obtained from the X-ray Photon Correlation Spectroscopy (XPCS) technique at the European Synchrotron Radiation Facility (ESRF).

I. INTRODUCTION

A. Glass and supercooled liquid states

Glasses have a disordered, out-of-equilibrium structure and slow relaxation dynamics. The glassy state formed through a kinetic transition from a supercooled metastable liquid. A liquid can be cooled down up to a point where the thermodynamically stable configuration is the crystalline state. Nevertheless, if cooled fast enough, crystallization can be avoided and thus the liquid becomes a so-called supercooled metastable liquid. If the temperature is further decreased, the viscosity in the supercooled liquid increases so that it takes a longer time for it to equilibrate after a change of external conditions, up to the point when it can no longer do so. It is precisely at this moment that a transition to the glassy state occurs, at a temperature T_g , which is dependent on the rate at which the material is cooled (Fig 1).

Once in the glass state, materials exhibit slow structural changes (compared to other states such as the liquid state). These are slow structural relaxation processes referred to as physical aging. The properties of glasses and their long-time evolution are governed by the relaxation dynamics, the most relevant characteristic being the relaxation time scale, which can drastically change due to small changes in temperature and structural state.

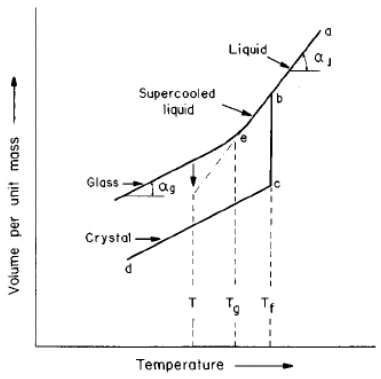

FIG. 1. Specific volume over temperature for liquid, supercooled liquid, glass and crystal states. Transition to the glass state at temperature T_g [1].

Our aim here is to get insight into the behavior of the relaxation dynamics in the glass and supercooled liquid states. The fact that crystallization can be avoided in good glass-forming materials allows us to study both the supercooled liquid and glass states.Metallic glasses (MGs) will be the object of our study. These are disordered alloys that exhibit properties of high strength, high hardness, large elastic region and soft magnetic properties [2–4]. Their unique homogeneous liquid-like structure make these materials good candidates for new advanced manufacturing and nanotechnology applications.

B. Dynamics of glasses and supercooled liquids

Viscosity is a macroscopic quantity that results from the mobility of molecules inside a material. In the case of glasses and particularly of MGs, mobility decreases upon cooling. In supercooled liquid viscosity can vary in ten orders of magnitude within a narrow temperature range [5] . On the other hand, the structural relaxation time is a microscopic parameter that measures the time scale of the atomic mobility and, therefore, how long it takes a system to recover its equilibrium configuration after a perturbation. In general, when the system is in the supercooled liquid state, relaxation time decreases as the temperature increases, as they also do the macroscopic dynamical properties such as viscosity [6].

One of the aims of the experiment is to measure the structural relaxation time τ_α and the shape parameter β of both an MG and a high-entropy MG (HEMG) in order to compare them and see whether they behave differently. This can be done experimentally by obtaining the Intermediate Scattering Function, which is how we will address the motion in the liquid and glass states [7].

In disordered systems, the Intermediate Scattering Function ϕ(q,t) gives information about the dynamics of the scattering particles inside the material, that as said previously, can be described by the τ_α and β parameters [6]. The function is defined in *eq* 1 but what we obtained experimentally is the square of the ISF, which we refer to as g^2.

$$\phi(q,t) = f(q,T)exp[-(t/\tau_\alpha)^\beta] \quad (1)$$

II. EXPERIMENTAL METHODS: XPCS TECHNIQUE

When an atom is illuminated with coherent, monochromatic light, it will emit scattered photons, leading to an interference pattern. In the case of samples that present random fluctuations (such as metallic glasses and supercooled liquids) this interference pattern is referred to as a speckle pattern [8]. We are only interested in the photons coming from scattered light, since they have information about the structure of the glass and the temporal evolution of the speckle patterns will allow us to obtain the ISF.

In order to set the energy of the radiation used in the XPCS experiment we need to account for the electronic state transitions of the elements present in our materials that can produce fluorescence. The incident X-rays must not have an energy immediately above the energy necessary to excite the fluorescent emission of any of the elements present in the compound, which we want to avoid as it is a source of incoherent photons that will decrease the contrast of the speckle patterns. We will work with energies below the edge, so as not to get fluorescent photons and we will set a threshold of energy at about half the energy we are working with. In that way, we expect that the photons that we will get at the detector must be of the energy of the incident beam, since they come from elastic scattering.

In the experiment we used two 2D pixel photon detectors. Only a small range of wavenumbers q will be detected and afterwards studied. Therefore, the orientation of the detector is of paramount importance: it is to be placed at a certain angle with respect to the incident beam according to Bragg's law (*eq* 2).

$$Q = 4\pi sin(\theta)/\lambda \quad (2)$$

After collecting data for a period of time δt, the average correlation between images taken at different times t_1 and t_2 is computed with *eq* 3, which is exactly the g^2 function described above.

$$g^2(t_1,t_2) = \sum_p \frac{\langle I_p(t_1) I_p(t_2)\rangle}{\langle I^2(t)\rangle} \quad (3)$$

This results in the so-called two-time plot, which can be seen in the schematics of the XPCS experimental set-up shown in Fig.2

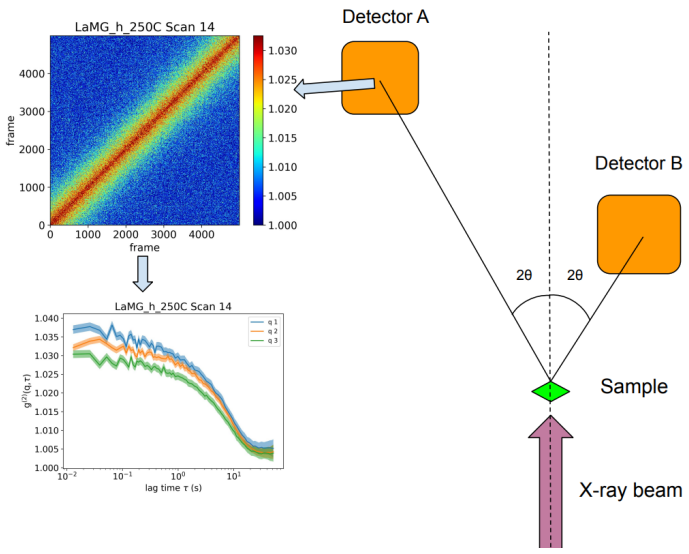

FIG. 2. Schematics of the XPCS experiment in beamline ID10 at ESRF.

After setting the energy of the incident beam and the position of the detectors, we mounted the metallic glass ribbons inside a furnace under vacuum atmosphere in the position shown in Fig 2. The furnace has kapton windows to allow the transmission of the incident and scattered photons. The experiment will consist in applying a constant heating rate of $1K/min$ to the metallic glass, in order to get insight to the dynamics of the materials as temperature increases. We only used the data collected by the detector A, *Pilatus*. Detector B was useful to calibrate the set-up and gave us information about what stage of crystallisation was the sample at all temperatures.

III. RESULTS

The assumption of a Kohlrausch-Williams-Watts (KWW) function for the ISF (*eq* 1) leads to

$$g^2 = c \cdot exp[(-2 \cdot t/\tau_\alpha)^\beta] + b \quad (4)$$

where parameters c and b refer to the contrast and baseline parameters, which correspond to the plateaus at the start and at the end of the g^2 function (See Fig 3) [9, 10]. The contrast and baseline parameters are basically dependent on the experimental setup and the density and thickness of the samples. This conditions are not expected to change along the heating ramp. Therefore, we can set constant the values of b and c for a given sample, and then. With this data, we have fit the τ_α and β parameters, obtained as a function of the temperature.

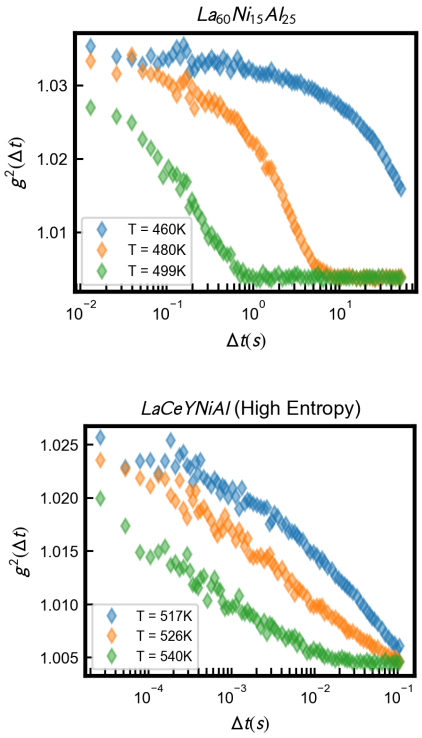

FIG. 3. g^2 function (eq 4) over Δt for $La_{60}Ni_{15}Al_{25}$ MG (Top) and $LaCeYNiAl$ HEMG (Bottom), for three different temperatures for the supercooled liquid state, with starting temperature close to T_g (blue).

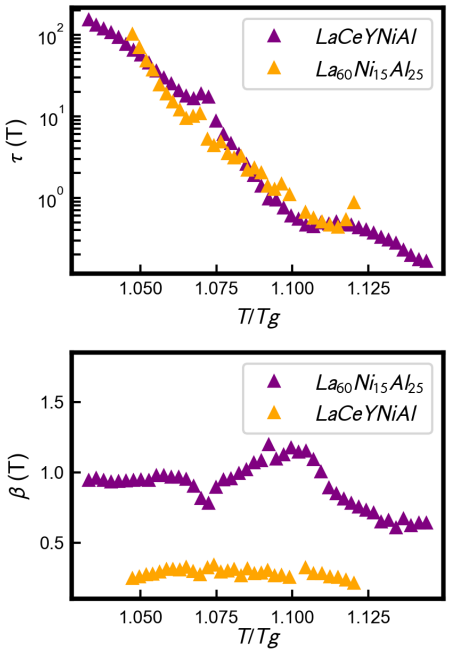

FIG. 4. Comparison of the relaxation time (Top) and the shape parameter (Bottom) over normalised temperature (T/T_g), for $La_{60}Ni_{15}Al_{25}$ MG (T_g=445 K) and $LaCeYNiAl$ HEMG (T_g=492 K)

In Fig 3, we show the g^2 function at different temperatures and the fitted τ_α and β parameters for the La MG and HEMG samples with a fixed contrast and baseline.

As shown in Fig 4, the relaxation time of the two materials show a very similar behavior if the temperature is normalized by the T_g of each material. This suggests that the viscosity change with temperature, the activation energy for flow and the liquid fragility are similar in both liquid alloys. Contrarily, the shape exponent is near a value of 1 for the La MG and around 0.3-0.4 for the high entropy counterpart. A β=1 corresponds to a single, well-defined relaxation time, while a $\beta < 1$ indicates the presence of a distribution of microscopic relaxation times. Parameter τ_α is in this latter case the average value of the distribution. Although these are just preliminary results, it seems that the high entropy effect is reflected in the presence of a wide distribution of relaxation times. This broad distribution of the times may have its origin in a liquid structure formed by a large variety of local configurations.

IV. CONCLUSIONS

We have determined experimentally the timescale of the atomic-scale structural relaxation along the transition from the glass state to the supercooled liquid state of two glass-based metallic glasses ($La_{60}Ni_{15}Al_{25}$ and $LaCeYNiAl$). The relaxation time is observed to decrease from the order of minutes down to less than one second, corresponding to the change from a solid-like glass to a viscous liquid. At lower temperatures we obtained higher relaxation times, which confirms the glass state nature at this temperature range. This can be seen directly from the g^2 function. We have obtained slower decorrelation over time at lower temperatures. As for higher temperatures, decorrelation becomes faster, which is indicative of the faster dynamics. At the range of temperatures analyzed, the samples have not yet crystallized. This is because we observe no increase in the relaxation time at any point after the previous drop for the supercooled liquid state. A preliminary analysis of the results suggests that the dynamics of the HEMG show a much lower shape exponent β, indicating the presence of a much broader relaxation spectrum compared to the conventional MG.

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Citations and References

[1] Zanotto, Edgar. (1998). Do cathedral glasses flow?. American Journal of Physics. 66. 392-395. 10.1119/1.19026.

[2] Schroers, J. (2010). Processing of bulk metallic glass. Advanced materials, 22(14), 1566-1597.

[3] Chen, M. (2011). A brief overview of bulk metallic glasses. NPG Asia Materials, 3(9), 82-90.

[4] Best, James Evenson, Zach Yang, Fan Dippel, Ann-Christin Stolpe, M. Gutowski, Olof Hasib, M. Tarik Li, Xiaopeng Kruzic, Jamie. (2019). Structural periodicity in laser additive manufactured Zr-based bulk metallic glass. Applied Physics Letters. 115. 031902. 10.1063/1.5100050.

[5] Debenedetti, P. G., Stillinger, F. H. (2001). Supercooled liquids and the glass transition. Nature, 410(6825), 259-267.

[6] Ruta, B., Pineda, E., Evenson, Z. (2017). Relaxation processes and physical aging in metallic glasses. Journal of Physics: Condensed Matter, 29(50), 503002.

[7] Kurzthaler, C., Leitmann, S., Franosch, T. (2016). Intermediate scattering function of an anisotropic active Brownian particle. Scientific reports, 6(1), 1-11.

[8] Narayanan, Theyencheri Konovalov, O.. (2020). Synchrotron Scattering Methods for Nanomaterials and Soft Matter Research. Materials. 13. 752. 10.3390/ma13030752.

[9] Amini, N., Yang, F., Pineda, E., Ruta, B., Sprung, M., and Meyer, A., Intrinsic relaxation in a supercooled ZrTiNiCuBe glass forming liquid, Physical Review Materials, vol. 5, no. 5, 2021.

[10] Dyre, J. C. (2006). Colloquium: The glass transition and elastic models of glass-forming liquids. Reviews of modern physics, 78(3), 953.