Atomic diffusion in liquid Ni, NiP, PdNiP, and PdNiCuP alloys

S. Mavila Chathoth and A. Meyer^{a)}

Physik Department E13, Technische Universität München, 85747 Garching, Germany

M. M. Koza

Institut Laue-Langevin, 38042 Grenoble, France

F. Juranyi

*Physikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken, Germany
and Paul Scherrer Institut, 5232 Villigen, Switzerland*

(Received 20 August 2004; accepted 23 September 2004)

We investigated the self-diffusion of Ni in liquid Ni, Ni₈₀P₂₀, Pd₄₀Ni₄₀P₂₀, and Pd₄₃Ni₁₀Cu₂₇P₂₀ at temperatures up to 1795 K with incoherent, quasielastic neutron scattering. Values of measured self-diffusion coefficients vary over the accessible temperature ranges as a function of composition only within 10%. Although mixing has a drastic effect on the liquidus temperature and the undercooling capabilities, a relation between these properties and the atomic diffusion in the liquid is not observed. Apparently, diffusive motion is governed by the packing fraction of the atoms, that is very similar in these dense liquids. © 2004 American Institute of Physics.

[DOI: 10.1063/1.1825617]

PdNiCuP alloys exhibit an exceptional bulk glass-forming ability.^{1–4} This comes along with a self-diffusion of the atoms at the liquidus temperature T_{liq} that is about two orders of magnitude slower as compared to simple liquids and most alloys.⁵ In order to suppress crystallization on undercooling in hard-sphere like metallic systems mixing of various elements is required for glass formation. We performed quasielastic neutron scattering experiments on pure Ni and glass forming Ni₈₀P₂₀, Pd₄₀Ni₄₀P₂₀, and Pd₄₃Ni₁₀Cu₂₇P₂₀ alloys in order to investigate the effects of mixing on the Ni self-diffusion in the equilibrium liquid.

The alloys were prepared from a mixture of pure Ni, Pd, and Cu metals by arc melting under argon atmosphere. In a second step, P was added in an induction melting furnace. The melts were subject to B₂O₃ flux treatment in order to remove oxide impurities. The solidus and liquidus temperatures were measured by differential scanning calorimetry and are in accordance with literature values.^{6,7} The liquidus temperatures are $T_{liq}=863$ K in Pd₄₃Ni₁₀Cu₂₇P₂₀, $T_{liq}=972$ K in Pd₄₀Ni₄₀P₂₀, and $T_{liq}=1171$ K in Ni₈₀P₂₀. The melting temperature of pure Ni is 1727 K. For the neutron time-of-flight experiments, thin-walled Al₂O₃ containers were used that provide a hollow cylindrical sample geometry with a 22 mm diameter, a 40 mm height, and a wall thickness of 0.6 mm in the case of Ni and NiP, and of 1.2 mm in the case of PdNiP and PdNiCuP. For the chosen sample geometries and wavelengths of the incoming neutrons, the samples scatter less than 8%. Effects of multiple scattering, which would alter the data especially toward low q , could not be detected.

PdNiP was investigated on the spectrometer FOCUS at the Paul Scherrer Institute. In an experiment on the spectrometer IN6 at the Institute Laue-Langevin, dynamics in PdNiCuP, NiP, and Ni were measured. The setups with wavelengths of the incident neutrons of $\lambda=5.4$ Å (FOCUS) and 5.1 Å (IN6) allowed an accessible wave-number range q of about 0.4 to 1.6 Å⁻¹ at zero energy transfer. Regarding the scattering cross sections of the individual elements, in this q

range the signal is dominated by the incoherent scattering of Ni. In PdNiCuP incoherent scattering on the Cu atoms contributes with about 20% to the signal. Following the arguments in Ref. 8, the diffusion coefficients of the Ni and Cu atoms are quite similar.

The liquids were measured at temperatures ranging from their liquidus temperature up to 1795 K. In the case of PdNiP the furnace on FOCUS did not allow measurements above 1400 K. In the case of PdNiCuP data below 1255 K were taken from Ref. 8. Run durations at each temperature were 2–4 h on IN6 and 10 h on FOCUS. At each temperature empty cell measurements were performed. The IN6 Nb resistance furnace was calibrated *in situ* with the melting temperatures of the Ni and NiP samples; hence, we estimate errors in the temperature values of this experiment to be smaller than ± 5 K.

The scattering law $S(q, \omega)$ was obtained by normalization to a vanadium standard, correction for self-absorption and container scattering, and interpolation to constant wave numbers q . Further, $S(q, \omega)$ was symmetrized with respect to the energy transfer $\hbar\omega$ by means of the detailed balance factor. Fourier transformation of $S(q, \omega)$, deconvolution of the instrument resolution, and normalization with the value at $t=0$ gave the time correlation function $\Phi(q, t)$.

Figure 1 displays the normalized density correlation functions $\Phi(q, t)$ of the liquid alloys. The final decay towards 0 in $\Phi(q, t)$ [Fig. 1(a)] can be described with an exponential function, $f_q \exp(-t/\tau_q)$, as expected for normal liquids.⁹ f_q denotes the Debye–Waller factor and τ_q the relaxation time. In dense, glass-forming liquids the structural relaxation from a plateau in $\Phi(q, t)$ to zero is usually described by a stretched exponential function, $f_q \exp[-(t/\tau_q)^\beta]$, as a result of a non-linear coupling of density fluctuations caused by feedback effects in the dense liquid.¹⁰ Fits with a stretched exponential function to the high-temperature data revealed a stretching exponent β that approaches unity with increasing temperature. Systematic changes of β as a function of the alloy's composition could not be detected.

^{a)}Electronic mail: ameyer@ph.tum.de

FIG. 1. Density correlation functions $\Phi(q, t)$ in the structural relaxation regime in liquid Ni, $\text{Ni}_{80}\text{P}_{20}$, $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, and $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ at different temperatures. (a) $\Phi(q, t)$ shows an exponential decay at high temperatures (lines). (b) Rescaled $\Phi(q, t; T)/f_q(T)$ of $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$: A time-temperature superposition holds over the entire temperature range. The solid line represents a fit with a stretched exponential function giving a stretching exponent $\beta=0.75$.

On approaching the liquidus temperature in liquid PdNiCuP alloys, the mode-coupling theory of the liquid-to-glass transition¹⁰ gives a consistent description of the dynamics that govern the mass transport.^{8,11} With an increasing relaxation time a plateau evolves in $\Phi(q, t)$. The decay from this plateau to zero exhibits then stretching with a stretching exponent $\beta_q \approx 0.75$. Rescaling of $\Phi(q, t)$ with f_q and of the time with τ_q [Fig. 1(b)] demonstrates that in PdNiCuP a time-temperature superposition holds from the liquidus temperature at 863 K even up to 1795 K. One should note that the final decay to zero of a stretched exponential function cannot be distinguished from an exponential decay.

An evaluation of density data^{4,12,13} and structure factors^{14–16} shows that Ni, NiP, PdNiP, and PdNiCuP are all densely packed liquids with very similar values of the packing fraction. A signature of dense packing in the dynamics is a $1/q^2$ dependence of the relaxation time τ_q not only in the hydrodynamic regime of $q \rightarrow 0$ but also at intermediate q .⁸ Figure 2 shows that the relaxation times of the four different liquids indeed follow a $1/q^2$ dependence over the measured q range. This allows us to derive a diffusion coefficient $D = 1/(\tau_q q^2)$.

Quasielastic neutron scattering data are not affected by convection effects, since dynamics are probed on significantly shorter time scales as the ones related to convective transport. Therefore, diffusion coefficients can be derived on an absolute scale. Since for the investigated samples the signal is dominated by the incoherent scattering on Ni, the data analysis gives the self-diffusion coefficient of the Ni atoms. Figure 3 displays self-diffusion coefficients in pure Ni, NiP, PdNiP, and PdNiCuP. For a comparison data of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ (Ref. 5) and of $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{10}$ (Ref. 8) measured at lower temperatures are shown as well.

FIG. 2. Relaxation times τ_q of structural relaxation in liquid Ni, NiP, PdNiP, and PdNiCuP. In all systems, $1/\tau_q$ exhibits a q^2 dependence (lines) also in an intermediate q range. The slope represents the Ni self-diffusion coefficient D .

Over the accessible temperature ranges there is an overall agreement in the Ni self-diffusion coefficients within $\pm 10\%$. The agreement is even better for temperatures above 1390 K: There, diffusion coefficients of NiP and PdNiCuP are equal within the error bars. Absolute values in NiP and PdNiCuP, respectively, range from $1.96 \pm 0.06 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $2.09 \pm 0.11 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1390 K to $4.65 \pm 0.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $4.74 \pm 0.18 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1795 K. Replacing more than 85% of the Ni atoms by Pd and Cu has, at least in this temperature range, no resolvable effect on the diffusion of the Ni atoms. At temperatures around 1000 K, data for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ overlap.⁵ Differences in the diffusion coefficients of the two alloys are not larger than the error bars.

Even in pure Ni the value of $3.80 \pm 0.06 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1795 K is only 20% below the diffusion coefficients of the NiP and PdNiCuP alloys. Close to the melting point, $D_{\text{Ni}} = 3.27 \pm 0.04 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1735 K. This value is in good agreement with a prediction from a hard-sphere calculation that gives $3.90 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.¹⁷

In hard-sphere-like liquids, one expects that the self-diffusion coefficient can be expressed in terms of shear viscosity η via the Stokes-Einstein relation $D = k_b T / (6\pi a \eta)$ with a reasonable value of the hydrodynamic radius a . In PdNiCuP this relation holds with $a = 1.15 \text{ \AA}$:⁸ the covalent radius of the Ni atom. In PdNiP, diffusion coefficients calcu-

FIG. 3. Ni self-diffusion coefficients in pure liquid Ni and liquid NiP, PdNiP, and PdNiCuP alloys as obtained by quasielastic neutron scattering. The arrows indicate the corresponding liquidus temperatures.

lated from viscosity data are systematically about 20%–30% below the measured diffusion coefficients.¹⁸ This effect increases to about 40% in pure Ni, taking the viscosity data from Ref. 19. As compared to the findings in bulk glass-forming ZrTiNiCuBe alloys, where this deviation is more than two orders of magnitude at the liquidus temperatures²⁰ a 40% effect is small. However, these deviations from the Stokes–Einstein relation suggest that influences of short-range order on the liquid dynamics cannot be fully neglected.

Our findings are in accordance with results of recent molecular dynamics simulations on binary hard-sphere liquids, that address the question of mixing effects on structural relaxation.²¹ There, at a given packing fraction, mixing only causes measurable and systematic changes in the diffusion coefficients at packing fractions that are close to the critical packing fraction of mode-coupling theory. In Pd₄₃Ni₁₀Cu₂₇P₁₀, extrapolations give a corresponding critical temperature at about 710 K.⁸ However, for quasielastic neutron scattering on the alloys discussed here, crystallization prevents access to this interesting regime.

In conclusion, we measured Ni self-diffusion coefficients in liquid Ni and liquid NiP, PdNiP, and PdNiCuP alloys with quasielastic neutron scattering. In these liquids, an increasing number of components leads to a continuous decrease of the liquidus temperature, the critical cooling rate for glass formation and the atomic mobility at the liquidus temperature. The diffusion coefficient at the corresponding liquidus temperature is nearly two orders of magnitude smaller in PdNiCuP as compared to pure Ni. At a constant temperature, however, the replacement of more than 85% of the Ni atoms in NiP by Pd and Cu has no resolvable effect on the Ni self-diffusion coefficient. In these dense liquids, atomic transport is controlled by the packing fraction, that is very similar in these alloys.

The authors acknowledge financial support by the German DFG (SPP Phasenumwandlungen in mehrkomponentigen Schmelzen) under Grant No. Me 1958/2-2.

- ¹A. Inoue, N. Nishiyama, and H. Kimura, *Mater. Trans., JIM* **38**, 179 (1997).
- ²N. Nishiyama and A. Inoue, *Appl. Phys. Lett.* **80**, 568 (2002).
- ³J. Schroers, W. L. Johnson, and R. Busch, *Appl. Phys. Lett.* **77**, 1158 (2000).
- ⁴I.-R. Lu, G. P. Görlner, and R. Willnecker, *Appl. Phys. Lett.* **80**, 4534 (2002).
- ⁵A. Meyer, R. Busch, and H. Schober, *Phys. Rev. Lett.* **83**, 5027 (1999).
- ⁶I.-R. Lu, G. Wilde, G. P. Görlner, and R. Willnecker, *J. Non-Cryst. Solids* **250–252**, 577 (1999).
- ⁷G. Wilde, G. P. Görlner, R. Willnecker, and G. Dietz, *Appl. Phys. Lett.* **65**, 397 (1994).
- ⁸A. Meyer, *Phys. Rev. B* **66**, 134202 (2002).
- ⁹J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
- ¹⁰W. Götzke and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
- ¹¹V. Zöllmer, K. Rätzke, F. Faupel, and A. Meyer, *Phys. Rev. Lett.* **90**, 195502 (2003).
- ¹²K. C. Chow, S. Wong, and H. W. Kui, *J. Appl. Phys.* **74**, 5410 (1993).
- ¹³J. Brillo and I. Egry, *Int. J. Thermophys.* **24**, 1155 (2003).
- ¹⁴N. Mattern, H. Hermann, S. Roth, J. Sakowski, M.-P. Macht, P. Jovari, and J. Jiang, *Appl. Phys. Lett.* **82**, 2589 (2003).
- ¹⁵Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980).
- ¹⁶T. Schenk, D. Holland-Moritz, V. Simonet, R. Bellissent, and D. M. Herlach, *Phys. Rev. Lett.* **89**, 075507 (2002).
- ¹⁷P. Protopoulos, H. C. Andersen, and N. A. D. Parlee, *J. Chem. Phys.* **59**, 15 (1973).
- ¹⁸A. Griesche, M.-P. Macht, J.-P. Garandet, and G. Froberg, *J. Non-Cryst. Solids* **336**, 173 (2004).
- ¹⁹Y. Sato, T. Nishizuka, T. Talamizawa, K. Sugisawa, and T. Yamamura, *Proceedings of the 16th European Conference on Thermophysics, London, 2002*.
- ²⁰A. Meyer, W. Petry, M. Koza, and M.-P. Macht, *Appl. Phys. Lett.* **83**, 3894 (2003).
- ²¹G. Foffi, W. Götzke, F. Sciortino, P. Tartaglia, and Th. Voigtmann, *Phys. Rev. Lett.* **91**, 085701 (2003).