Journal of Alloys and Compounds 509S (2011) S18–S22

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Assessment of rheological and thermodynamic properties of the $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass around glass transition using an indentation creep technique

V. Keryvin[a,b,*], Y. Gueguen[a], C. Bernard[a,b]

[a] LARMAUR ERL CNRS 6274, Université de Rennes 1, 35042 Rennes, France
[b] LIMATB EA 4250, Université de Bretagne Sud, 56321 Lorient, France

ARTICLE INFO

Article history:
Received 8 September 2010
Received in revised form
13 December 2010
Accepted 15 December 2010
Available online 23 December 2010

Keywords:
Shear viscosity
Activation energy
Activation volume
Metallic glass
Glass transition
Correlation factor
Indentation
Creep
Rheology
Thermodynamics
Shear modulus

ABSTRACT

The thermodynamic and rheological properties of the $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass are explored by means of an indentation creep technique around the glass transition. We have developed a dedicated instrumented indentation apparatus allowing to assess the mechanical properties at elevated temperatures. The analysis of results is made possible by using the viscoelastic solutions of contact mechanics. We also analyse the thermodynamics of creep around glass transition to estimate the activation free energy changes from the activation free enthalpy changes via the shear modulus – temperature data. The shear viscosity values extracted using this technique allow for the derivation of activation energies (free enthalpy 210 kJ/mol, enthalpy 456 kJ/mol, entropy 410 J/mol/K) for the flow process. All these properties were found to closely match with those obtained using conventional techniques for viscosity measurements. Compared to the latter, the indentation creep technique requires small volumes and samples are easy to prepare. It is therefore expected that such a technique might be employed for the study of glass transition in metallic glasses.

1. Introduction

In glassy materials (silicates, amorphous alloys, glassy polymers..), the knowledge of viscosity is of paramount importance. Interest is mostly twofold. Firstly, the temperature dependence of viscosity along with the effects of the stress or the strain rate (Newtonian or non Newtonian behaviour) or of the environnement (oxidation *e.g.*), in the supercooled liquid range (SCLR) below the crystallisation temperature, allows for the determination of a processing window. Inside this window, processing is made easier for forming these materials, otherwise brittle at lower temperatures, into simple or more complex geometries. Secondly, it gives some powerful insight into the physical nature of glasses, including their structure (short-to-medium range order, packing...) and the thermodynamics of flow (activation energies and volumes).

Bulk metallic glasses (BMG) are relatively recently discovered materials exhibiting extraordinary mechanical properties including strength, yield strain, resilience, hardness or fracture toughness [1–3]. They are unfortunately usually brittle at room temperature or quasi-brittle in unconstrained conditions such as tension or compression. Therefore, conventional machining or forming at room temperature are either too costly or precluded. As for other glassy materials, forming in the SCLR is possible, even if the oxidation and crystallisation issues are to be handled with more caution than for silicate glasses or glassy polymers for instance, and processes have been recently proposed [4]. Applications of BMG to MEMS (Micro Electro Mechanical Systems) devices are currently a promising way [5] and some storage/data systems have already been reported [6].

In all these applications, viscosity measurements are required as the main processing parameters. As for the physical insight one can get from viscosity, it should be put into parallel with that from elasticity measurements [7,8].

Compared to other measurement techniques, indentation creep allows to characterize small volumes of materials in a non destructive way. In this paper, we show that the use of indentation creep experiments, along with the knowledge of the temperature dependence of elastic moduli, provides a rapid, robust and relevant tool for exploring the thermodynamics of the glass transition in BMG as well as the steady state shear viscosity.

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* Corresponding author at: LIMATB EA 4250, Université de Bretagne Sud, 56321 Lorient, France. Fax: +33 297874572.
E-mail address: vincent.keryvin@univ-ubs.fr (V. Keryvin).

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doi:10.1016/j.jallcom.2010.12.114

2. Theoretical background to creep and indentation creep

In this section, we provide the necessary theoretical background to creep and indentation creep to allow for the correct interpretation of the experimental results presented in the subsequent sections.

2.1. Thermodynamic approach to creep

In this paragraph, we present two methods to describe the creep phenomenon based on a thermodynamic approach.

The first method is based on the concept of hierarchically correlated motion [9] and considers that the faster molecular movements occur before, and trigger, the slower ones. Let τ be the characteristic relaxation time of the simplest elementary motions involved in the deformation process, an Arrhenius-type equation for its thermal behaviour writes:

$$\tau = \tau_0 \exp\left(\frac{\Delta G_a}{RT}\right) \quad (1)$$

where ΔG_a is the free activation enthalpy associated with the flow process, T is the temperature, R the gas constant and τ_0 a multiplicative constant. Then the characteristic time for molecular mobility in the disordered condensed matter τ_{mol} (corresponding to the mean duration of a structural unit jump over a distance equal to its dimension – experimentally available) is given by (see Refs. [9,10] for details):

$$\tau_{mol} = A\tau^{\frac{1}{b}} \quad (2)$$

where A is a constant and b is the so-called correlation factor which can be regarded as a structural parameter characterising the correlation between the different atomic or molecular movements occuring in the glass. When $b = 0$ any movement of a structural unit requires the motion of all the other units (maximum order, perfect correlation), while when $b = 1$ all the movements are independent on each other (the maximum disorder corresponding to a Maxwell model for relaxation, or to a single characteristic time of the classical Debye relaxation process). Differentiation of Eq. (2) with respect to temperature, recalling that the directly available thermodynamical parameter is the activation enthalpy $\Delta H_a = \partial \ln\tau_{mol}/(\partial/RT)$, one obtains:

$$\Delta G_a = b\Delta H_a + T\left.\frac{\partial \Delta G_a}{\partial T}\right|_{\sigma} - \left[\frac{T\Delta G_a}{b} + RT^2\log\tau_0\right]\left.\frac{\partial b}{\partial T}\right|_{\sigma} \quad (3)$$

where $\ll |_{\sigma} \gg$ denotes partial differentiation keeping the stress σ as constant.

In temperature ranges where ΔG_a and b change little with temperature, which is the case, for instance, above the transition range, the former equation reduces to:

$$\Delta G_a = b\Delta H_a \quad (4)$$

This equation, shows that in the common case where $b = 0.5$, the apparent energy for the relaxation process is about twice the value of the relevant free enthalpy energy.

The second method is based on the classical theory of thermally activated flow phenomena, which considers the existence of two independent contributions acting together to overcome the energy barrier, ΔG_0, associated with the flow process. One of this contribution, ΔG_a, has a purely thermal origin and is derived from the thermally activated atomic, or molecular, movements; the other, ΔW_a, is due to the applied stress so that:

$$\Delta G_0 = \Delta G_a + \Delta W_a \quad (5)$$

Schoeck [11] considered that the height of the barrier, ΔG_0, to be overwhelmingly of elastic origin. ΔG_0 is therefore taken to be proportional to the shear modulus μ and depends only on temperature T. A straightforward relationship between the temperature derivates of ΔG_0 and μ leads to:

$$\frac{\partial \Delta G_0}{\partial T} = \frac{\Delta G_0}{\mu}\left.\frac{\partial \mu}{\partial T}\right|_{\sigma,s} \quad (6)$$

where s denotes the structure of the glass.

Others assumptions that can be found in [12], allow for a formal equivalence with the first method and Eq. (4) giving the value of the correlation factor, b, as

$$b = \left(1 - \frac{T}{\mu}\frac{\partial \mu}{\partial T}\right)^{-1} \quad (7)$$

Let us recall that Eq. (4) is valid in the ranges where b is constant, that is in the glassy state and in the super cooled liquid range, and not at the glass transition,

2.2. Indentation-creep

In this paragraph, the key equations modelling the indentation test are presented.

Sneddon [13] established the relationship between the applied load P_e and the penetration depth h for a rigid indenter, a linear isotropic homogeneous material of shear modulus μ and Poisson's ratio ν and a frictionless contact.

$$P_e(t) = \frac{\mu}{1-\nu} \times F \times h(t)^n \quad (8)$$

where F and n are constant values related to the indenter geometry and t is the time.

The problem of linear viscoelastic contact was later addressed by Lee and Radok [14] then Hunter [15], using the method of functional equations, by substituting the elastic parameters μ and ν in Eq. (8) by their viscoelastic time-dependent counterparts υ and G. However as pointed out by the same authors, this procedure is relevant when the boundary conditions, which are time-dependent, allow for a monotonic increase of the contact area [16]. Ting [17] proposed a solution for different indenter geometries and different contact area histories. This challenging to use method can be written easily for a monotonic increase of the contact area:

$$P(t) = \frac{1-\nu}{\mu}\int_0^t \psi(t-s)\frac{\partial P_e(s)}{\partial s}\,ds \quad (9)$$

where P is the applied load, P_e is the elastic solution of Eq. (8), and ψ is a function defined by:

$$\psi^* = \frac{G^*}{1-\upsilon^*} \quad (10)$$

where f^* denotes the Laplace–Carson transform of f.

Using Eq. (8) and (9), we get:

$$P(t) = F\int_0^t \psi(t-s)\frac{\partial h^n(s)}{\partial s}ds \quad (11)$$

This latter expression being equivalent to

$$P^* = F\psi^*(h^n)^* \quad (12)$$

Let the function ξ defined by $\psi^*\xi^* = 1$; we get:

$$(h^n)^* = \frac{P^*}{F}\xi^* \quad (13)$$

which is equivalent to:

$$h^n(t) = \frac{1}{F}\int_0^t \xi(t-s)\frac{\partial P(s)}{\partial s}ds \quad (14)$$