

## Diffusion of Hydrogen in Amorphous Ni-Zr Alloys

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**Abstract.** Amorphous alloys Ni<sub>64</sub>Zr<sub>36</sub> and Ni<sub>36</sub>Zr<sub>64</sub> structure and hydrogen mobility are researched by the molecular dynamics method. The analysis of structure factors and partial distribution functions of atoms revealed hydrogen affects the short order parameters of the disordered systems. Diffusion coefficients of hydrogen are shown to depend on its concentration.

### Introduction

Amorphous alloys used as materials for producing and storage of high purity hydrogen are very prospective and have been widely researched by scientists. However, the published literature data on hydrogen diffusion in amorphous alloys are few and have considerable divergence probably due to neglecting of the hydrogen concentration affect on its mobility and short order structure of alloy.

The solubility of hydrogen in amorphous alloys is higher than in polycrystalline similar structure samples [1, 2]. The diffusion coefficient of hydrogen in amorphous materials depends on its concentration and usually deviates from the Arrhenius law [2].

Unlike a crystal alloy, where interstice volumes are presented discretely only by tetrahedron and octahedron cavities, the distribution of small and big interstice cavities in an amorphous alloy is close to a Gaussian function [3, 4]. Thus the distribution function form of hydrogen energies in the amorphous alloys cavities is close to the RDFA (Radial Distribution Function of Atoms) main peak form which is approximated also by a Gaussian function [5]. It had been shown [1,6], that the ability of amorphous alloys' of hydrogen absorption is determined by the number and size of cavities for hydrogen implantation, as well as by the contents of hydride forming elements (Ti, Zr, Hf, etc.). Besides the hydrogen diffusion coefficient considerably depends on its concentration in amorphous alloys.

### Molecular Dynamics Calculations

Molecular dynamics method (MD) for short order structure analysis and hydrogen transport in the amorphous Ni-Zr alloys is used in this work. The model system unlike [7, 8] contained 640 (360) particles of nickel, 360 (640) particles of zirconium and 1(2) particles of hydrogen in the cubic cell. The movement equations integrating were carried out by time steps of  $1.1 \cdot 10^{-15}$  s using the Verlet method [9]. Inter-particle potentials and numerical values of pair potentials factors have been taken from the [10, 11] publications.

Hydrogen diffusion coefficients in the amorphous Ni-Zr alloys were calculated in the 298-798K temperature interval by the mean square root displacement of particles  $\langle \Delta R^2(t) \rangle$  for a large number of steps.

Disorder systems short order is characterized by the radial distribution function of atoms  $g(r)$  (RDFA) which determines the location probability of any atom at a distance  $r$  from the chosen interference atom and described by the well-known formula:

$$g_{ij}(r) = (\Delta N)L^3/4\pi r^2 \Delta r N$$

where  $\Delta N$  — the number of particles in a spherical layer thickness  $\Delta r$  on a distance  $r$  from the chosen particle;  $L$  — the cube edge length of a in the basic cell and  $N$  — number of its particles.

## Results and Discussion

Computer modelling results of the Ni-Zr and Ni-Zr-H amorphous alloys structure and properties are shown in Figs. 1,2 and presented in the Table 1.

The structural factors of  $\text{Ni}_{64}\text{Zr}_{36}$  (alloy 1) and  $\text{Ni}_{36}\text{Zr}_{64}$  (alloy 2), with hydrogen and without are shown on Fig. 1. All curves have diffused interference maxima proper for an amorphous state. It verifies such a state as well when hydrogen absorption take place at low and high contents of hydride forming element and hydrogen in an alloy. Increasing the number of H — atoms in a MD-model for 1- alloy initially results in structural factor peaks displacement to the low dispersion vectors (S) and in main peak height (h) increasing. Then the displacement vice versa results in the high S- and low h-values. It testifies to the number of H-atoms affects to amorphous alloys structure. All peaks of a(s) became more relief, oscillations extend to higher scattering vectors. The authors [12,13] proved that icosahedrons type of atoms packing is dominating in amorphous metals structure where high polyhedron concentration with coordination number 12 take place. The main structural factor maximum height and form of the bifurcated second peak are determined by contacting polyhedrons number and their type of bond [14]. For alloy 2 which has a content close to  $\text{NiZr}_2$  (curve 1), the position of the two first maxima of a(s)-curve corresponds to the interference lines average position for crystal  $\text{NiZr}_2$  compound. The amorphous alloy short order therefore can be described with the help of a coordinating icosahedron cluster, which is the basic structural unit of  $\text{NiZr}_2$  crystal. Hydrogen in such a structure can be located in numerous tetra-cavities, formed by Ni and Zr atoms [15]. Hydrogen atom incorporation in the MD-model (curve 2) results due to penetration of hydrogen into numerous cavities of the amorphous structure. Hydrogen atoms probably form with Zr some kind of quasi crystal  $\text{ZrH}_2$  lattice [6]. This supposition reveals in a better resolution of short and long diffraction maxima (3,6 curves) for alloys with high contents of Zr and H atoms.

Partial  $g_{ij}(r)$  radial distribution functions of model systems and short order parameters are presented in Fig. 2 and in the table. For all low and zero hydrogen alloys, the shortest interatomic distance of Ni-Ni pair remains constant (0.240nm), decreasing up to 0.230nm when H increases up to two atoms. Interatomic distances of N-Zr and Zr-Zr pairs considerably decrease with growth of Zr and H concentration. We note that  $r_{\text{Ni-Ni}}$  and  $r_{\text{Zr-Zr}}$  are close to Ni and Zr atoms diameters (0.244 nm and 0.324 nm) correspondently, and the distance between Ni-Zr atoms is somewhat less than the sum of the Ni and Zr atoms radii, that is confirmed by diffraction experiment results [16]. This fact confirms bond formation between these elements due to hybridization of vacant 3d – electron band of Ni and 4d-band of Zr [17].

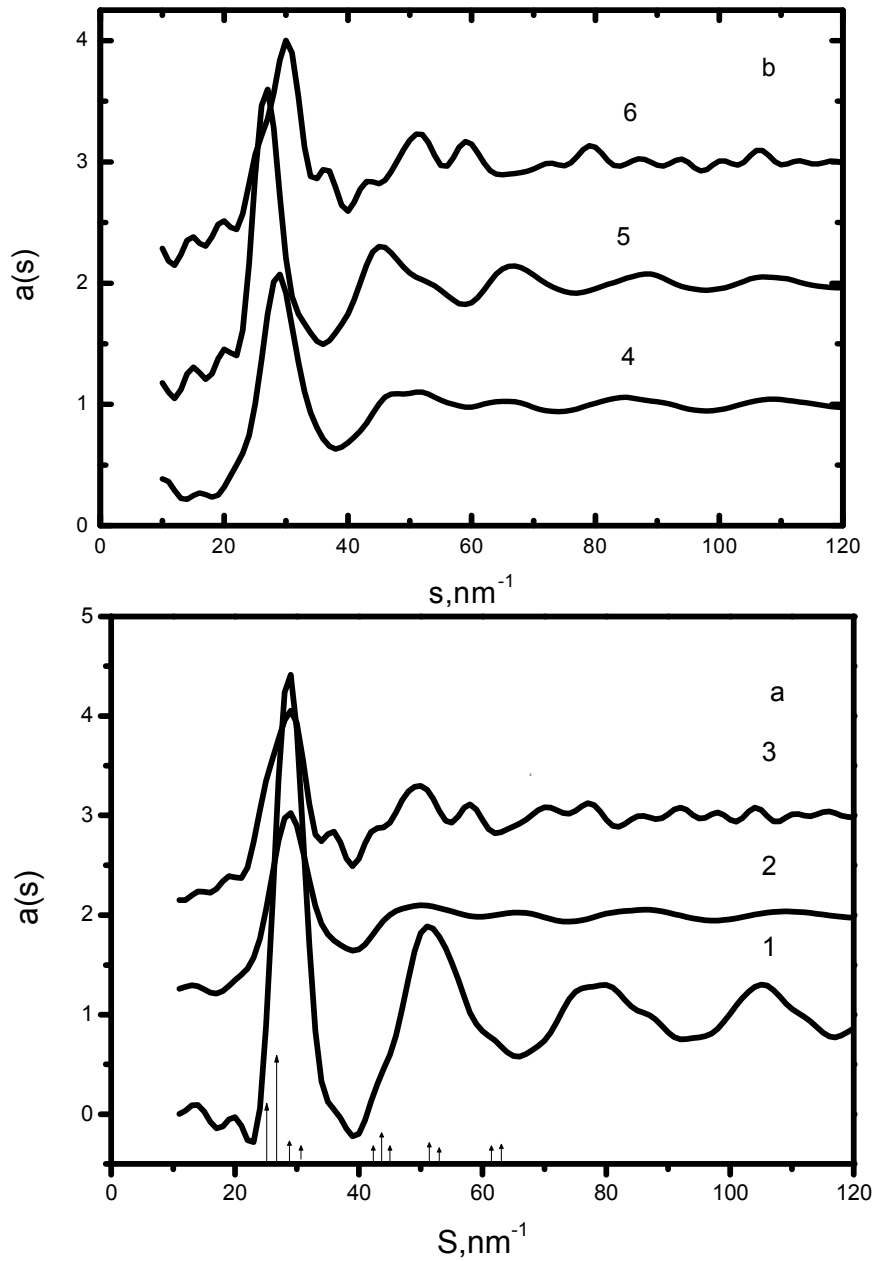


Figure 1. Amorphous alloys structure factors with hydrogen and without:  
 a)  $\text{Ni}_{36}\text{Zr}_{64}$ (1),  $\text{Ni}_{36}\text{Zr}_{64}+1\text{H}$ (2),  $\text{Ni}_{36}\text{Zr}_{64}+2\text{H}$ (3);  
 b)  $\text{Ni}_{64}\text{Zr}_{36}$ (4),  $\text{Ni}_{64}\text{Zr}_{36}+1\text{H}$ (5),  $\text{Ni}_{64}\text{Zr}_{36}+2\text{H}$ (6)  
 (arrows indicate the interference lines of  $\text{NiZr}_2$  crystal)

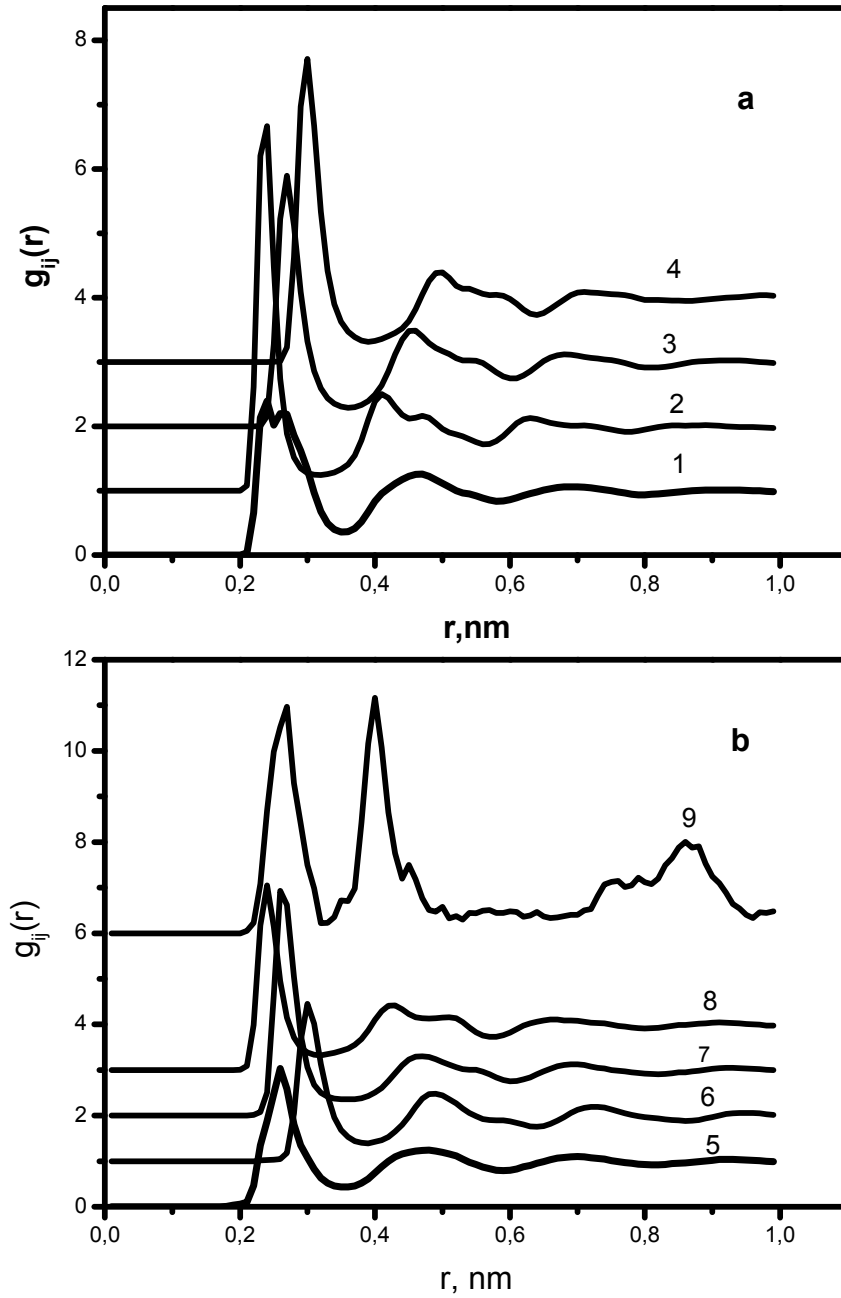


Figure 2. Radial distribution functions  $g_{ij}(r)$  of  $\text{Ni}_{64}\text{Zr}_{36}$  alloy:  
1, (a) - no hydrogen; 5, (b) - one hydrogen atom.  
Partial  $g_{ij}(r)$ : 2,8 - Ni-Ni; 3,7 - Ni-Zr; 4,6 - Zr-Zr; 9 - H-H

Table 1. Short range order parameters of amorphous alloy in Ni-Zr and Ni-Zr-H systems

System	Partial RDFA			$D_H$ at 298K
	Ni-Ni	Ni-Zr	Zr-Zr	
	r, [nm]	r, [nm]	r, [nm]	[ $\text{cm}^2\text{s}^{-1}$ ]
$\text{Ni}_{64}\text{Zr}_{36}$	0.238	0.270	0.301	
$\text{Ni}_{36}\text{Zr}_{64}$	0.240	0.261	0.290	
$\text{Ni}_{64}\text{Zr}_{36} < 1\text{H}_2 >$	0.240	0.266	0.310	$1.2 \cdot 10^{-5}$
$\text{Ni}_{64}\text{Zr}_{36} < 2\text{H}_2 >$	0.240	0.26	0.29	$1.7 \cdot 10^{-4}$
$\text{Ni}_{36}\text{Zr}_{64} < 1\text{H}_2 >$	0.241	0.265	0.297	$8.9 \cdot 10^{-5}$
$\text{Ni}_{36}\text{Zr}_{64} < 2\text{H}_2 >$	0.230	0.250	0.280	$2.1 \cdot 10^{-4}$

Calculated diffusion coefficients of hydrogen for amorphous Ni-Zr-H alloys are presented in the Table. The value of  $D_H$  varies from  $2 \cdot 10^{-4}$  up to  $1.2 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ , in the same limits, as diffusion coefficients of H atoms in an icosahedron TiNiZr alloy [18]. As it follows from the Table,  $D_H$  grows with increase of hydride forming element Zr concentration and H atoms in the MD-model. The activation energy of hydrogen diffusion for amorphous  $\text{Ni}_{64}\text{Zr}_{36}$  alloy was estimated in the 298-768K temperature interval. A value of  $E=0.1\text{eV}$  was obtained. This result on H atoms diffusion may be explained by various energy position [1,19] in the disordered materials. Deep potential wells acts like traps (octa-cavities) and are occupied by hydrogen initially. Then hydrogen occupies interstices with high energy values (tetra-cavities) and an abrupt increase of  $D_H$  is observed.

### Summary

Amorphous alloys  $\text{Ni}_{64}\text{Zr}_{36}$  and  $\text{Ni}_{36}\text{Zr}_{64}$  structure and hydrogen mobility are researched by MD method. The analysis of structure factors and partial distribution functions of atoms revealed hydrogen affects the short range ordered parameters of the disordered systems Diffusion coefficients of hydrogen depend on its concentration.

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