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Editor's Choice

# Atomic self-diffusion in TiNi

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ABSTRACT

The projector augmented wave method was applied to investigate the energetics of point defect formation at finite temperatures and the Ni-vacancy jumps in the intermetallic *B*2-TiNi alloy. It was shown that the effective formation energy of the Ni-vacancy (1.14 eV) is significantly lower than that of Ti-vacancy (1.74 eV); however, the antistructural atoms are dominant defects irrespective of alloy composition. The obtained results reveal that the migration barrier of the Ni-vacancy to the nearest-neighbor site is less (0.19 eV) than that for the Ni-vacancy jump to the next-nearest-neighbor site (1.64 eV). The Ni-vacancy implements two sequential nearest-neighbor jumps with short-lived intermediate configuration and some of such jumps initiate six-jump cycles of the Ni-vacancy along [0 0 1] and [1 1 0] directions with [0 0 1] bent mechanism as preferential one. In the latter case the calculated migration barrier of 0.82 eV is found to be in good agreement with experiment. The energy barrier for four-jump cycle flat mechanism is calculated by 0.27 eV higher. It is shown that the Ni-vacancy diffusion in *B*2-TiNi is strongly dominated by both six-jump cycle [0 0 1] bent and flat mechanisms at low temperatures but the contribution of the next-nearest-neighbor jumps become important with temperature increase.

## 1. Introduction

It is known that Ti-Ni shape memory alloys (SMAs) are attractive for theoretical study because of their potentials in technological applications [1]. They exhibit unique mechanical properties as shape memory effect (SME) and super-elasticity and therefore can be used as electrical switches, electronic connectors, fine medical wires, dental and bond implants, and various SME based fixation devices. Many processes in the engineering alloys such as phase transition, dislocation climbing, etc. and their mechanical properties are related to the atomic diffusion [2,3]. The knowledge of the diffusivity and its anisotropy is very important for understanding the deformation process in alloys, diffusion-barrier properties, etc. Information about migration barriers and diffusion mechanisms is needed to get much better insight on the oxidation and hydrogenation of materials. Besides, the interrelation of point defect structures and atomic mobility with alloy functional properties is important for numerous practical applications. In this connection the impurity diffusion and self-diffusion in materials remains in a focus of both experimental and theoretical studies – see [2–13] and references therein. However, these phenomena are far from complete understanding even in binary alloys with the *B*2-phase [3,5–10].

In spite of diffusion of light interstitial elements, substitutional impurities, self-diffusion of alloy components being under long intense study by experimental methods, some obtained results remain contradictory. Experimentally the diffusion coefficient ($D$) can be measured by different methods such as radiotracer method, Auger electron spectroscopy, etc. [14–16]. The activation energy ($Q$) of the diffusion is determined by using the Arrhenius equation [2,4]. However, the experimental values of both diffusion coefficients and activation energies vary greatly due to the presence of impurities in the samples (it is difficult to prepare experimentally the crystal with high purity), availability of tracer elements, surface oxidation or other factors. Density functional theory (DFT) combined with the transition state theory (TST) represent a reliable methodology to understand the impurity diffusion and self-diffusion mechanisms in different systems [4,11–13]. The advantage of such calculations is possibility to screen the influence of the lattice imperfection using an ideal pure system.

The experimental determination of the temperature diffusion coefficients and the activation energies for atomic diffusion in Ti-Ni alloys were performed in several studies [14–20]. In particular, in [14] their determination was based on interdiffusion measurements in multiphase diffusion couples of different compositions. In [15–18] solid-state reactions in thin Ti–Ni films, multilayers

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and in mechanically alloyed powders were investigated. In general, the results of these investigations were found in good agreement with each other. The activation energy of 142 ± 6 kJ mol$^{-1}$ (1.47 ± 0.06 eV) was obtained for crystalline Ti-Ni alloys in [14]. Besides, a pre-exponential factor $D_0$ had the order of magnitude of $10^{-7}$ m$^2$ s$^{-1}$ [14]. Slightly lower value of the activation energy (115–135 kJ mol$^{-1}$) was obtained in [15–18] when the diffusion partly or fully took place in the amorphous phase. It should be noted that much lower activation energy of 84 ± 25 kJ mol$^{-1}$ was obtained in [17] for the grain-boundary diffusion of Ni in Ti. On the other hand, the activation energy of the diffusion in *B*2-TiCo alloy [21] was substantially higher (265 ± 11 kJ mol$^{-1}$) than that measured in TiNi [14–18]. This difference was interpreted by the effect of phase and/or grain boundaries that could result in too lower activation energy in TiNi. Thus, from mentioned above papers it was established: (i) the diffusion coefficient in Ti–Ni alloys is determined by Ni diffusion because Ti atoms diffuse to one-two order slower than Ni atoms, (ii) the activation energy for self-diffusion in Ti-Ni is very small compared to other intermetallic *B*2-alloys.

Furthermore, in [19] the self-diffusion of $^{63}$Ni in Ni–50.07 at.% Ti alloys was measured between 783 and 1288 K using a radiotracer technique that is the most precise way to determine the diffusion coefficient. The activation energy of 155 ± 6 kJ mol$^{-1}$ (1.61 ± 0.06 eV) was obtained that is a little bit higher than the values measured in earlier papers [14–18]. The Arrhenius function in this system did not show any pronounced bending, and hence no diffusion anomalies could be identified. However, the "anomalous" diffusion takes place in pure β-Zr and β-Ti, presumably related to phonon softening [2]. A similar anomaly was observed in Ti–Ni alloys also [22]. In addition, from the pressure dependence of Ni diffusion in the same samples as in [19] it was demonstrated that the activation volume is zero within the experimental errors ($V_D = (0.01 \pm 0.13)\ V_0$) [20]. The following explanations of this fact was suggested: the low activation energy and the zero activation volume mean that the Ni-vacancy concentration is not pressure dependent, and the effective formation energy of vacancy ($E_v$) is small. The authors of [23,24] concluded from positron annihilation experiments that, in the process of the melt spinning, most of monovacancies are frozen in. On the other hand, Ni is a fast diffuser in β-Ti. The activation energy is 124 kJ mol$^{-1}$ [25]. Since Ni in *B*2-TiNi has only Ti nearest neighbors, it seems plausible that an interstitial-like mechanism of diffusion is valid for this alloy also. However, some authors think that it is impossible [19,26].

It is believed that the diffusion mechanism in *B*2-ordered alloys should be different from that in pure BCC metals because nearest-neighbor (NN) jumps of atoms can destroy long-range order in the arrangement of atoms. Different diffusion mechanisms such as atom jump to the next-nearest-neighbor (NNN) sites, four-jump cycles (4JC), six-jump cycles (6JC), antistructural bridge (ASB) and triple defect (TD) mechanisms were proposed in last decades for *B*2-alloys [6,8–10,27]; however, common trends were not established. It is necessary to point out that the atomic mechanisms of diffusion were intensively investigated by theoretical methods in *B*2-NiAl. In particular, Mishin et al. [6] indicate that ASB mechanism has the lowest activation volume and migration barrier ($E_m$) although it requires some degree of antisite disorder in the alloy. At the same time the activation energy related to the ASB mechanism in stoichiometric NiAl alloy differs only by 0.1 eV from that for NNN mechanism. Further, it was confirmed [8] by the first-principles calculations that NNN jump of a Ni vacancy has a lower energy barrier compared to 6JC mechanism but ASB one was not recalculated there. In general, authors of [8] conclude that the NNN mechanism for the Ni vacancy jump can operate in competition along with other mechanisms in *B*2-NiAl. The triple-defect mechanism was suggested in [9] based on the agreement between the experimental data and the atomistic calculations. The activation energy $Q$ = 3.18 eV calculated for this mechanism using empirical EAM potentials agrees well with value of 3.0 ± 0.07 eV obtained from radiotracer experiments in the same work. Chen et al. Ref. [10] considered five diffusion mechanisms including NNN jump, 6JC [1 1 0], 6JC [1 0 0] flat, 6JC [1 0 0] bent and triple-defect diffusion using molecular dynamic simulation with modified analytic embedded-atom method. The smallest activation energy of 2.769 eV was calculated for TD mechanism also. It is interesting that in [10] the energy profiles for all 6JC mechanisms have six peaks structure whereas three and four peak curves were obtained in [8]. The atomic configuration after the Ni-vacancy jump to NN site is stable but it was found unstable in [8]. Furthermore, the Ni-vacancy formation energy (1.169 eV) is quite higher compared to the value of 0.68 eV calculated in [6]. It is seen that the information about Ni-vacancy diffusion mechanisms even for the most studied NiAl alloy remains contradictory. The studies of self-diffusion in case of other *B*2-alloys are insufficient.

Several words should be said about measurements of vacancy formation and activation energies in *B*2-TiNi. Two values of vacancy formation energy $E_{v1}$ = 0.78 ± 0.02 eV and $E_{v2}$ = 0.97 ± 0.05 eV were evaluated from the positron annihilation spectroscopy (PAS) [28]. The investigations were conducted in the temperature interval of 480–900 K. Based on calculated interatomic force constants in [29], authors of [28] supposed that the first of the above energy values is related to the formation energy of vacancy on the Ni-sublattice, and the second one – on the Ti-sublattice. Almost the same value as $E_{v1}$, $E_v$ = 0.77 ± 0.08 eV, was measured recently in [30] using positron Doppler broadening method; however, the defect type (Ni or Ti vacancies) was not identified. It is necessary to point out that the positron lifetime spectra measured in [31] did not reveal the positron trapping by structural defects in TiNi at temperatures lower than 500 K. A larger value of $E_v$ (1.48 eV) for Ni-vacancy than the presumed above cited experimental one, resulted from calculation by molecular dynamic method in [32]. The calculations by the plane wave pseudopotential method within the density functional theory [33] reveal a lower value of Ni-vacancy formation energy (1.09 eV) for high-temperature *B*2-TiNi phase. The calculated vacancy formation energy on the Ti-sublattice (1.74 eV [33]) is quite higher than the experimental value of 0.97 eV [28]. At the same time the difference between vacancy formation energies on one and the other sublattices is 0.65 eV [33], in agreement with ~0.67 eV calculated in [32].

The activation energy for Ni-vacancy migration was also obtained by PAS method based on measurement of annealing vacancies induced by electron irradiation [28]. It was shown that the migration barrier is as small as 0.7 ± 0.1 eV in *B*2-TiNi. The larger value of 0.87 eV was determined in [34] based on resistivity of quenched alloy samples $Ti_{49.4}Ni_{50.6}$. To the best of our knowledge, there is only one theoretical estimation of $E_m$ (1.272 eV) in *B*2-TiNi for 6JC mechanism [32]. This calculation was performed for fixed cubic volume containing 1024 atoms. According to Ref. [32], the interstitial mechanism for Ni diffusion in TiNi needs a relatively high energy because it involves a Ni–Ni dumbbell, oriented in the ⟨1 1 1⟩ direction, centered on a Ti site and having one or two adjacent antisite Ti atoms on the Ni-sublattice.

Thus, the self-diffusion mechanisms in TiNi are barely studied from a theoretical point of view. In view of a controversy between experimental and previous theoretical results, more pointed theoretical investigations of migration barriers and point defect energies are necessary to get better insight on the Ni-vacancy diffusion mechanism in *B*2-TiNi alloy, and are provided by the present study.