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Aging and structural relaxation of hyper-quenched $Mg_{65}Cu_{25}Y_{10}$ metallic glass

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ABSTRACT

The structural relaxation, glass transition and crystallization processes of $Mg_{65}Cu_{25}Y_{10}$ metallic glass are studied by Differential Scanning Calorimetry (DSC) and Mechanical spectroscopy. The relaxation model derived from the mechanical measurements is compared with the kinetics of these transformations obtained from the DSC curves. The structural relaxation kinetics is found to be controlled by the glassy dynamics following an Adams–Gibbs–Vogel function. The glass transition and crystallization kinetics are controlled by the dynamics of the supercooled melt following a Vogel–Fulcher–Tammann behaviour. The results suggest that the microscopic processes responsible of structural relaxation and aging below the glass transition correspond to the same processes generating the α-relaxation peak.

1. Introduction

Physical properties of metallic glasses (MG) can be deeply affected by the relaxation state attained during the previous thermal history [1]. The high cooling rates usually needed to bypass crystallization result in glasses with high fictive temperatures (T_f). This as-quenched state is characterized by large amounts of excess free volume and internal stresses in the glass structure and it can be stabilized through annealing or physical aging. In Mg, Ca and Ce-based metallic glasses, where the glass transition temperature (T_g) is found below 450 K, the structural relaxation processes are active even at room temperature. A clear understanding and description of the processes driving structural relaxation is then a fundamental knowledge in designing the annealing protocols in order to obtain the desired properties and in predicting the time evolution of the physical properties under working conditions.

In Ref. [2] we described the relaxation spectrum of $Mg_{65}Cu_{25}Y_{10}$ glass by means of mechanical spectroscopy. The elastic complex modulus measured in the multi-frequency tests was well described by considering that the system follows a Vogel–Fulcher–Tammann (VFT) function in the supercooled liquid state

$$\tau_e(T) = \tau_0 \exp\left(\frac{B}{(T - T_0)}\right) \quad (1)$$

and an Adams–Gibbs–Vogel (AGV) function [3] in the out-of-equilibrium glassy state

$$\tau_{ne}(T) = \tau_0 \exp\left(\frac{B}{T(1 - T_0/T_f)}\right) \quad (2)$$

with parameters $B = 5750$ and $T_0 = 260$ K taken from viscosity data [4] and $\tau_0 = 2.4 \times 10^{-15}$ s determined from the position of the maximum of the loss peak in the equilibrium supercooled liquid region. The fictive temperature changed from $T_{f2} = 437$ K in the as-quenched state to $T_{f1} = 412$ K in a relaxed state obtained by isothermal annealing. The onset of glass transition was observed by DSC at $T_g = 416$ K when heating at 10 K/min. The relaxation time given by Eqs. (1) and (2) correspond to the main structural relaxation time of the system (α-relaxation). Below T_g, the dynamics of the glass are arrested in an Arrhenius behaviour while, above T_g, the VFT function reproduces the diverging slowing down of the dynamics when approaching glass transition.

The microscopic processes leading to structural relaxation and physical aging of metallic glasses are not at all clear. Mechanical spectroscopy at low frequencies (0–200 Hz) shows that the internal friction increases in the same temperature region were structural relaxation of as-quenched samples takes place [5,6]. In many systems it is considered that the structural relaxation is driven by secondary relaxations faster than the main relaxation of the glass [7–9]. Evident secondary relaxations have been found in Pd-based and La-based systems [6]. In other systems, the increase of internal friction is observed as a low temperature excess wing of the equilibrium α-relaxation peak in the viscoelastic loss modulus

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[10–12]. In Ref. [2] the excess wing of $Mg_{65}Cu_{25}Y_{10}$ glass was well described as the high frequency tail of the α-relaxation once arrested in the non-equlibrium dynamics given by Eq. (2).

If the microscopic processes driving structural changes during annealing or aging of metallic glasses are the same processes generating internal friction in mechanical spectroscopy experiments, the determination of the relaxation model would be a useful tool for understanding such phenomena. In this paper we will compare results of Differential Scanning Calorimetry (DSC) and Dynamo-Mechanical Analysis (DMA) of $Mg_{65}Cu_{25}Y_{10}$. The measurements were performed in samples with different relaxation states obtained by annealing or by room-temperature aging. The aim of the work is to check if the structural changes occurring during annealing and aging of as-quenched samples are explained by the relaxation model proposed in Ref. [2] and, therefore, if they can be fundamentally described by Eqs. (1) and (2).

2. Materials and methods

Samples were produced as thin ribbons by melt-spinning. Cu and Y pure metals were pre-alloyed by arc-melting under Ti-gettered Ar atmosphere. Pure Mg was added in an induction furnace in order to prevent its volatilization. The melt was then injected on the Cu wheel spinning at 40 m/s perimeter velocity producing rapidly quenched metallic ribbons with thickness of 33 ± 4 μm. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 404 F3 Pegasus and in a Perkin Elmer DSC-7. In order to assess the kinetics of the reactions the DSC curves were performed with heating rates from 5 to 60 K/min on the as-quenched sample and from 0.5 to 60 K/min on the aged samples. Mechanical spectroscopy was performed on a TA-instruments Q800 DMA. Tests were carried on in tensile geometry applying a preload (static force) of 0.08 N at a frequency of 1 Hz. Oscillating strains of 1 μm amplitude were applied by loading and unloading around this static value with the required dynamic force. The length of the ribbon pieces was of 10 mm.

The measurements were performed on as-quenched, relaxed and aged samples. The as-quenched samples were stored several weeks at room temperature before the measurements, the fast physical aging observed during the first days after the production of rapidly-quenched $Mg_{65}Cu_{25}Y_{10}$ glass [13] is then expected not to affect the results. The relaxed samples measured by DMA were obtained by annealing isothermally during 30 min at 410 K while being under tensile constant load of 0.08 N. This procedure is expected to release most part of quenched-in internal stresses and suppress sensible structural changes when annealing with the heating rates used in the DSC and DMA experiments (0.5–60 K/min). The aged samples were obtained by keeping the ribbons in a humidity-free environment during 20 and 24 months.

3. Results

Fig. 1 shows the signature of structural relaxation of as-quenched samples measured by DSC and DMA. The blue lines correspond to the as-quenched samples. Above 365 K, the increase of the loss modulus measured at 1 Hz corresponds well with the onset of the exothermic signal of the structural relaxation. Between 365 K and 400 K the loss modulus $E''(\omega, T)$ shows an evident hump in the same region where the structural relaxation is detected by the DSC signal. Here it should be noted that the change of frequency in DMA experiments, and the change of heating rate in both DSC and DMA would shift the temperatures were the different phenomena are observed. However, from the comparison of DSC and DMA measurements, it seems plausible that the same microscopic events generating internal friction are also responsible of the structural changes stabilizing the system.

For the 5 K/min DSC scan depicted in the figure, the glass transition region is detected between 408 K and 428 K. Above this temperature the system reaches internal equilibrium. The maximum of the loss modulus peak, which would mark the dynamic glass transition corresponding to a frequency of 1 Hz, is observed near 440 K well above the glass transition detected by DSC, which would correspond to the dynamic glass transition at frequencies approximately 100 times lower [14].

For the relaxed samples (red lines) the release of heat during annealing is completely absent in the DSC signal, this means that the system remains basically in the same isoconfigurational state below T_g. In the loss modulus, the low temperature hump is suppressed but the increase of internal friction is still observed as a low-temperature wing of the equilibrium. This means the microscopic processes generating internal friction are also activated in the relaxed state but, in this case, they do not lead the system to a change of state.

Fig. 2 shows the change in the intensity and onset of structural relaxation between as-quenched samples and samples stored 20 months. It can be observed that, after the fast physical aging observed during the first weeks after production [13], $Mg_{65}Cu_{25}Y_{10}$ is continuously evolving towards more and more stable states due to aging at room temperature. Fig. 2 inset shows the change in the onset temperatures of structural relaxation and glass transition when applying different heating rates. In this case the measurements correspond to samples stored 24 months.

The activation energies of the structural relaxation, glass transition and crystallization processes have been calculated by the Kissinger method, the calculated values are $E_r = 148$ kJ/mol, $E_g = 303$ kJ/mol and $E_x = 208$ kJ/mol respectively. Fig. 3 shows the Kissinger plots of as-quenched, 20-months and 24-months

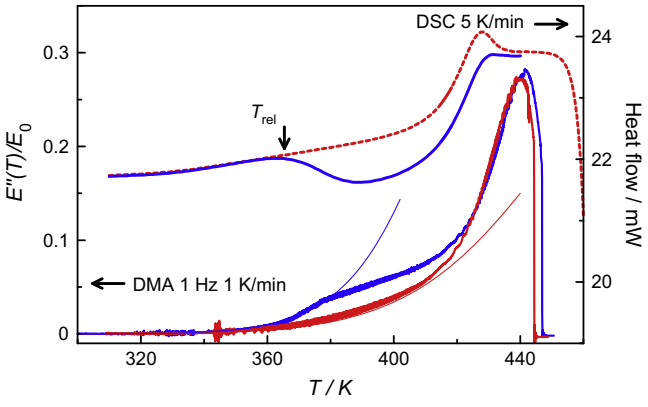

Fig. 1. DSC and DMA runs obtained for the as-quenched (blue) and relaxed (red) samples. Thin lines correspond to the $E''(T)/E_0$ calculated from the CC-function and the proposed non-equilibrium dynamics $\tau_{ne}(T,T_f)$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

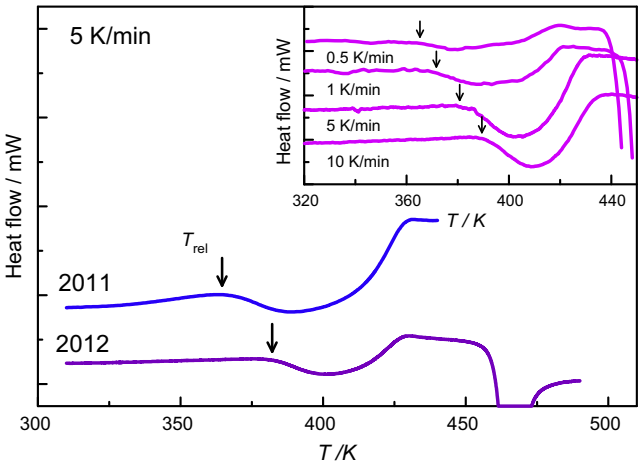

Fig. 2. DSC curves obtained for as-quenched (blue), 20-months aged (purple) and 24-months aged (magenta). The inset shows the temperature shift of structural relaxation and glass transition as function of the applied heating rate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)