

## Pressure-Induced Structural Relaxation in Amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>: The Formation Volume for Diffusion Defects

G. Ruitenberg,<sup>1</sup> Paul De Hey,<sup>1</sup> F. Sommer,<sup>2</sup> and Jilt Sietsma<sup>1</sup>

<sup>1</sup>Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands

<sup>2</sup>Max-Planck Institut für Metallforschung, Stuttgart, Germany

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Structural relaxation induced by hydrostatic pressure is experimentally observed for the metallic glass Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>. The pressure dependence of the structural state is displayed in the shape of the glass-transition peak that is measured by means of differential scanning calorimetry after annealing treatments at 563 K and pressures up to 0.75 GPa. Quantification of the effect using the free-volume theory yields a formation volume of  $5.9 \pm 0.5 \text{ \AA}^3$  for defects in this glass. In combination with the previously determined pressure dependence for the Au diffusivity, a value of  $5 \pm 4 \text{ \AA}^3$  is derived for the migration volume for Au diffusion. [S0031-9007(97)04805-9]

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Structural relaxation in metallic glasses under the influence of an elevated temperature is a well-known phenomenon that has been widely studied (e.g., [1]). Within the amorphous structure, changes occur that lead to significant changes in physical properties, which are particularly pronounced in the atomic-transport properties viscosity and diffusivity [2]. Although pressure, similar to temperature, is liable to induce structural relaxation as well, experimental studies of pressure-induced structural relaxation are very few [3]. The pressure dependence of the structural state of metallic glasses is particularly of interest when regarding the diffusion process, since it can give insight into the formation volume for defects. Combined with the pressure dependence of the diffusivity, which yields the so-called activation volume, the migration volume for diffusion can also be derived. A separate determination of these two quantities adds to the understanding of the diffusion process.

In the present Letter the phenomenon of structural relaxation induced by pressure will be investigated for the metallic glass Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>. Experimental evidence obtained by means of differential scanning calorimetry (DSC) after annealing samples at hydrostatic pressures up to 0.75 GPa directly shows the occurrence of pressure-induced structural relaxation. The state of relaxation that is reached during these treatments is quantified by means of the free-volume theory [2,4]. This results in the determination of the formation volume for defects in amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>. Combining the result with the pressure dependence of the diffusivity of gold determined previously on the same samples [5] yields a quantitative estimate for the migration volume for diffusion of Au in amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> as well.

Experiments were performed on a set of amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> ribbons, being the very ribbons on which previously the pressure effect of the diffusivity has been measured [5]. The ribbons were first brought in metastable equilibrium, without inducing crystallization, by anneal-

ing at ambient pressure and a temperature of 563 K during 10 000 s. Under these conditions equilibrium is reached in approximately 5000 s [6]. Subsequently, the samples were annealed for 43 200 s at  $563.0 \pm 0.1$  K and hydrostatic pressures up to 0.75 GPa ( $\pm 0.01$  GPa) in order to determine the Au diffusivity [5]. The annealing time of 43 200 s can be assumed to be long enough to attain the pressure-dependent equilibrium defect concentration, even if structural relaxation is retarded at high pressure. After the pressure anneal each ribbon was cooled down under pressure to room temperature in about 20 min. After a storage period at ambient temperature and pressure, on each ribbon differential scanning calorimetry experiments are performed on a Perkin-Elmer DSC-2 at a heating rate of 40 K/min. The sample weights in these experiments range from 6 to 14 mg.

The peak height of the glass transition has been shown to be a measure for the state of relaxation of the material at the beginning of the DSC-scan. Chen [7] was among the first to show this effect, for amorphous PdNiP. A similar relation between the structural state and the glass-transition peak has also been observed for other classes of amorphous materials, e.g., for amorphous polystyrene [8]. It has been interpreted and quantified in terms of the free-volume model in Refs. [9] and [10]. Figure 1 shows the experimental DSC traces, given here as the change in the apparent heat capacity  $\Delta C_p(T) = C_p(T) - C_p(350 \text{ K})$  with  $C_p(350 \text{ K}) = 23.0 \text{ J/mol K}$  at the start of the measurement, for samples that were annealed at the pressures indicated. The glass-transition peak that appears at approximately 610 K exhibits a distinct dependence on the pressure that was applied. Figure 1 therefore directly shows the pressure-dependent state of relaxation that the material reaches after the pressure anneal at 563 K. At room temperature and ambient pressure this structural state persists, even for the period of about four years that elapsed between the pressure anneals and the DSC experiments.

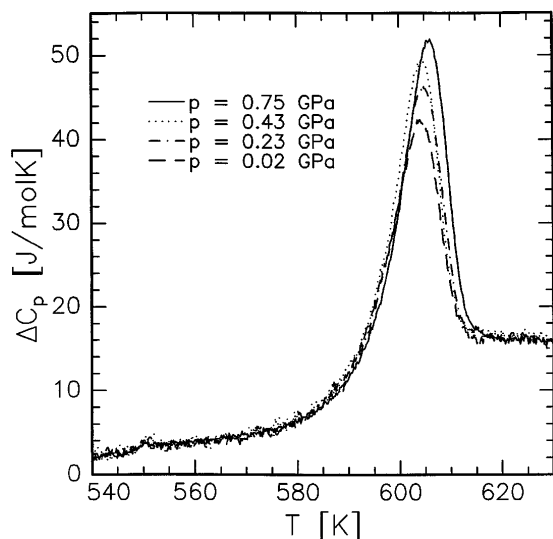


FIG. 1. Experimental differential scanning calorimetry traces for amorphous  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  annealed at 563 K and the pressure indicated.

As a quantification of the state of relaxation we will use the defect concentration  $c_D$  in connection with the free-volume theory [4]. A series of studies on amorphous  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  has shown the validity of this approach for the description of the relaxation behavior [2,6,10]. The change in defect concentration due to structural relaxation during a DSC scan is governed by the differential equation [2,11]

$$\frac{dc_D}{dt} = -k_r c_D [c_D^2 - (c_D^{\text{eq}})^2]. \quad (1)$$

In this equation  $t$  denotes time and  $k_r$  is a temperature-dependent rate factor for structural relaxation. The defect concentration in metastable equilibrium is denoted by  $c_D^{\text{eq}}$ . The defect concentration during a DSC scan is calculated by integrating Eq. (1) with the boundary condition of an initial defect concentration  $c_0$  at the start of the scan ( $T = 350$  K at  $t = 0$ ). According to the free-volume theory [4] the defect concentration is related to the reduced free volume  $x$  by  $c_D = \exp(-1/x)$ . The calculated DSC signal is then obtained by assuming the observed heat flow, given here as  $\Delta C_p(T)$ , to be proportional to  $dx/dT$  [9]. In the approach to the temperature-dependent equilibrium  $c_D^{\text{eq}}$  the glass-transition peak becomes apparent in  $dx/dT$  [9]. The exact shape and position of the peak, in particular its height, depend strongly on the initial defect concentration  $c_0$ . The monotonous relation between the glass-transition peak height and the defect concentration  $c_0$  at the start of the DSC scan [10] enables one to use the DSC as a device to measure the defect concentration in a sample. In Ref. [10] numerical values are given for all parameters involved.

The calculated DSC traces are shown in Fig. 2. The low-temperature slope in the DSC signal that is visible in both the experimental and calculated curves is due to chemical short-range-ordering effects [10]. The only

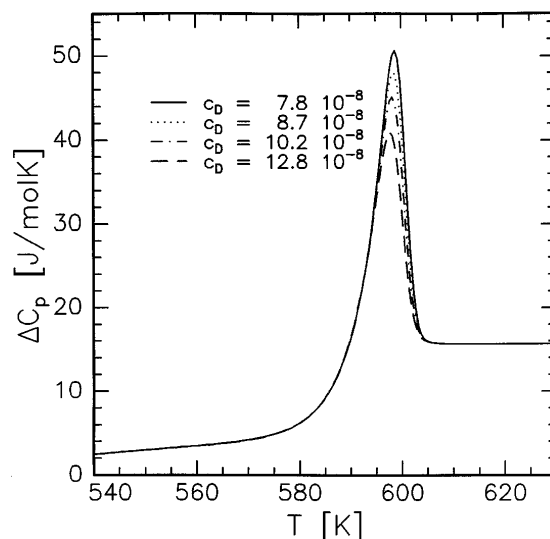


FIG. 2. Calculated DSC traces, according to Eq. (1), for the initial defect concentrations indicated.

fit parameter that is used to match these curves with the experimental curves of Fig. 1 is the initial defect concentration  $c_0$ , which in the present study is the defect concentration after each of the pressure anneals. The resulting defect concentration as a function of the pressure  $p$  is presented in Fig. 3. The difference in the glass-transition peak heights after the anneals at  $p = 0.02$  GPa and after  $p = 0.75$  GPa (Fig. 1) corresponds to a reduction of the defect concentration of approximately 40% after the high-pressure anneal (Fig. 3), whereas the diffusivity was shown to reduce by approximately a factor of 3 in Ref. [5]. The accuracy of the defect concentration is estimated at 10%.

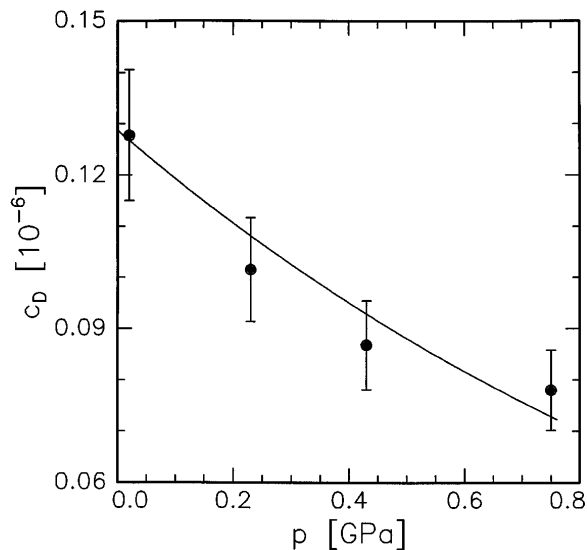


FIG. 3. The defect concentration as a function of hydrostatic pressure. The solid line gives a fit of Eq. (4), with  $\Delta V_f = 5.9 \text{ \AA}^3$ , to the data determined from the results shown in the Figs. 1 and 2.

The Arrhenius-like temperature dependence of the diffusivity in metallic glasses that has been observed experimentally (e.g., [12]) gives rise to a description of the diffusion process as thermally activated events taking place at specific sites in the structure. It has been shown in Ref. [2] that the use of the defect concentration  $c_D$  in connection with Eq. (1) for the concentration of these sites yields an adequate reproduction of the temperature and time dependence of the diffusivity. The important topics in the research on diffusion in metallic glasses are the actual nature of these defects, and the way the atoms use the defects to perform a diffusion event. Experimentally attainable quantities that are of great value for this research are the pressure dependence of the diffusivity [12] and the isotope effect on the diffusivity [13]. We will now discuss the implications of the pressure-induced structural relaxation for the pressure dependence of the diffusivity.

In a general expression, using  $k_D$  as a rate factor, the diffusivity  $D$  is given by

$$D = k_D c_D. \quad (2)$$

The factor  $k_D$  incorporates both the frequency at which diffusion events occur at each defect, and the effective jump distance. It can be described, due to the thermal activation of the process, by

$$\begin{aligned} k_D &= k_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \\ &= k_0 \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta E_m}{kT}\right) \exp\left(-\frac{p\Delta V_m}{kT}\right), \end{aligned} \quad (3)$$

in which  $k_0$  is a pre-exponential factor,  $k$  is Boltzmann's constant,  $T$  is the temperature,  $p$  is the hydrostatic pressure, and the quantities  $\Delta G_m$ ,  $\Delta S_m$ , and  $\Delta E_m$  give the free energy, the entropy, and the internal energy of activation for the diffusion event, with the index denoting "migration."  $\Delta V_m$  is the migration volume, being the temporary volume change necessary for the diffusion event to take place. Note that at ambient pressure  $p\Delta V_m$  is very small, viz. on the order of  $10^{-5}$  eV.

For substitutional diffusion in crystals, the defect concentration equals the vacancy concentration, the temperature dependence of which is determined by the formation enthalpy  $\Delta H_f$ . The pressure dependence is governed by the formation volume  $\Delta V_f$ . In metallic glasses, only the *temperature* dependence of  $c_D$  has been investigated in detail; on the *pressure* dependence of the defect concentration so far no experimental data are available. The most plausible description of the pressure dependence is to incorporate a Boltzmann factor  $\exp(-p\Delta V_f/kT)$ , with  $\Delta V_f$  the formation volume for diffusion defects. For Pd<sub>40</sub>Ni<sub>40</sub>P<sub>40</sub> in the metastable equilibrium state,  $c_D$  can therefore be given by

$$c_D(T, p) = \exp\left(-\frac{B_T}{T - T_0}\right) \exp\left(-\frac{p\Delta V_f}{kT}\right), \quad (4)$$

in which  $B_T = 3300$  K and  $T_0 = 355$  K are constants derived in Ref. [2]. The solid line in Fig. 3 is a fit of  $c_D$  according to Eq. (4), assuming a pressure-independent value for the only fit parameter  $\Delta V_f$ . The satisfactory fit shown in Fig. 3 is obtained with  $\Delta V_f = 5.9 \pm 0.5 \text{ \AA}^3$ , and it shows the validity of Eq. (4).

The diffusivity as a function of  $p$  has been experimentally studied for a number of glasses [5,12,14]. From  $D(p)$  the activation volume  $\Delta V$  is derived by

$$\Delta V = -kT \frac{\partial \ln D}{\partial p}. \quad (5)$$

With the use of the Eqs. (2), (3), and (4)  $\Delta V$  can be shown to consist of a migration part and a formation part, according to

$$\Delta V = -kT \frac{\partial \ln k_D}{\partial p} - kT \frac{\partial \ln c_D}{\partial p} = \Delta V_m + \Delta V_f. \quad (6)$$

The present study has yielded quantitative information on the diffusion process in amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>. The formation volume for diffusion defects has been observed to be  $5.9 \text{ \AA}^3$ , which is about  $0.35\Omega_{\text{Au}}$ , with  $\Omega_{\text{Au}}$  the atomic volume of gold ( $\Omega_{\text{Au}} = 16.9 \text{ \AA}^3$  [15]). Combining the present result with the value  $\Delta V = 11 \pm 4 \text{ \AA}^3$  found previously for Au diffusion in these samples [5], we conclude the migration volume for Au diffusion to be  $\Delta V_m = 5 \pm 4 \text{ \AA}^3$  [16], or  $\sim 0.3\Omega_{\text{Au}}$ . Therefore, Au diffusion in this metallic glass is characterized by a formation volume that is smaller than found for crystalline gold ( $0.52\text{--}0.65\Omega_{\text{Au}}$  [17]) and a migration volume that is distinctly nonzero, and somewhat larger than in crystalline gold ( $0.15\Omega_{\text{Au}}$  [15]).

In conclusion, pressure-induced structural relaxation is observed in amorphous Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> after anneals at 563 K and hydrostatic pressures up to 0.75 GPa. A quantitative interpretation of this effect yields a value of  $5.9 \pm 0.5 \text{ \AA}^3$  for the formation volume of diffusion defects in this glass, and a value of  $5 \pm 4 \text{ \AA}^3$  for the migration volume for Au diffusion.

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