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Relaxation of rapidly quenched metallic glasses: Effect of the relaxation state on the slow low temperature dynamics

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Abstract

The relaxation spectrum of rapidly quenched $Mg_{65}Cu_{25}Y_{10}$ metallic glass ribbons is studied by mechanical spectroscopy at temperatures below and around the glass transition. The comparison between hyper-quenched and relaxed samples is used to examine the origin of the low temperature "excess wing" of internal friction commonly observed in mechanical spectroscopy of metallic glasses. The results show that the excess wing can be attributed to access of the system to the broad α-relaxation process while evidence of secondary relaxations is not found. This suggests that in this glassy system the activation energies of structural relaxation and low temperature deformation are directly related to the activation energy of the main relaxation process of the glassy state.

Keywords: Dynamic mechanical analysis; Internal friction; Mechanical properties; Metallic glasses; Relaxation

1. Introduction

The relaxation dynamics of metallic glass-forming alloys influences the fundamental properties of these materials. The liquid phase dynamics near the glass transition temperature T_g can be well described by the temperature dependence of the α-relaxation time τ, defined as the timescale for shear viscosity relaxation. Upon increasing the temperature above T_g supercooled liquids experience a rapid decrease in τ and viscosity η. Among other factors, such as the thermodynamic stability of competing crystalline phases [1] or the topological proximity of liquid and crystalline structures, the viscosity of the supercooled liquid strongly determines the glass-forming ability (GFA) and the thermal stability of metallic glasses [2]. The behavior of viscosity close to T_g is also responsible for the flow and shape formability of metallic glasses at high temperatures [3–5].

Below T_g glasses are in an out of equilibrium state. As a consequence, the glassy state is not stable and the system continuously evolves towards more relaxed configurations. The glassy state resulting from the quenching process relaxes down to more energetically favorable states by means of structural rearrangements with a broad spectrum of activation energies [6]. The available thermal energy determines which of these rearrangement processes are accessible and their characteristic times. The time evolution of the system due to structural relaxation at temperatures below T_g is termed physical aging and has important technological consequences in glassy materials.

In metallic glasses relaxation processes accessible at temperatures well below T_g are usually observed as an excess wing of the loss modulus measured by mechanical spectroscopy [7–10]. Since the earliest studies of Chen et al. [11] these processes have been known to be responsible for the aging and relaxation of glassy metals, even at temperatures

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well below the T_g. These relaxation mechanisms involve annihilation of excess free volume and internal stresses of fast quenched metallic glasses [12] and they may induce changes in the mechanical properties increasing the rigidity and, in some alloys, provoking a transition from ductile to brittle fracture behavior [13,14].

Recently it has been proposed that secondary relaxations observed by mechanical spectroscopy are intimately linked to the so-called shear transformation zones (STZs), both events showing similar activation energies [15,16]. The current theories state that the main microscopic mechanism of permanent deformation of metallic glasses is the activation of STZs, which are local regions of tens or hundreds of atoms undergoing inelastic shear distortion. The operation of STZs seems to play a fundamental role in both homogeneous and inhomogeneous deformation of glassy alloys [17] and it has been a topic of intense research for the last decade.

In this paper we analyze the relaxation processes in $Mg_{65}Cu_{25}Y_{10}$ metallic glass below and above the T_g by means of mechanical spectroscopy using a dynamo-mechanical analyzer (DMA). $Mg_{65}Cu_{25}Y_{10}$ alloy is one of the first bulk metallic glass-forming compositions discovered in the 1990s and it shows an excellent GFA. This material can be solidified in completely glassy rods 7 mm in diameter [18] and it is characterized by high thermal stability. The temperature gap between the glass transition, $T_g \sim 420$ K, and crystallization is about 50 K when heating the sample at a constant rate of 20 K min^{-1}.

The high stability of the supercooled liquid has allowed a detailed study of the kinetic behavior of the liquid state by several different techniques. The viscosity $\eta(T)$ of the $Mg_{65}Cu_{25}Y_{10}$ melt above T_g was found to follow a Vogel–Fulcher–Tammann (VFT) function

$$\eta(T) = \eta_\infty exp\left(\frac{B}{(T - T_0)}\right) \quad (1)$$

with $B = 5750$ K and $T_0 = 260$ K [18]. Calculation of the fragility parameter [19], defined as

$$m = \left.\frac{d\log(\eta)}{d(T_g/T)}\right|_{T=T_g} = \frac{BT_g}{(T_g - T_0)^2 \ln 10} \quad (2)$$

gives a value of $m = 41$ using the viscosity data and taking $T_g = 420$ K. This value of m places this alloy as a liquid with intermediate fragility among the metallic glass-forming melts, which have fragility parameter values ranging from 20 to 80 [20].

Below the T_g $Mg_{65}Cu_{25}Y_{10}$ glass shows a significant degree of aging even at room temperature T_R [14]. Calorimetric, X-ray diffraction and positron annihilation measurements of rapidly quenched foils [21] showed that the amount of frozen-in excess free volume decreases significantly in samples stored for several days at T_R compared with samples stored at liquid nitrogen temperature. This indicates that some relaxation mechanisms are already activated at T_R. Direct measurement of the physical aging has recently been reported in the case of fast quenched $Mg_{65}Cu_{25}Y_{10}$ metallic glass [22,23], which was found to lead to a slowing down of structural relaxation by a factor of ten in less than 3 h. This fast aging seems to be universal in metallic glasses [24] and is related to the release of internal stresses stored during the fast quenching process.

Here we use mechanical spectroscopy to determine the low frequency relaxation spectrum of $Mg_{65}Cu_{25}Y_{10}$ from T_R up to temperatures above the calorimetric T_g. DMA measurements provide the complex elastic modulus $E^*(T,\omega) = E'(T,\omega) + iE''(T,\omega)$ as a function of temperature T and applied oscillation frequency $\omega = 2\pi f$. The real part of the elastic modulus, the storage modulus, gives information on the changes in material stiffness while the imaginary part, the loss modulus, reflects the amount of internal friction at each temperature and frequency. The aim of the work is to analyze the differences between relaxed and as-quenched samples, the latter corresponding to a glassy state very far from equilibrium. For this reason we used thin glassy ribbons rapidly quenched by melt spinning. The very high cooling rates of this rapid solidification technique provide the hyper-quenched samples required. In Section 3, data obtained from single and multi-frequency DMA experiments as well as from calorimetric measurements will be presented. The specific features of performing mechanical spectroscopy of thin ribbons in tensile geometry will be discussed. In Section 4, the results will be analyzed in order to determine the relaxation spectrum of $Mg_{65}Cu_{25}Y_{10}$. The internal friction at low temperature will be interpreted as activation of the main relaxation process corresponding to glassy states with different fictive temperatures. In contrast to similar studies on other metallic glasses it will be shown that a secondary relaxation is not detected in the investigated frequency range.

2. Experimental

Samples were produced as thin ribbons by melt spinning. Cu and Y pure metals were pre-alloyed by arc melting under a Ti-gettered Ar atmosphere. Pure Mg was added in an induction furnace in order to prevent its volatilization. The melt was then injected onto a Cu wheel spinning at 40 m s^{-1} perimeter velocity producing rapidly quenched metallic ribbons with a thickness of 33 ± 4 μm. Differential scanning calorimetry (DSC) was performed in a Perkin Elmer DSC-7 with a resolution below 1 μW. Mechanical spectroscopy was performed on a TA Instruments Q800 DMA. The tests were carried out in tensile geometry applying a preload (static force) of 0.08 N. 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 10 mm, which means a relative strain oscillation amplitude of approximately $\varepsilon = 10^{-4}$. The applied frequencies ranged from 0.3 to 30 Hz. The DMA measurements were performed on as-quenched and relaxed samples. The as-quenched samples were stored for several weeks at room temperature before