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Dynamic mechanical properties in a $Zr_{46.8}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{27.5}$ bulk metallic glass

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Abstract

The dynamic mechanical response was investigated in a bulk metallic glass $Zr_{46.8}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{27.5}$ (called Vit4). Mechanical spectroscopy was performed either using continuous heating or isothermal measurements. A main visco-elastic relaxation is observed before the onset of crystallization. A drastic decrease of the storage modulus and a maximum of the loss modulus indicate this relaxation in the amorphous state. The very large activation energy ($E_A = 4.5$ eV) and the very high value of the pre-exponential factor ($\tau_0^{-1} = 2.5 \times 10^{-35}$ s) indicate that this relaxation involves the collective movement of a large number of atoms, as in many amorphous materials (polymers, oxide or molecular glasses). Master curves are plotted, indicating that the time–temperature superposition principle is obeyed. These master curves can be described using a physical model based on the concept of quasi-point defects. Finally, the elastic, visco-elastic and visco-plastic contributions to the deformation are separated and discussed.

Keywords: Bulk metallic glass; Mechanical spectroscopy; Visco-elasticity

1. Introduction

Manufacturing of bulk metallic glasses has now become fairly routine with the fabrication in the past decade of several families of extremely good glass forming multicomponents alloys such as ternary Pd–Ni–Cu [1], La–Al–Ni [2], Mg–Cu–Y [3], quaternary Pd–Ni–Cu–P [4–6], Zr–Ni–Cu–Al [7] or quinary Zr–Ti–Cu–Ni–Al or Zr–Ti–Cu–Ni–Be [8–18]. This last family is now commercially available with two particular compositions: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (called Vit1) and $Zr_{46.8}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{27.5}$ (called Vit4) and is well documented. This last bulk metallic glass is especially attractive due to its large supercooled liquid region, typically 100 K. This region is located between the glass transition temperature T_g and the temperature corresponding to the onset of crystallization T_x. This crystallization phenomenon, due to the non-equilibrium state of these alloys, can be more or less complex. Whereas a short annealing near the glass transition will cause a reversible structural relaxation, a prolonged annealing, especially at high temperature, induces either phase separation and crystallization or directly formation of crystalline particles [13–19]. In Vit4 it has been shown previously [20] that the formation of stable crystalline phases ($NiZr_2$, $CuZr_2$ and $ZrBe_2$) can be preceded by that of a quasicrystalline phase which is depleted in Be. In view of the importance of the thermal stability of amorphous alloys with respect to crystallization for engineering applications, the influence of changes in microstructure and properties during crystallization have therefore to be studied. An investigation of the mechanical properties is evidently important due to the nature of the application for components in mechanical systems.

In bulk metallic glasses, mechanical properties are fairly well documented, either at room temperature or in the glass transition region [21–28]. While at low temperature only a limited deformation is observed, very large deformations can be achieved at high temperature, i.e. in the glass transition region. Most of the performed experiments are quasi-static

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tests: tensile or compressive tests, creep tests or viscosity measurements. In order to get detailed information on the atomic mobility involved on the deformation, mechanical spectroscopy is a very suitable technique [29]. A periodic stress $\sigma = \sigma_0 \cos(\omega t)$ with an angular frequency ω is applied to the sample and the induced deformation $\varepsilon = \varepsilon_0 \cos(\omega t - \phi)$ is recorded. The complex modulus $G^* = \sigma^*/\varepsilon^* = G' + iG''$ or the complex compliance $J^* = \varepsilon^*/\sigma^* = J' - iJ'' = 1/G^*$ are directly connected to the atomic mobility. Such experiences have been carried out either at a single frequency and the authors talk about internal friction measurements or in a large frequency range and then the term "mechanical spectroscopy" is used. In crystalline solids, mechanical spectroscopy is a powerful tool for the investigation of crystal lattice defects (points defect, dislocations, . . .) and information on the associated apparent activation energies can be deduced. In amorphous materials, mechanical relaxations are observed, but their physical origin is not so clear. In amorphous polymers, sub-T_g relaxation (called β or γ relaxation) are often associated to local movements and the main (or α) relaxation is intimately connected to the onset of flow. In oxide glasses, the α relaxation is also observed, but the β relaxation is not systematically present and, when it occurs, it can be due to the presence of water or local movements of foreign ions. In bulk metallic glasses, different investigations have been reported [30–46]. However, a lot of questions are still open, for instance: (i) what is the influence of structural relaxation and crystallization on the complex modulus? (ii) In the amorphous state, what is the temperature evolution of both the real part and the imaginary part of the modulus (respectively, called the storage modulus and the loss modulus)? (iii) Do we observe one or several relaxations? (iv) What are the parameters associated to these relaxations (apparent activation energy and pre-exponential factor)? (v) What are the respective parts of elastic, anelastic and visco-plastic components in the mechanical response? (vi) Do relaxation curves exhibit a Debye character (i.e. with a single relaxation time)? (vii) Angel [47] introduced a fragility parameter to characterize the amorphous materials; for bulk metallic glasses, only a few data have been reported and, for instance, no indication has been given for the Vit4.

So, the aim of the present work is to give some answers to these different questions. Vit4 has been retained due to its large supercooled liquid region which enables a good stability.

2. Experimental procedure

Amorphous cylinders of Vit4 ($Zr_{46.8}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{27.5}$) have been prepared in CRETA-CNRS (Greno-

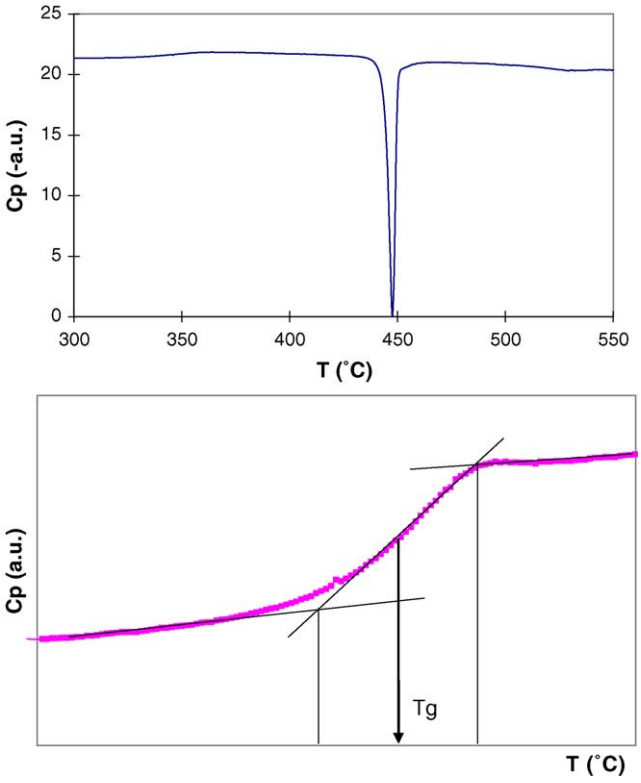

Fig. 1. DSC thermogram of the Vit4 taken during continuous heating at 3 K min^{-1}.

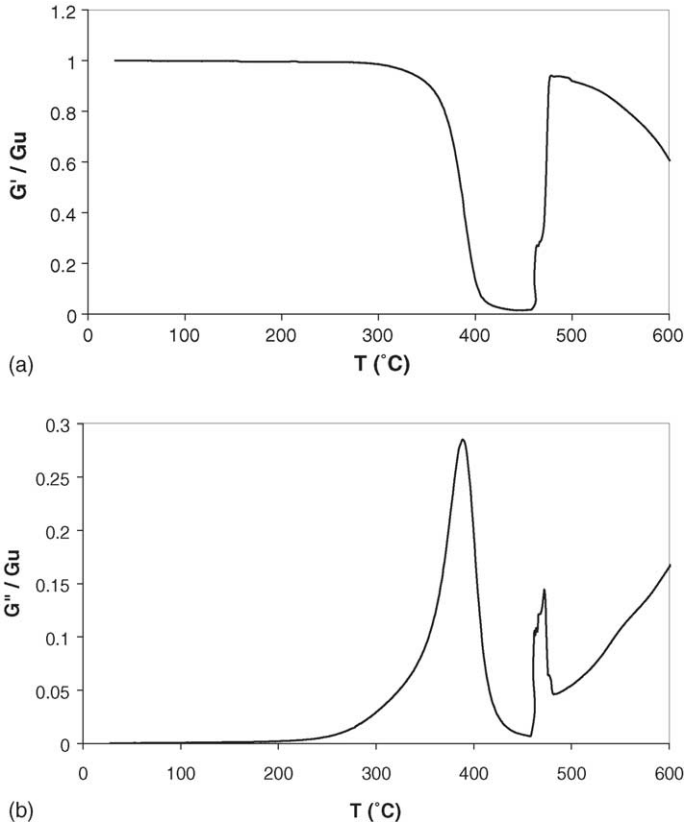

Fig. 2. Dependence of the normalized shear modulus of Vit4 as a function of temperature. G_u is the unrelaxed shear modulus. The measurement frequency is 0.3 Hz. The heating rate is 3 K min^{-1}. (a) Storage modulus; (b) loss modulus.