Activation Volume for Hf Diffusion in an Amorphous $Ni_{0.54}Zr_{0.46}$ Alloy

A. Grandjean,[1] P. Blanchard,[2] and Y. Limoge[1]
[1]*Section de Recherche de Métallurgie Physique, C.E. Saclay, Gif-sur-Yvette Cedex, France*
[2]*Section de Caractérisation Physique des Matériaux, C.E.N. Grenoble, Av des Martyrs, Grenoble, France*

(Received 6 March 1996)

In this Letter we present the results of a diffusion study of Hf in a $Ni_{0.54}Zr_{0.46}$ amorphous alloy. We have measured the diffusion properties with and without pressure, up to 1 GPa. From these measurements we can deduce an Arrhenius behavior of the diffusion, with an activation energy of 0.76 eV and a pre-exponential factor of 7.4×10^{-17} m^2/s. The activation volume amounts to 8.5 Å^3. Activation volume and energy are related by the Keyes relationship. We then discuss to what extent presently proposed diffusion mechanisms, point defects, or collective processes can be tested against these results. [S0031-9007(96)02084-4]

PACS numbers: 66.30.–h, 81.05.Kf, 81.15.Cd

In equilibrium crystalline solids atomic diffusion takes place by mechanisms involving point defects and thermally activated jumps. On the other hand, diffusion in equilibrium liquids does not involve point defects. Therefore starting with single crystals and increasing the degree of disorder toward the liquid state, the diffusion mechanism must switch from a localized event involving a defect to a homogeneous and collective process. We want to know whether diffusion in amorphous metallic alloys is defect mediated or due to a collective mechanism. The existence of point defects is well established in covalent glasses, and has recently been shown in a Lennard-Jones model of glasses [1]. However, their contribution to atomic transport is still a matter of debate in both cases [2,3], despite a 13-year-old proposal of a vacancy mechanism in amorphous alloys [4]. The crucial question of the effect of the pressure upon the diffusion coefficient D, namely, whether it is compatible with a vacancy formation volume, is still controversial [5,6].

Early measurements under high pressures have shown an activation volume, defined as $\Delta V = -kT[\delta \ln(D)/\delta p]$, of the order of one atomic volume, Ω, for self diffusion in a $(FeNi)_{0.80}(PB)_{0.2}$ amorphous alloy [5]. But later experiments led to a *negative* value, of the order of -0.1Ω, in a cobalt based glass [6]. On the contrary recent results gave positive values, between 8 and 20 Å^3, for Co diffusion in Ni_xZr_{1-x} glasses $(0.42 < x < 0.62)$ [7]. These contradictions can be due to the difficulties inherent to diffusion experiments in glasses, since the metastability implies small mean squared displacements. The difficulties are even higher in the high pressure environment involving strong surface contamination, difficult temperature control, and shorter durations. We decided to make new and very carefully controlled determinations of ΔV for self-diffusion in a properly chosen amorphous alloy, using the best available techniques at all steps of the experiments. We chose to study self-diffusion in a $Ni_{0.54}Zr_{0.46}$ glass for this class of alloy is believed to be prone to display collective diffusion behavior, hence a low ΔV according to some authors [8]. Given the well known chemical and size similarities between Zr and Hf we have used the Hf as a tracer for the Zr, since we can in this case use the SIMS (secondary ion mass spectrometry) method to determine the concentration profiles, as done in Ref. [7].

Experimental procedures.—Given the very small mean squared displacements accessible in amorphous alloys, which renders any surface contamination very detrimental, we chose the use of buried tracer layers. The SIMS method is well suited in this case, and, in addition to analyzing the whole concentration profile, allows checking the Gaussian nature of the diffusion as well as detecting possible spurious artifacts.

In order to optimize the quality of the samples themselves with respect to purity, composition, and structure, they were prepared by ion sputtering in a UHV deposition chamber including two computer controlled ion guns working with high purity argon gas. A rotating target holder permitted switching one of the targets between two different elements, here Zr and Hf. In this way we can insert buried layers of $Ni_{0.54}Hf_{0.46}$ inside the $Ni_{0.54}Zr_{0.46}$ matrix. The composition was controlled to 1% atomic. The amorphous layers were deposited on Si(100) wafers covered by 200 nm of SiO_2. In order to improve the precision of the depth determination we used two buried layers 4.5 nm thick each, in a sample of 130 nm total thickness. The total impurity content of the targets was given as better than 10 ppm for Ni, 500 ppm for Hf (excluding Zr), and 600 ppm for Zr (mainly as Fe, excluding oxygen). Differential thermal dilatation between substrate and sample, of the order of a few 10^{-6} at most, corresponds to a negligible stress level of a few tens of MPa, at most, during the diffusion annealings.

The crystallization temperatures of our samples at a heating rate of 1 °C/min, for example, 813 K for $Ni_{0.60}Zr_{0.40}$ or 770 K for $Ni_{0.46}Zr_{0.54}$, were checked by electron microscopy and x-ray studies, and found in good agreement with literature results [9]. We have relaxed the samples at 330 °C before the diffusion anneals [10], and controlled that they were indeed relaxed. Among other tests we used varying annealing times for Hf diffusion, from 20 to 100 h at the same temperature (see Fig. 1). The pressure experiments were done in a Bridgman-type high pressure cell according to the procedure developed in Ref. [5]. The pressure needed to detect a change of D being of the order of 100 MPa at least, the experiments done under vacuum, at ambient pressure, or at 20 MPa, can all be told zero pressure experiments. The temperature is measured by a chromel thermocouple *inside* the pressure vessel, which enabled the temperature to be known to better than 1 °C [5].

The SIMS determination of the Hf diffusion profile was done in a Cameca ion microproble, model I.M.S. 3f, using 5 keV Xe primary ions, while the sample was flooded by O_2. After annealing under pressure an oxide layer about 6 nm thick was found. The bulk oxygen contamination detected by SIMS and ESCA (electron spectroscopy for chemical analysis) was not significantly higher than in the nonannealed samples. The determination of the true tracer profile was further improved by correcting the experimental profile from the perturbations introduced by the irradiation damage of the primary Xe^+ beam [11]. A complete description of the experimental procedure is given in Ref. [10].

Results.—We show in Fig. 1 the results obtained for the diffusion coefficient of Hf tracer in a $Ni_{0.54}Zr_{0.46}$ alloy at zero pressure. The measurements were done in a standard furnace under vacuum, except for the one at 412 °C, obtained in the high pressure setup at 20 MPa, in order to control the coherency between the two sets of measurements, with and without pressure. Figure 2 gives the results obtained as a function of pressure at a temperature of 412 °C. In both cases the uncertainty amounts to 20%, from the reproducibility of the results as well as from the analysis of the possible errors.

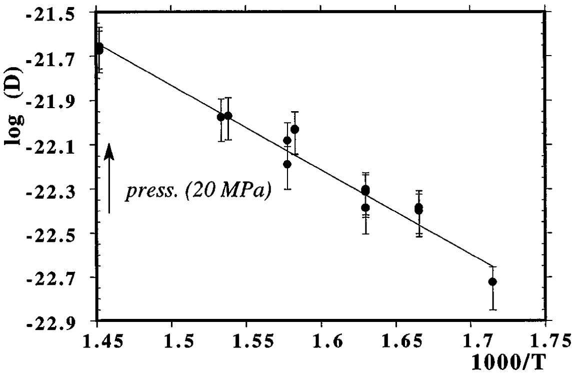

FIG. 1. Arrhenius plot of diffusion coefficients for Hf transport in $Ni_{0.54}Zr_{0.46}$ at negligible pressure. The value at 412 °C was obtained in the high pressure setup, at 20 MPa. The durations of the annealings were 10 h at 412 °C, 40 h and 70 h at 376 °C, 50 h at 358 °C, 90 h at 356 °C, 20 h, 80 h, and 100 h at 338 °C, 50 h at 325 °C, and 100 h at 308 °C.

The pre-exponential factor D_0 had a value of 7.4×10^{-17} m^2/s, the activation energy Q amounted to 0.76 eV per atom, and the activation volume ΔV was 8.5 Å^3. In this system the mean atomic volume is 16 Å^3 and the Zr atomic volume is 23 Å^3. The results at ambient pressure are in good agreement with those published by Wu on a $Ni_{0.49}Zr_{0.51}$ glass [12]. On the other hand, the activation volume corresponds only partly to the results of Höfler in Ni_xZr_{1-x} glasses quoted above and shown in Table I [7].

It has been shown by Keyes [13] under the hypothesis that the activation energy corresponds to a strain energy of the solid during the activated step of diffusion, and in the limit of the macroscopic elasticity, that Q and ΔV are related by $\Delta V = k\chi Q$, with χ the compressibility of the material and k a coefficient of the order of 4–5 related to the Grüneisen constant g by $k = 2g - 0.66$ [13]. Indeed in this approach the activation volume is due to the pressure effect on the elastic constants, i.e., to the anharmonicity of the interatomic interactions. This result can also be obtained in the framework of the dynamical theory of the jump [14]. Strictly speaking the Keyes relationship should then work only for an interstitial mechanism or the migration part of a vacancy one. However, diffusion experiments show in this last case that it works for the whole diffusion event, i.e., including also the formation part. Using simple models of interatomic interaction one can check that it works also for the vacancy formation energy, with a coefficient k of the same order of magnitude [13]. Experimentally k is found to be almost independent of the material, and of the mechanism, but to depend on the structure: it is larger in compact metals than in noncompact ones, amounting to 5.5 in fcc against 2.3 in bcc [10]. The general validity of the relation comes from the fact that the anharmonicity of the interactions affects in a parallel manner the pressure variation of the elastic constants, relevant in a macroscopic deformation, and the variation with interatomic distances of the Kanzaki forces at work during defect formation and migration. In this respect it seems probable that the relations should work in

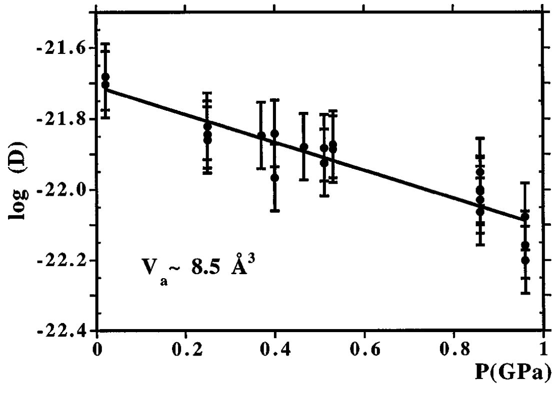

FIG. 2. Pressure effect upon diffusion of Hf tracer at 412 °C in a $Ni_{54}Zr_{46}$ glass.

TABLE I. Activation energies, activation volumes, and Keyes coefficients for Co [7] and Hf (this work) diffusion in Ni_xZr_{1-x} amorphous alloys. The last column shows the value of the coefficient k involved by the Keyes relationship.

Tracer	x	Q (kJ/mol)	ΔV (Å^3/at.)	$\Delta V/\chi Q$
Co	0.42	154	8.9	2.8
	0.52	187	20	5.2
	0.57	162	18	5.4
	0.62	165	7.9	2.3
Hf	0.54	73	8.5	5.3

all materials, including glasses, whatever the mechanism involved, provided the activation energy has a strain part as main term.

It is therefore not surprising to get a value of $k = 5.3$ in our $Ni_{0.54}Zr_{0.46}$ alloy, metallic glasses being almost as compact as fcc phases. We have shown in the last column of Table I the value of k in Ni_xZr_{1-x} glasses, according to Höfler *et al.* [7] and us. This relationship is also obeyed in a $Fe_{40}Ni_{40}P_{14}B_6$ amorphous alloy, with $k \cong 4$ [5]. Therefore some of Höfler's results appear doubtful. Among the four values of ΔV published, two of them, those for $x = 0.52$ and 0.57, comply with the Keyes rule with $k = 5.2$. But the other two appear a bit too small. Moreover the jump from 18 to 8 Å^3 between $x = 0.57$ and 0.61 is hard to explain since the activation energy, on the contrary, varies smoothly with concentration [12].

Can we now deduce from these two results some clue to the mechanism of diffusion? Proposals have been made in two directions: a point defect mechanism, vacancy or interstitial, as in crystals, or a collective mechanism as in liquids, generally of an unspecified nature. In the second hypothesis, proposals are made on the basis of experimental data, the pre-exponential factors D_0 [8,15]. Alternatively collective excitations specific to the amorphous state have been claimed, from a theoretical point of view, to constitute a possible mechanism.

In crystalline metals for a vacancy mechanism, activation energy and cohesion are quite nicely related by the Van Liemp rule stating that $Q \cong 0.14 T_m$, Q in kJ/mol, T_m the melting temperature. In hexagonal Zr the intrinsic activation energy is deduced to be of the order of 3.1 eV [16]. In this respect our present finding, 0.76 eV for self-diffusion, is small. Conversely, according to Keyes, the activation volume also is quite small as compared to the Zr atomic volume. At first our results as compared to pure Zr do not seem to be in favor of a vacancy mechanism. Moreover in crystals whenever a jump mechanism prevails, the pre-exponential term is given by $D_0 = \beta f \nu a^2 \exp(\Delta S/k)$, β being a numerical coefficient, f the correlation factor, of the order of one, a the jump distance, ν the so-called attempt frequency, k the Boltzmann factor, and ΔS the activation entropy. In the hypothesis of a simple defect mechanism an entropy of the order of a few k is expected.

Assuming the D_0 expression to be valid, and using measured D_0's, one can calculate ΔS, and, under various assumptions, transpose it into a number of atoms involved. In a $Fe_{24}Zr_{76}$ glass, similar to the present one, it has been proposed that the ΔS deduced in this way can be transformed into an activation volume by assuming that it corresponds to the entropy variation due to the density fluctuation during the activated step. One gets then $\Delta V = \alpha \Delta S/\chi$ with χ the compressibility and α the volume dilatation coefficient. In this system D_0 amounts to 7×10^6 m^2/s, and corresponds, according to the authors, to an activation volume of 60Ω, or 60 atoms involved, pointing to a strongly collective mechanism [8]. However, this is a very high activation volume which is clearly ruled out by all ΔV measured presently. Moreover D_0 terms are prone to large experimental errors and cannot, except in the simplest cases, be directly related to the atomic mechanism, particularly in disordered systems [3]. The proposals made on these bases seem to us too fragile to be followed in the absence of other reasons [10].

On the other hand, two kinds of excitations specific to the glassy materials have been detected in experiments or numerical simulations. The first one observed at low temperature, of the order of 10% of the glass temperature at most, corresponds to groups of 10 to 40 atoms, involved in bistable positions [17]. The tunneling transitions between the two equilibrium positions, distant in energy by 10^{-4} eV, are responsible for the well known linear excess of specific heat below 1 K, and at a higher temperature anharmonic excitations in the double wells produce a peak in the C_v/T^3 curve [18]. Conversely at a much higher temperature, at or above the glass transition, it has been shown that small groups of atoms, 3 to 5, could exchange their position [19], in manner reminiscent of the ring mechanism proposed for crystals by Zener [20] and much later detected by Nguyen in bcc metals [21].

It can be proposed that these excitations can form the base of a defectless mechanism. However, for providing a diffusion mechanism two conditions must be met. At first they must be present in a sufficient concentration so each atom can participate in several of them. This is probably not a severe requirement for high temperature events, but is far from proved in the other case. One has also to assume that these excitations are described by a very broad distribution, in order to match the proper energy scale of diffusion, say from 1 to 2 eV. In both cases a more precise test against our results is not possible since we do not know their thermodynamical properties. In this respect molecular dynamics simulations would be of a great help, for the determination of theoretical activation energy and volume.

However, the defect hypothesis is not necessarily ruled out by the very low activation parameters we have obtained. Indeed the self-diffusion in *hexagonal* Zr can only be understood if the role of *extrinsic vacancies* trapped by Fe impurities, unavoidable in Zr, is taken into account [16]. These extrinsic vacancies are believed [22] to be at the origin of the very low, 1.1 eV, apparent activation energy observed between 1100 and 900 K in αZr, which in this case corresponds simply to the migration term [23]. We have built a simple model taking into account this effect [10]. By fitting the model to the experimental behavior of αZr, we found a true activation energy of 3.1 eV, matching well the melting point in agreement with Hood [16], a solution energy of Fe amounting to 1.15 eV and an Fe-vacancy binding energy of 1.4 eV, all values in agreement with the estimations of King [22].

In the present glass, either due to the high concentration of nickel or to the unavoidable iron impurity, the same extrinsic effect is possible. Using our model, and taking simply into account the disordered state which implies a smaller energy scale, and then a lower temperature range, we have obtained a good fit of our present diffusion data for an intrinsic activation energy of 2.2 eV, a binding energy of 1.4 eV, and a solution energy of 0.7 eV. The apparent activation energy amounts now to 0.8 eV, in good agreement with our value. The question now is to verify whether the iron impurity can have the same effect in the glass as in the αZr. In this respect experiments in crystalline Ni-Zr alloys would be much more interesting. Following the Keyes rule this small activation energy will probably correspond to a small activation volume. A symmetric case is known in crystalline Al-Cr and Al Mn alloys, where a large activation energy due to a strongly repulsive solute-vacancy interaction has been found, linked to a very large activation volume [24] by a Keyes relationship involving $k = 4.6$.

In conclusion, we propose therefore that in $\mathrm{Ni}_x\mathrm{Zr}_{1-x}$ glasses the activation volume for self-diffusion is positive and of the order of, but less than, the relevant atomic volumes. The activation volume and energy are related by the Keyes relationship for the same reasons as in crystals, independently of the diffusion mechanism. Since both conclusions are valid in the other main class of amorphous alloy [5], the metal-metalloid one, they are likely to be valid for all metallic glasses. We have shown that the relatively small activation volume and energy we have measured are not incompatible with a vacancy mechanism if the extrinsic regime of diffusion due to Fe impurities, well known in αZr, is supposed to work also in this glass. The collective proposal based on D_0 values have been shown to be incompatible with experimental results. For a meaningful comparing of our results with the theoretical proposals of a collective mechanism, however, we need more detailed information on their characteristics.

[1] J.M. Delaye and Y. Limoge, J. Phys. (Paris) **3**, 2063 (1993).
[2] J.M. Delaye and Y. Limoge, J. Phys. (Paris) **3**, 2079 (1993).
[3] J.L. Bocquet, G. Brebec, and Y. Limoge, in *Physical Metallurgy*, edited by R.W. Cahn and P. Haasen (North-Holland, Amsterdam, 1996).
[4] Y. Limoge, G. Brebec, and Y. Adda, *Proceedings of the International Conference on Diffusion in Metals and Alloys, Tihany, Hungary, 1982*, edited by F.J. Kedves, (1983), p. 285.
[5] Y. Limoge, Mater. Sci. Forum **15–18**, 517 (1987); Acta Metall. Mater. **38**, 1733 (1990).
[6] F. Faupel, P.W. Hüppe, and K. Rätzke, Phys. Rev. Lett. **65**, 1219 (1990).
[7] H.J. Höfler, R.S. Averback, G. Rummel, and H. Mehrer, Philos. Mag. Lett. **66**, 301 (1992).
[8] H. Kronmüller and W. Frank, Radiat. Eff. Defects Solids **108**, 81 (1989).
[9] K.H.J. Buschow and N.M. Beekmans, Phys. Rev. B **19**, 3843 (1979).
[10] A. Grandjean and Y. Limoge, Acta Metall. (to be published).
[11] Y. Limoge, Le Vide les Couches Minces **24**, 167 (1985).
[12] H.M. Wu, Ph.D. thesis, University of Illinois, 1991.
[13] R.W. Keyes, J. Chem. Phys. **29**, 467 (1958).
[14] C.P. Flynn, *Point Defects and Diffusion* (Clarendon Press, Oxford, 1972), p. 306.
[15] S.K. Sharma, S. Banerjee, K.K. Jain, and A.K. Jain, J. Mater. Res. **4**, 603 (1989).
[16] G.M. Hood, J. Mater. Nucl. **135**, 292 (1985).
[17] H.R. Schober, C. Oligschleger, and B.B. Laird, J. Non-Cryst. Solids **156–158**, 965 (1993).
[18] U. Buchenau *et al.*, Phys. Rev. B **46**, 2798 (1992).
[19] H. Miyagawa and Y. Hiwatari, Phys. Rev. A **44**, 8278 (1991).
[20] C. Zener, J. Appl. Phys. **22**, 372 (1952).
[21] V.D. Nguyen and Y. Adda, Philos. Mag. A **56**, 269 (1987).
[22] A.D. King, G.M. Hood, and R.A. Holt, J. Mater. Nucl. **185**, 174 (1991).
[23] J. Horvath, F. Dyment, and H. Mehrer, J. Mater. Nucl. **126**, 206 (1984).
[24] G. Rummel *et al.*, Z. Metall. **86**, 131 (1995).