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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

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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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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:

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

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):

$$\tau_{mol} = A\tau^{\frac{1}{b}} \tag{2}$$

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:

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

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:

$$\Delta G_a = b\Delta H_a \tag{4}$$

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:

$$\Delta G_0 = \Delta G_a + \Delta W_a \tag{5}$$

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:

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

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

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

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.

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

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:

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

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

$$\psi^* = \frac{G^*}{1-\upsilon^*} \tag{10}$$

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

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

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

This latter expression being equivalent to

$$P^* = F\psi^*(h^n)^* \tag{12}$$

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

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

which is equivalent to:

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

Eq. (11) and (14) therefore give the relationships between the load and the penetration depth for a linear viscoelastic solid. We consider now the case of the indentation creep loading for which the load history is given by a step loading $P(t) = P_0 H(t)$ where H is the Heaviside function. Eq. (14) becomes:

$$h(t) = \sqrt[n]{\frac{\xi(t)}{F} P_0} \tag{15}$$

The ξ function is defined by:

$$\xi^* = \frac{1}{\psi^*} = (1 - \upsilon^*) J^* \tag{16}$$

To have access to the creep shear compliance J, the classical assumption [18,19] is to take υ as a constant and we will take it as 0.5 as the shear flow is incompressible and predominant at large times which are considered in our study.

$$h(t) = \sqrt[n]{\frac{J(t)}{2F} P_0} \,\text{and}\, J(t) = 2F \frac{h^n(t)}{P_0} \tag{17}$$

For the spherical indenter used in this study, the parameters are $F = 8\sqrt{R}/3$ where R is the ball radius, and $n = 3/2$ [20].

Assuming a Maxwell like model for the shear viscous flow, the shear compliance, J, tends for long times towards t/η where η is the shear viscosity, so that the derivative of h^n tends towards a constant value. We get

$$\eta = \frac{P_0}{2F} \left[\frac{dh^n}{dt} \right]^{-1} \tag{18}$$

3. Materials and experiments

The $Pd_{40}Ni_{40}P_{20}$ (at.%) bulk metallic glass is studied in this paper. An alloy ingot was prepared by arc melting pure metals in a purified argon atmosphere. BMG rods with diameter of 4.5 mm were prepared by repeated melting of their molten alloys fluxed with B_2O_3. The formation of a single glassy phase was confirmed by X-ray diffraction. The glass transition temperature, T_g, is 576 K (differential scanning calorimetry, DSC, 20 K/min) [21].

Depth sensing indentation creep experiments were performed by means of a laboratory made apparatus described in Ref. [20]. Our laboratory has developed an equipment operating in the micro-indentation range, with applied loads between 0.01 and 15 N, consisting in a hot chamber equipped with an alumina tube and a sapphire indenter, and allowing for a better than 2 K accuracy along a 10 mm testing zone. The whole equipment is situated in a vibration-free and air disturbance-free environment. The load is applied using a piezoelectric actuator and the penetration depth is measured with a capacitive sensor having a resolution of 10 nm. The load fluctuation is less than ±12 mN. The maximum target temperature is 1473 K, with a thermal stability within 1 K variation up to 1323 K. Samples were cut into 10 mm thick disks. Surfaces were prepared with usual grinding techniques (SiC paper and diamond paste till 1 μm for mirror-like surfaces). All the indentation tests were performed at constant load and constant temperature with loads ranging from 1 to 13 N and temperatures ranging from 550 to 600 K. Before each test, samples were annealed during at least 30 min at the test temperature in order to stabilize the glass structure and to stabilize the temperature field of the machine frame (±1 K). Then the initial load was applied at a high rate (0.2 N/s) and was maintained to the test load when this one was achieved. The displacement, h, was recorded as a function of time. For a given temperature and a given load, up to three tests were performed. The temperature and load ranges for the tests carried out in the present study have been chosen in order to, firstly, include the T_g and, secondly, generate exploitable data. Let us recall that, in previous work [20] it has been shown that imposing different constant loads in the [0–13 N] range did not influence the viscosity measurement. That is why, in order to obtain exploitable curves, higher temperatures were preferably associated to lower loads to prevent too rapid tests. The indenter used was a 1.5 mm in diameter sapphire spherical indenter.

The apparent shear viscosity, η, was calculated using Eq. (18) in the steady state regime.

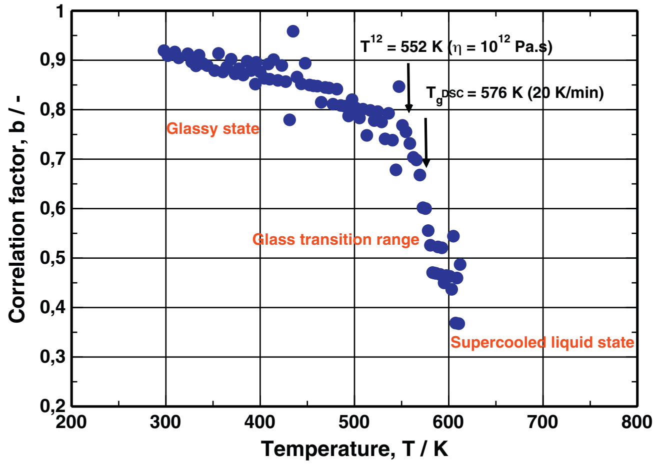

Fig. 1. Variations of the correlation factor around the glass transition temperature.

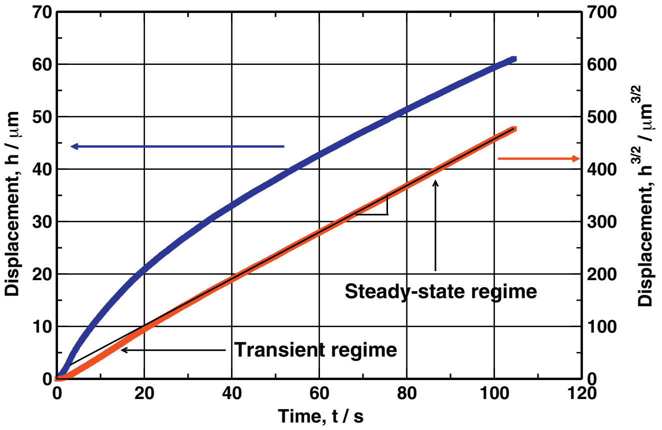

Fig. 2. Spherical indentation creep at 585 K. Displacement versus time with the two regimes.

4. Results and discussion

The evaluation of the correlation factor, b, using Eq. (7), was performed by means of the temperature variations data of the shear modulus[1] from Ref. [22]. They are plotted in Fig. 1. In the glassy state, below T_g, b is higher than 0.9 while in the supercooled liquid state (above T_g) it is close to 0.45, a value quite lower than that of window glass [23] or a ZrCuAlNi BMG [24]. Fig. 2 presents an example of the displacement h recorded during a spherical indentation creep test at 585 K. Like for standard creep, there exist two regimes: the transient one for which the displacement rapidly increases and a steady state regime where the function $h^{3/2}$ is a linear function of time. This slope give then access to the shear viscosity as given by Eq. (18).

Fig. 3 presents the changes in viscosity with temperature as determined by indentation creep measurements at different

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[1] Actually from the shear resonance frequencies whose square fits with the elastic shear modulus.

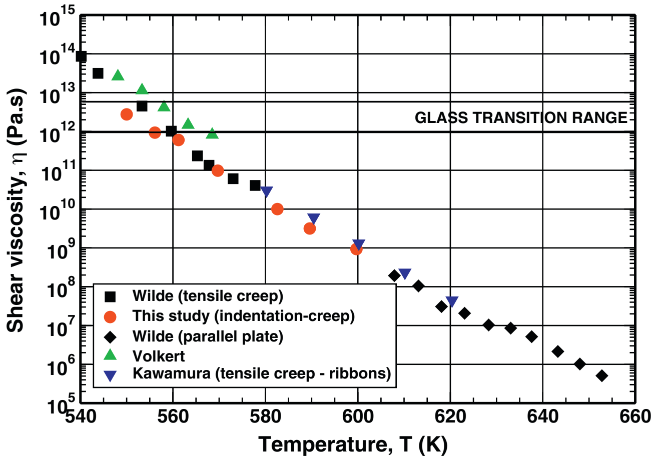

Fig. 3. Changes in shear viscosity with temperature given by indentation creep measurements along with results from the literature.

temperatures. On this graph the glass transition range is classically described by viscosity values in the [10^{12};$10^{12.6}$] Pa·s range, corresponding to a [548;556]K temperature range, which is classically slightly lower than the glass transition temperature (576 K) obtained by DSC [25]. It was proposed to be attributed to a degradation of the glass structure by ultrasounds [26]. Data available from the literature are also reported for the same composition [27,28] and for a very similar one [29,30]. A remarkable agreement is found between these results and our work.

Assuming an Arrhenius-like dependence of viscosity with temperature,

$$\eta = \eta_0 \exp\left(\frac{\Delta H_a}{RT}\right) \tag{19}$$

we therefore obtain an activation enthalpy ΔH_a of 456 kJ/mol (4.7 eV). This value is relatively close to that reported in other works [27,31] and comparable to Zr-based alloys [24]. Given this latter value along with that of the correlation factor b in the supercooled liquid range, using Eq. (4), we get the value of activation free enthalpy ΔG_a of 210 kJ/mol (2.2 eV). The activation entropy at ΔS_a, is then given by the following equation:

$$\Delta G_a = \Delta H_a - T\Delta S_a \tag{20}$$

Its value is 410 J/mol/K in the SCLR. The variations of ΔG_a and ΔS_a with temperature are shown on Fig. 4. Recalling that their determination is valid above and below the glass transition, we therefore observe a decrease in the free activation enthalpy and an increase in the activation entropy, going from the glassy state to the SCLR.

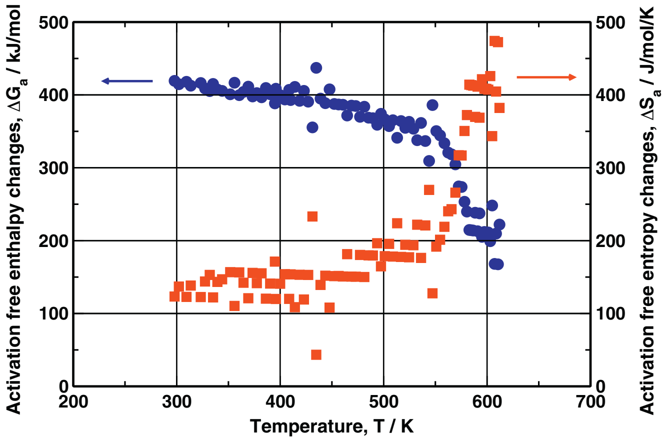

Fig. 4. Changes in activation entropy.

Table 1
Thermodynamical parameters (activation enthalpy, activation free enthalpy, activation entropy, activation volume and fragility) extracted from the indentation creep test either by Nemilov's method or by our approach.

	Nemilov's approach	This work
ΔH_a (kJ/mol)	456	
T_g (K)	552 (T_g^{12})	576 (T_g^{DSC})
ΔG_a (kJ/mol)	174	210
ΔS_a (J/mol/K)	510	410
V_a (10^{-6} m^3/mol)	5.45	–
V_a (Å^3/atom)	9.1	–
m	43	43

The variations of η with temperature above T_g allow for the determination of the fragility index m popularized by Angell [32]. This value is the slope of logη vs log (T_g^{12}/T) at T_g^{12} where T_g^{12} is the temperature for which $\eta = 10^{12}$ Pa s (here 552 K). High values of m qualify the material as a fragile glass-former (or "short" glass, as called by glass-makers) while low values mean that it is a strong glass-former (or "long" glass). In our case $m = 43$ a value close to that of Kawamura and Inoue [28].

Nemilov [33] proposed a pragmatic approach for estimating the activation energies at T_g only based on the viscosity–temperature curve. It is interesting to compare the results of such an approach with our results which are based on this latter curve and on the elasticity data. From Nemilov [33,34], we have:

$$\begin{aligned} &\Delta G_a = 316 T_g^{12} \quad && \Delta S_a = -316 + \left(\frac{\Delta H_a}{T_g^{12}}\right) \\ &V_a = \frac{\Delta G_a}{\mu} && m = 16.5\left(\frac{1+\Delta S_a}{38R}\right) \end{aligned} \tag{21}$$

where V_a is the activation volume, otherwise determined by $V_a = -\,\partial\Delta G_a/\partial\sigma$ with conventional creep experiments and temperature jumps, and μ is the shear modulus (32 GPa @ T_g^{12} from Ref. [8]). The values for the parameters of the thermally activated viscous flow process are reported in Table 1 and are very comparable from one to another. The value of V_a, with the crude approximation of the atomic radii for a crystalline alloy (1.57 Å in our case), allows to estimate the number of atoms to be involved in the flow process to be around one, which is much lower than reported values in Zr-based alloys [24,35]. The theory of Nemilov, which is mostly based on Maxwell's model for flow and somehow restricted to covalent glasses [33,34], may therefore be inadequate for capturing some of the flow features relevant to metallic glasses. Therefore, getting access to the activation volume is precluded by employing the indentation creep technique. Conventional creep measurements remain mandatory. These values may provide insight on the plasticity carriers at low or high homologous temperatures, the shear transformation zones, especially its size [1].

5. Summary

In this study, we have successfully employed the indentation creep technique to assess the rheological and thermodynamic properties of a bulk metallic glass around its glass transition. The shear viscosity values extracted using this technique allow, either solely with Nemilov's approach [33,34] or with the additional knowledge of the temperature variations of the shear elastic moduli, for the derivation of activation energies (enthalpy, free enthalpy, entropy) for the flow process. All these properties were found to closely match with those obtained using conventional techniques for viscosity measurements. The advantages of the indentation creep technique lie in the possibility of using small volumes of material, the easiness of sample preparation and the small time required to extract viscosity values spanning a large interval. It is therefore expected that such a technique might be employed for the study of glass transition in metallic glasses.

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References

[1] C.A. Schuh, T.C. Hufnagel, U. Ramamurty, Acta Mater. 55 (12) (2007) 4067–4109.
[2] V. Keryvin, Y. Nadot, Y. Yokoyama, Scripta Mater. 57 (2007) 145–148.
[3] V. Keryvin, V.H. Hoang, J. Shen, Intermetallics 17 (4) (2009) 211–217.
[4] J. Schroers, Adv. Mater. 22 (14) (2010) 1566–1597.
[5] G. Kumar, H.X. Tang, J. Schroers, Nature 457 (7231) (2009) 868–872.
[6] J. Schroers, Acta Mater. 56 (3) (2008) 471–478.
[7] T. Rouxel, J. Am. Ceram. Soc. 90 (10) (2007) 3019–3039.
[8] T. Ichitsubo, E. Matsubara, H. Chen, J. Saida, T. Yamamoto, N. Nishiyama, J. Chem. Phys. 125 (2006) 154502-1.
[9] R. Palmer, D. Stein, E. Abrahams, P. Anderson, Phys. Rev. Lett. 53 (10) (1984) 958–961.
[10] J.M. Pelletier, J. Perez, J.L. Soubeyroux, J. Non-Cryst. Solids 274 (1–3) (2000) 301–306.
[11] G. Schoeck, Phys. Status Solidi 8 (2) (1965) 499.
[12] T. Rouxel, J.-C. Sanglebœuf, M. Huger, C. Gault, J.-L. Besson, S. Testu, Acta Mater. 50 (7) (2002) 1669.
[13] I.N. Sneddon, Int. J. Eng. Sci. 3 (1965) 47–57.
[14] E.H. Lee, J.R.M. Radok, J. Appl. Mech. 27 (1960) 438–444.
[15] S.C. Hunter, J. Mech. Phys. Solids 8 (1960) 219–234.
[16] M. Vandamme, F.J. Ulm, Int. J. Solid Struct. 43 (10) (2006) 3142–3165.
[17] T.C.T. Ting, J. Appl. Mech. 33 (4) (1966) 845–854.
[18] M. Sakai, S. Shimizu, J. Non-Cryst. Solids 282 (2–3) (2001) 236–247.
[19] Y.-T. Cheng, C.-M. Cheng, Mater. Sci. Eng. R 44 (2004) 91–149.
[20] C. Bernard, V. Keryvin, J.-C. Sanglebœuf, T. Rouxel, Mech. Mater. 42 (2010) 196–206.
[21] Y. He, R.B. Schwarz, J.I. Archuleta, Appl. Phys. Lett. 69 (13) (1996) 1861–1863.
[22] A.S. Bains, C.A. Gordon, A.V. Granato, R.B. Schwarz, J. All. Comp. 310 (2000) 20–23.
[23] J. De Bast, P. Gilard, Comptes rendus de recherche IRSIA, Tech. rep., Travaux du centre de l'industrie technique et scientifique belge [in French], 1965.
[24] V. Keryvin, E. Reynaud, Y. Gueguen, T. Rouxel, M.-L. Vaillant, C. Bernard, J.-C. Sanglebœuf, Y. Yokoyama, submitted for publication.
[25] V. Keryvin, M.-L. Vaillant, T. Rouxel, M. Huger, T. Gloriant, Y. Kawamura, Intermetallics 10 (11–12) (2002) 1289–1296.
[26] T. Ichitsubo, E. Matsubara, T. Yamamoto, H. Chen, N. Nishiyama, J. Saida, K. Anazawa, Phys. Rev. Lett. 95 (2005) 245501.
[27] G. Wilde, G.P. Gorler, R. Willnecker, H.J. Fecht, J. Appl. Phys. 87 (3) (2000) 1141–1152.
[28] Y. Kawamura, A. Inoue, Appl. Phys. Lett. 77 (8) (2000) 1114–1116.
[29] C.A. Volkert, F. Spaepen, Mater. Sci. Eng. 97 (1988) 449–452.
[30] C.A. Volkert, F. Spaepen, Acta Metall. 37 (5) (1989) 1355–1362.
[31] K. Schroter, G. Wilde, R. Willnecker, M. Weiss, K. Samwer, E. Donth, Eur. J. Phys. B 5 (1) (1998) 1–5.
[32] C.A. Angell, Science 267 (5206) (1995) 1924–1935.
[33] S.V. Nemilov, J. Non-Cryst. Solids 353 (52–54) (2007) 4613–4632.
[34] S. Nemilov, J. Non-Cryst. Solids 352 (26–27) (2006) 2715–2725.
[35] M. Bletry, P. Guyot, J.J. Blandin, J.L. Soubeyroux, Acta Mater. 54 (5) (2006) 1257–1263.