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Consistency of the free-volume approach to the homogeneous deformation of metallic glasses



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ABSTRACT

One of the most widely used approaches to model metallic-glasses high-temperature homogeneous deformation is the free-volume theory, developed by Cohen and Turnbull and extended by Spaepen. A simple elastoviscoplastic formulation has been proposed that allows one to determine various parameters of such a model. This approach is applied here to the results obtained by de Hey et al. on a Pd-based metallic glass. In their study, de Hey et al. were able to determine some of the parameters used in the elastoviscoplastic formulation through DSC modeling coupled with mechanical tests, and the consistency of the two viewpoints was assessed.

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1. Introduction

Understanding the physical basis of the homogeneous deformation of bulk metallic glasses is an important fundamental as well as practical subject. On a fundamental basis, there exists no consensus on the nature of the mechanism(s) responsible for the deformation of amorphous materials. In practice, the homogeneous mode is of interest, particularly for shaping operations on metallic glasses at high temperature. For the latter class of materials, one of the most widely used models to describe the homogeneous deformation is the free-volume model. It was proposed by Cohen and Turnbull [1–3] for liquids and applied to the glass-transition phenomenon, and was later adapted to the case of the deformation of metallic glasses by Spaepen [4]. In this framework, the carriers of plastic deformation are so-called flow defects, whose concentration c_f is given by:

$$c_f = \exp\left(-\frac{\gamma v^*}{v_f}\right) \quad (1)$$

where v^* is the critical free volume level, v_f is the average free volume per atom and γ is a geometrical factor allowing for the overlap of free-volume areas. The viscoplastic strain rate then writes:

$$\dot{\gamma} = c_f 2\nu \exp\left(-\frac{\Delta G^m}{kT}\right) \sinh\left(\frac{\tau \Omega}{kT}\right) \quad (2)$$

where ν is the atomic vibration frequency, ΔG^m is the migration free energy, τ is the shear stress and Ω is the activation volume. k and T have their usual meaning.

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This model leads to a satisfying rationalization of the dependency of glasses viscosity with temperature, by assuming that the average free volume writes:

$$v_f = \frac{T - T_0}{B} \gamma v^* \quad (3)$$

which allows us to write the Vogel–Fulcher–Tammann equation from the free-volume system, the VFT equation being commonly used to describe the temperature dependence the viscosity of undercooled liquids (see for example [5]). This equation is then interpreted as a temperature-dependent equilibrium concentration of defects, c_{eq} :

$$c_{eq} = \exp\left(-\frac{B}{T - T_0}\right) \quad (4)$$

where B and T_0 are material parameters. For a glass at sufficiently high temperature, if the free-volume level is higher than the equilibrium one, the so-called structural relaxation occurs. This phenomenon is notably accompanied by a density increase. The viscosity of the glass then increases linearly with time, which in the framework of the free-volume model can be understood as an annihilation of flow defects with a second-order kinetics, which writes [6–8]:

$$\dot{c}_f = k_r c_f (c_f - c_{eq}) \quad (5)$$

where k_r is the structural relaxation kinetic coefficient, which is thermally activated [8].

The stress–strain curve of a metallic glass deformed in the homogeneous mode exhibits stress overshoots whose amplitude increases with the strain rate. Various studies have investigated this phenomenon (see, for example, [9–11]), and from a free-volume perspective, it is due to an increase of the flow defect concentration. Several forms of the dependency of the flow defect concentration with strain have been studied, and based on their measurements coupling uniaxial tests and DSC results, de Hey et al. have shown [12] that the best description of the flow defect creation by strain is:

$$\dot{c}_f = a_x \dot{\varepsilon}_p c_f \ln^2(c_f) \quad (6)$$

where $\dot{\varepsilon}_p$ is the plastic strain-rate and a_x is the flow defect creation coefficient. This equation is derived from the free-volume model assuming $dv_f \propto d\varepsilon_p$. By coupling Eqs. (5) and (6), the kinetic of flow defect concentration, when a metallic glass is plastically deformed, is given by:

$$\dot{c}_f = a_x \dot{\varepsilon}_p c_f \ln^2(c_f) - k_r c_f (c_f - c_{eq}) \quad (7)$$

whose steady-state solution c_f^* writes:

$$c_f^* = c_{eq} + \frac{a_x}{k_r} \dot{\varepsilon}_p \ln^2 c_f^* \quad (8)$$

By coupling Eqs. (2) and (8), it is possible (see [13]) to deduce the ratio a_x/k_r and $\dot{\varepsilon}_{0,c}$, knowing the activation volume Ω and c_{eq} .

Assuming that the total strain is the sum of the elastic and viscoplastic contributions, it writes (in uniaxial conditions):

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + c_f \varepsilon_{0,c} \sinh\left(\frac{\sigma \Omega}{2\sqrt{3}kT}\right) \quad (9)$$

where E is the Young modulus. By coupling Eq. (9) with Eq. (7), it is then possible to model mechanical experiments [11]. By coupling this type of modeling with the approach based on the steady state [13], most of the parameters of the free-volume model—at a given temperature—can be deduced from mechanical results only, with the noticeable exception of the equilibrium flow defect concentration, c_{eq} .

The aim of the present paper is to examine the consistency of the elastoviscoplastic approach, by comparing the values found by de Hey et al. [12] for the various parameters of the model thanks to DSC measurements with the ones that can be deduced from a purely mechanical analysis of their results, following the method depicted in [11].

2. Structural parameters determination and comparison

In their study [12] of the structural modifications induced by plastic deformation of a PdNiP metallic glass in the homogeneous domain correlating tensile tests and DSC measurements, de Hey et al. have conducted one experiment that is particularly favorable to apply the mechanical analysis proposed in [11]. Indeed, using the results of uniaxial strain-rate jump experiments, it is possible to determine almost all the parameters of Eqs. (7) and (9), which include the structural relaxation coefficient k_r and the free-volume creation coefficient a_x . These two parameters were also determined by de Hey et al. thanks to the modeling of DSC curves, *i.e.* a thermodynamical approach.

However, for the model to be consistent, the values found by an approach and the others must be the same. In Fig. 1 are presented the data published by de Hey et al. for a tensile test involving strain-rate jumps between $\dot{\varepsilon} = 8.3 \times 10^{-5} \text{ s}^{-1}$ and $4.2 \times 10^{-5} \text{ s}^{-1}$. By adjusting the parameters of Eqs. (7) and (9), it is possible to obtain a rather satisfying fit of the

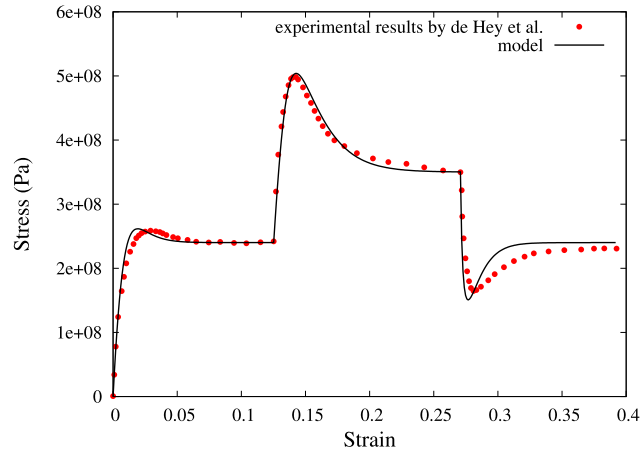


Fig. 1. Red dots: true stress vs. true strain curve obtained for a tensile test on a PdNiP metallic glass at 556 K by de Hey et al. [12], strain-rate cycling between $8.3 \times 10^{-5} \text{ s}^{-1}$ and $4.2 \times 10^{-5} \text{ s}^{-1}$. Black line: best fit obtained using the elasto-plastic formulation of the free-volume model obtained by coupling Eqs. (9) and (7). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Comparison of the results obtained from DSC analysis by de Hey et al. [12] thanks to the modeling of DSC and mechanical data, and the results obtained in the present study thanks to mechanical modeling only.

	Present study	de Hey et al.
$\Omega \text{ (}\text{\AA}^3\text{)}$	130	130
a_x	0.034	0.043
$k_r \text{ (s}^{-1}\text{)}$	6×10^{11}	3.2×10^{10}
$\varepsilon_{0,c} \text{ (s}^{-1}\text{)}$	5.47×10^9	
$E \text{ (GPa)}$	40	

experimental results (see Fig. 1 and Table 1). The model reproduces then correctly the overshoot and undershoot amplitude, and the value of the steady-state stress.

The value of the Young modulus used to reproduce the stress–strain curves was 40 GPa, whereas the measured value reported by de Hey et al. at room temperature is 96 GPa. Such a decrease of the Young modulus is generally understood as the signature of anelastic phenomena developing at high temperature. Indeed, when measured at high frequency (about 2 kHz), the elastic modulus shows very little variation (less than 5% on a Zr-based metallic glass in the glass-transition range), and in the same temperature interval, the value of the modulus decreases markedly with the measuring frequency (more than 50% at 1 Hz) (see [14,15]). However, the free-volume model cannot account for such anelastic effects and it is necessary to use the experimental modulus to model the stress–strain curves.

To evaluate the other material parameters—beyond the elastic modulus—from mechanical results only, it is necessary to determine a value of the equilibrium flow defect concentration at this temperature, as this parameter is free. The chosen value was $c_{\text{eq}} = 5.49 \times 10^{-15}$, as can be calculated using structural data proposed by Duine et al. [16] and used by Tuinstra et al. [17] for the same glass. Thanks to viscosity measurements conducted as creep tests on amorphous ribbons and assuming that the Newtonian viscosity dependency on temperature can be described thanks to the Vogel–Fulcher–Tammann equation, which writes:

$$\eta = \eta_1 \exp\left(\frac{B}{T - T_0}\right) \quad (10)$$

they obtained $B = 6600 \text{ K}$ and $T_0 = 355 \text{ K}$, these parameters being the same as in Eq. (4) that describes the dependency of the free volume on temperature.

Table 1 compares the values found in the present analysis and the ones obtained by de Hey et al. in [12] and Duine et al. in [16] (through the modeling of DSC and viscosity measurements).

It turns out that the activation volumes are in good agreement, and their large value points out the necessity to reinterpret the physical picture of the original free-volume interpretation, which was the jump of a single atom into a big enough hole, as such a large activation volume corresponds to several average atomic volumes. This observation has already been made by several authors (see for example [18,19]), and Argon proposed an analysis that led to similar stress/strain rate relationships, but based on the concept of shear transformation zone (see [20]), concept widely used in the community.

The values of the free-volume creation coefficient a_x found in both studies are close to one another (0.034 found here vs. 0.043 ± 0.004 found by de Hey et al.). On the other hand, the structural relaxation parameter k_r shows a larger discrepancy (6×10^{11} vs. $3.2 \times 10^{10} \text{ s}^{-1}$), which results in a significant difference in terms of a_x/k_r . This ratio is particularly sensitive

when applied to steady-state analysis (see [13]) and the values proposed by de Hey et al. (1.3×10^{-12} s) lead to results that are incompatible with their stress/strain rate experimental results in the steady state, for which a value of 1.4×10^{-13} s is required, based on the steady-state analysis.

This disagreement could be due to various errors. First, in the stress/strain rate experimental values. However, the stress error would then have to be more than 100 MPa and/or the error on the strain rate should be about $3 \times 10^{-5} \text{ s}^{-1}$ on the $4.2 \times 10^{-5} \text{ s}^{-1}$, both of them seem to be very large and unlikely.

A second possibility would be an error on the various material parameters of the free-volume model. Varying the activation volume between values that do not allow a satisfying fit of the data (from 30 to 230 \AA^3) and appear then as unrealistic, according to the method presented in [11], does not lead to variations of the predicted a_x/k_r ratio (1.4×10^{-13} s) of more than 0.01%, which is far from enough to account for the value deduced from de Hey et al.'s results. On the other hand, an increase in the flow defect concentration from 5.49×10^{-15} up to 5.49×10^{-14} would suffice. Hence, there may be somewhat significant errors in the parameters that were determined by Tuinstra et al. in [17] and Duine et al. [16] and used for comparison in the present study. Small incertitudes on the thermodynamical parameters can result in a rather large variation of k_r or c_{eq} , particularly concerning the activation energy or the temperature, as k_r has an Arrhenian behavior. Indeed, an error of 8% on the temperature and/or the activation energy would be sufficient to account for the discrepancy in k_r , whereas for c_{eq} an error of 6% on the parameter B or 4% on T_0 (see Eq. (4)) would bring the equilibrium flow defect concentration c_{eq} within margins compatible with the steady-state analysis as seen above. Obviously, a combination of lesser errors on all these parameters could also account for the a_x/k_r ratio discrepancy.

Alternatively, this could be the sign of an inconsistency of the viscoplastic formulation of the free volume model, but it would be necessary to rule out all the other previous possibilities before to come to this conclusion.

3. Conclusion

The free-volume theory provides a satisfying way to rationalize the mechanical behavior of metallic glasses in the homogeneous mode. The determination of the two parameters related to the free-volume kinetics (free-volume creation coefficient a_x and structural relaxation constant k_r) by DSC or mechanical modeling shows relatively good agreement, but points out probable errors, inferior to a few percent in the thermodynamical and kinetics parameters determination through DSC measurement and viscosity analysis. The free-volume model is then able to account quantitatively for mechanical as well as kinetic and thermodynamical results, on a rather phenomenological basis.

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