Ni self-diffusion in Zr-Ni(-Al) melts

D Holland-Moritz[1], S Stüber[2], H Hartmann[1], T Unruh[3] and A Meyer[1]

[1] Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt(DLR), 51170 Köln, Germany

[2] Physik Department E13, Technische Universität München, James-Franck-Str. 1, 85747 Garching, Germany

[3] Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM-II), Technische Universität München, 85747 Garching, Germany

dirk.holland-moritz@dlr.de

Abstract. We report on investigations on the atomic dynamics in melts of different binary Zr-Ni alloys and of the ternary glass-forming $Zr_{60}Ni_{25}Al_{15}$ alloy. The liquids are containerlessly processed in an electromagnetic levitator that is combined with quasielastic neutron scattering at the time of flight spectrometer TOFTOF of the FRM II. Ni self-diffusion coefficients are determined that exhibit an Arrhenius-type temperature dependence with comparatively large activation energies ranging between 0.64 and 0.90 eV. Although glass forming abilities and melting temperatures for these alloys exhibit large differences, the absolute values of the self-diffusion coefficients are similar at same temperature.

1. Introduction

Among numerous multi-component alloys forming (bulk) metallic glasses [1], one important class of alloys is based on the binary Zr-Ni system. The solidification behaviour of melts and consequently the glass formation process is strongly affected by the the atomic dynamics in the liquid. While for glass-forming Pd-(Ni-Cu-)P melts the viscosity is coupled with the diffusivity by the Stokes-Einstein relation above the critical temperature T_c of mode-coupling theory [2], for Zr-Ti-Cu-Ni-Be melts viscosity and diffusivity are decoupled above T_c and the liquidus temperature T_L [3]. Moreover these liquids exhibit considerably smaller values of the Ni self-diffusivity as Pd-(Ni-Cu-)P alloys at similar temperatures. In this work we present investigations on the Ni self-diffusion in melts of different binary Zr-Ni alloys and of the ternary glass forming alloy $Zr_{60}Ni_{25}Al_{15}$ by quasielastic neutron scattering. In order to avoid reactions of the Zr-based melts with crucible materaials and in order to cover a large temperature range including the metastable regime of undercooled liquids at temperature below the melting temperature, the samples are containerlessly processed by application of the electromagnetic levitation technique.

2. Experimental

Samples of the compositions $Zr_{64}Ni_{36}$, $Zr_{50}Ni_{50}$, $Zr_{36}Ni_{64}$ and $Zr_{60}Ni_{25}Al_{15}$ with a mass of approximately 1.5 g, were prepared from the constituents under an Ar-atmosphere (purity 99.9999 %) by arc melting.

The liquids are containerlessly processed within a He atmosphere (purity 99.9999 %) by employing the electromagnetic levitation technique. A special electromagnetic levitator was used, that has been designed for performing neutron scattering studies on the short-range order of undercooled metallic melts [4] and that has been adapted to the demands of quasielastic neutron scattering experiments [5] at the time of flight spectrometer TOFTOF [6] of the research reactor FRM II in Garching, Germany. A wavelength of the incident neutrons of λ = 5.1 Å was used. The instrumental energy resolution amounts to $\delta E \approx$ 95 µeV full width at half maximum (FWHM). It has been verified that even for strongly incoherent scattering samples like those of pure Ni, the precise determination of diffusion coefficients is not hampered by influences of multiple scattering, despite the large sample diameter [5].

3. Results and Discussion

Quasielastic neutron scattering experiments were performed for liquid $Zr_{64}Ni_{36}$, $Zr_{50}Ni_{50}$, $Zr_{36}Ni_{64}$ and $Zr_{60}Ni_{25}Al_{15}$ at different temperatures ranging from temperatures above the liquidus temperature T_L down to temperatures in the metastable regime of an undercooled melt below T_L. As an example, Figure 1 shows the quasielastic range of the scattering law $S(Q,\omega)$ for a $Zr_{50}Ni_{50}$ melt at two different temperatures (T = 1350 K and T = 1655 K) at a wave vector of Q = 1.0 Å^{-1}. The quasielastic signal can be well described with a Lorentzian function convoluted with the instrumental energy resolution function measured at 290 K with a Vanadium standard (lines in Figure 1). The full width at half maximum, Γ, of the Lorentzian function decreases with decreasing temperature.

For small momentum transfer (below $Q \approx$ 1.2 Å^{-1}) the measured signal is dominated by the incoherent scattering of the Ni atoms (incoherent scattering cross sections: σ_{inc}(Ni) = 5.2 barn, σ_{inc}(Zr) = 0.02 barn, σ_{inc}(Al) =0.256 barn) and the mean Ni self-diffusivity is related with Γ by $D = \Gamma Q^{-2}/2\hbar$. This allows to determine the Ni self-diffusivities in the different alloy melts, which are compiled as a function of temperature in Table 1 and which are plotted in figure 2. Also shown in figure 2 are results from former measurements of the Ni self-diffusivity in melts of pure Ni [5] and of the mean Ni and Ti self-diffusivity in melts of glass forming Zr-Ti-Ni-Cu-Be [3] alloys. It is evident that the data points for Zr-Ti-Ni-Cu-Be are on the same $D(T)$ curve as those of $Zr_{64}Ni_{36}$, suggesting a similar Ni diffusion mechanism in these systems.
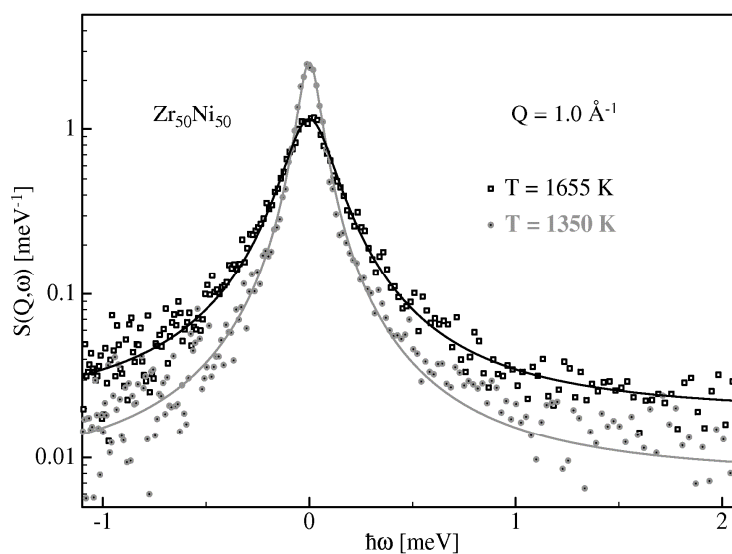
Figure 1. Scattering law for liquid $Zr_{50}Ni_{50}$ at Q = 1.0 Å^{-1} for two different temperatures (T = 1350 K and T = 1655 K).
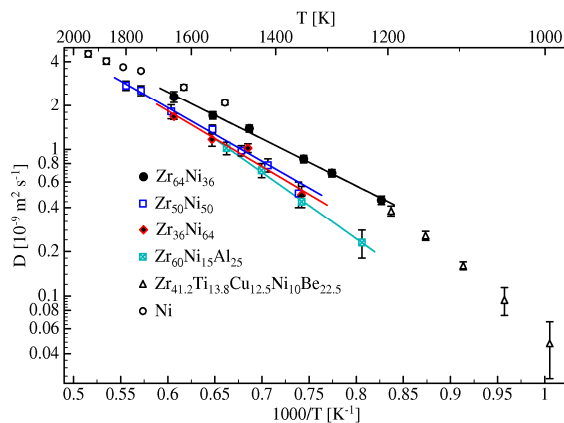
Figure 2. Temperature dependence of the Ni self-diffusivities in melts of Zr-Ni(-Al) and Ni [5] and of the mean Ni and Ti self-diffusivities in liquid Zr-Ti-Cu-Ni-Be [3].
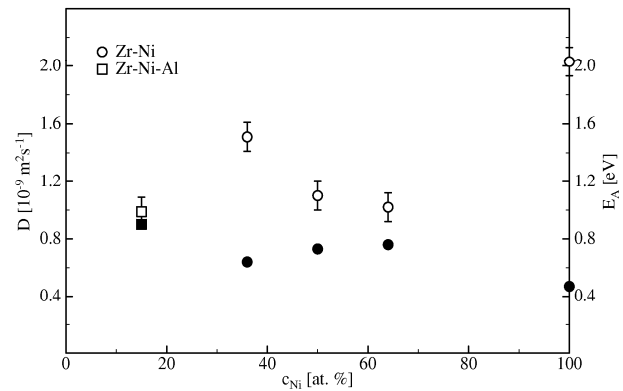
Figure 3. Dependence of the Ni self-diffusivities (open symbols) at constant temperature, T =1500 K, and of the activation energy, E_A, for Ni self-diffusion (full symbols) on the Ni-concentration for in liquid Zr-Ni (circles) and Zr-Ni-Al (squares).

Table 1. Ni self-diffusion coefficients, D, activation energies, E_A and prefactors, D_0, of different Zr-Ni(-Al) alloy melts measured by quasielastic neutron scattering.

Alloy	T [K]	D [10^{-9} m^2/s]	E_A [eV]	D_0 [10^{-7} m^2/s]
Zr$_{64}$Ni$_{36}$ (T_L = 1283 K)	1210 ± 5 1290 ± 5 1345 ± 5 1455 ± 5 1545 ± 5 1650 ± 5	0.44 ± 0.03 0.70 ± 0.04 0.90 ± 0.05 1.4 ± 0.1 1.7 ± 0.1 2.3 ± 0.2	0.64 ± 0.02	2.1 ± 0.3
Zr$_{50}$Ni$_{50}$ (T_L = 1533 K)	1355 ± 5 1415 ± 5 1475 ± 5 1545 ± 5 1655 ± 5 1750 ± 5 1800 ± 5	0.5 ± 0.1 0.78 ± 0.08 0.98 ± 0.08 1.4 ± 0.1 1.8 ± 0.2 2.5 ± 0.2 2.7 ± 0.2	0.73 ± 0.03	3.1 ± 0.6
Zr$_{36}$Ni$_{64}$ (T_L = 1343 K)	1350 ± 5 1460 ± 5 1545 ± 5 1650 ± 5	0.49 ± 0.07 1.0 ± 0.1 1.2 ± 0.1 1.7 ± 0.1	0.76 ± 0.11	3 ± 2
Zr$_{60}$Ni$_{15}$Al$_{25}$ (T_L = 1215 K)	1240 ± 5 1350 ± 5 1430 ± 5 1510 ± 5	0.23 ± 0.05 0.44 ± 0.04 0.72 ± 0.08 1.0 ± 0.1	0.90 ± 0.02	1.1 ± 0.2

For all Zr-Ni melts $D(T)$ shows an Arrhenius-type behavior, $D = D_0 \exp(-E_A/k_BT)$, in the investigated temperature regimes. The values of E_A and D_0 determined for the different alloy melts are

given in Table 1. These values are large as compared to activation energies for Ni self-diffusion observed in other melts. For instance, our former investigations on pure Ni gave E_A(Ni) = 0.47 eV [5]. For liquid $Al_{80}Ni_{20}$ a value of E_A(Al-Ni) = 0.36 eV is reported [7]. The determination of partial structure factors of molten $Zr_{64}Ni_{36}$ by elastic neutron scattering by isotopic substitution [8,9] indicates a short-range order different from the icosahedral short-range order observed for a large variety of metallic melts [10]. The short-range order in liquid $Zr_{64}Ni_{36}$ is characterized by a large local density of packing as indicated by high nearest neighbor coordination number of $Z \approx 13.9$. This may give rise to the large activation energy for atomic diffusion observed here for the Zr-Ni based melts.

Figure 3 shows the dependence of the Ni self-diffusivity in the Zr-Ni and Zr-Ni-Al alloys as a function of the Ni-concentration, c_{Ni}, at constant temperature, T = 1500 K, as calculated from the Arrhenius fits. Moreover the activation energies E_A are plotted as function of Ni-concentration. For $Zr_{50}Ni_{50}$, $Zr_{36}Ni_{64}$, and $Zr_{60}Ni_{15}Al_{25}$ D values of approx. $1 \cdot 10^{-9}$ m^2/s are determined, while for $Zr_{64}Ni_{36}$ and even more so for pure Ni [5] slightly higher values are obtained. The activation energies show the opposite dependence on c_{Ni}. Nevertheless, the composition dependence of the Ni self diffusivity in the investigated Zr-Ni(-Al) melts is small, especially when taking into consideration the strong compostion dependence of the melting temperatures. It is also noteworthy, that the addition of Al as a third alloy component has only a minor impact on the Ni selfdiffusivity.

4. Conclusions

We have investigated the Ni self-diffusivity in melts of different Zr-Ni(-Al) alloys by quasielastic neutron scattering. The temperature dependence of the Ni-self diffusivity is described by an Arrhenius law with activation energies for atomic diffusion that are high as compared to those determined in melts of pure Ni and $Al_{80}Ni_{20}$. This may be a result of a high local density of packing observed by elastic neutron scattaring investigations on $Zr_{64}Ni_{36}$ [8].

References

[1]   Inoue A and Takeuchi K 2004 *Mat. Sci Eng. A* **375-377** 16
[2]   Mavila Chathoth S, Meyer A, Koza M M and Juranyi F 2004 *Appl. Phys. Lett.* **85** 4881
[3]   Meyer A, Petry W, Koza M and Macht M-P 2003 *Appl. Phys. Lett.* **83** 3894
[4]   Holland-Moritz D, Schenk T, Convert P, Hansen T and Herlach D M 2005 *Meas. Sci. Techn.* **16** 372
[5]   Meyer A, Stüber S, Holland-Moritz D, Heinen O and Unruh T 2008 *Phys. Rev. B* **77** 092201
[6]   Unruh T, Neuhaus J and Petry W 2007 *Nuclear Instruments and Methods A* **580** 1414
[7]   Horbach J, Das S K, Griesche A, Macht M-P, Frohberg G and Meyer A 2007 *Phys. Rev. B* **75** 174304
[8]   Holland-Moritz D, Stüber S, Hartmann H, Unruh T, Hansen T and Meyer A, submitted for publication
[9]   Voigtmann T, Meyer A, Holland-Moritz D, Stüber S, Hansen T and Unruh T 2008 *Europhysics Letters* **82** 66001
[10]   Kelton K F, Greer A L, Herlach D M and Holland-Moritz D 2004 *MRS Bulletin* **12**, 940