Atomistic Simulation of Structural Evolution at Long Time Scales: Diffusion of Aluminum in Nickel at a Low Concentration Limit

Yuranan Hanlumyuang[*1, 2]

[1] Department of Materials Engineering, Faculty of Engineering, Kasetsart University,
Bangkok, 10900, Thailand

[2] Materials Innovation Center, Faculty of Engineering, Kasetsart University, Bangkok,10900, Thailand

*Email: yuranan.h@ku.th

Abstract

The diffusivity of aluminum in a Ni-Al system at a low concentration limit was studied using the compounded computational methods of (1) the Autonomous Basin Climbing method, (2) the nudged elastic band method, and (3) the on-the-fly Kinetic Monte Carlo method. The probable diffusion pathways were determined using the Autonomous Basin Climbing method, while the corresponding activation barriers were obtained from the nudged elastic band method. The on-the-fly Kinetic Monte Carlo method was then utilized to account for all hopping events and calculate associated escaped time. The tracer diffusion coefficient was calculated from tracking atomic species locations while accumulating associated escaped time intervals. The diffusion prefactor and effective activation energy of aluminum diffusion in a nickel matrix were determined from curve fitting to an Arrhenius equation. Our numerical results are in same order of magnitudes with a set of available published data, indicating the predictability of the compounded computational methods and transferability to other kinetics problems.

Keywords : Atomistic simulation, Long time scales evolution, Solid-state diffusion.

Introduction

Ni-based superalloys are important materials in materials science community in the past half-century. The materials have become ubiquitous in power plant applications because of their ability to withstand mechanical degradation and chemical resistance at high temperature. Various microstructural kinetics of Ni-based superalloys are underlying causes to mechanical and chemical properties of Ni-based superalloys [1-2]. For example, the superior creep resistance properties of the Ni-based superalloys arise from what is as the (γ /γ') microstructure that consists of the face-centered cubic solid solution matrix phase γ and embedded ordered precipitate phase γ' [2]. Dislocations in these materials have to rely on climbing over hard precipitates in order to response to an external stress. The presence of solute in the matrix phase then plays a crucial role in

assisting vacancy diffusion that in turn aids dislocation climbing [3]. The high chemical resistance assuring the longevity of the materials during service operation is due to the existence of a thin alumina layer at the surface of the superalloys. This chemical protection imparted by the oxide layer is a result of slow diffusion in the lattice of the alumina [4]. The formation of the oxide layer is determined largely by the diffusion of aluminum in the γ phase. The aluminum oxide layers nearing crack tips also influence embrittlement of the superalloys [5]. Growth of the internal oxide at these interfaces is the case of limited tensile leading to brittle failures. From the aforementioned mechanisms, solid-state diffusion, is a common factor in microstructural kinetics leading to both rich and poor properties of the superalloys. Fundamental understanding of solid-state diffusion mechanism in Ni-based superalloys is then

key imperative to ensure endurance and safe usages the superalloys.

In order to understand solid-state diffusion mechanism of materials, molecular dynamics (MD) has been considered a common computational tool for simulating dynamics of atomic systems. Despite successes in simulating dynamical evolution of atomic systems with traditional MD, simulating long-time dynamical behaviors in materials like fatigues and creeps with traditional MD is still limited by its small timesteps, far from realistic timescale. The MD methods are then inefficient for studying dynamics that span over hours or years. However, it is known that the potential energy surface (PES) of a certain material system reveals useful information about structural evolutions and rates of reactions. In this paper, we propose an alternative and compounded computational routine designed to circumvent the time-scale issue, and apply them to calculate diffusivity of aluminum in a nickel matrix that represents a low-concentrated Ni-Al alloy. Our compounded routines consist a set of methods, namely (1) the autonomous basin climbing (ABC) method, (2) nudged elastic bands (NEB) method, and (3) on-the-fly Kinetic Monte Carlo (OKMC) method. The ABC method offers a solution to a basin trap problem common in MD simulations. The potential surface of a material system is key to any physical kinetic behavior. It provides all the possible stable states and activation barriers of transition among states. In order to determine accurate activation barriers and minimum energy paths, the NEB method is utilized. The NEB method uses a number of connected atomic configuration replica as an elastic band, which in a relaxed configuration resembles a minimum energy pathway [6]. Lastly, the OKMC framework allows for laboratory time scale calculations. From known initial and final states obtained from the NEB method, a hopping event will be chosen from all possible reaction pathways with appropriate probabilities. The correlation between the

probabilities of a success solid-state reaction to time intervals is a direct result of the KMC workflow [7].

The compounded ABC, NEB, and OKMC simulation workflows are applicable to study various kinetics phenomenon such as creep, fatigue of material, and growth in materials, among others [8-10]. The present paper is aimed at applying the methods to study solid-state diffusion of aluminum in the matrix of nickel where the concentration of aluminum is low. Particularly, the quantity termed the tracer diffusion coefficient is investigated. The purpose of the paper is two-fold. The first one is to provide insights into numerical values of the tracer diffusion coefficient data in the Ni-based superalloys. The tracer diffusion coefficients are fundamental to the interdiffusion and self-diffusion coefficients in NiAl, hence relating to other aforementioned kinetic mechanisms [11]. The second purpose of the work is to build a solid foundation to a novel computational framework in order to expand our study into more complex kinetic mechanisms, such as diffusion assisted crack growths, creeps in nanocrystal, and void nucleation, among others.

In the following sections, brief outlines of the ABC, NEB, and OKMC will be discussed. More comprehensive discussions of each methods can be found in [6-7, 12]. In the later section, the applications of the compounded methods to the solid-state diffusion problem in a Ni-based superalloy are then presented. Numerical results of the compounded computational methods will be shown to overcome limitations of traditional MD methods and achieve a realistic timescale within reasonable computational time intervals. Comparisons of the tracer diffusion coefficient among our values, another simulated results [4], and published experimental values [13-15] will be discussed.

THEORY AND RELATED WORK

The ABC method that we use here was first introduced by Kushima *et al.* for computing the

viscosity of supercooled liquids [12] and later implemented by adding the extension of the algorithm by Fan *et al.* to improve the number of transition pathways. Fan explored the method and used it to investigate anisotropic diffusion of point defects in hcp Zr [9]. It has been shown that the time evolution and atomic configuration of the reaction can be predicted quite accurately using the method. After using the ABC method for finding neighboring states, the NEB method can be used to determine an activation energy among the states. The activation energies are essential information for calculating rates of transition among available states. Figure 1 illustrates the ABC method using a schematic one-dimensional PES. The following algorithm is the basis of ABC method for finding neighboring states of an atomic evolution:

1) Select initial local minima at r_{min}.

2) Activate a penalty function $\psi_1(r) = W \exp[-(r - r_{min})^2/2\sigma^2]$, hence total system energy is $\Phi_p^1 = \Phi + \psi_1$. W and σ are constants which determine the strength and spatial extent of the activation respectively.

3) Relax the overall excited system the overall exited system to minimize Φ_p^1 in order to obtain a new atomic configuration.

4) Repeat 2) and 3) with $\Phi_p^2 = \Phi_p^1 + \psi_2$, $\Phi_p^3 = \Phi_p^2 + \psi_3$, until local minima is identified and sufficient amounts of minima have been sampled.
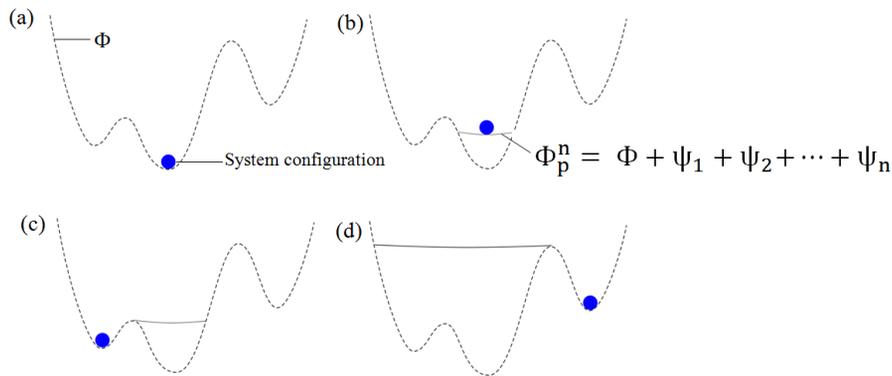

Figure 1. An illustration explains the ABC method. (a) An initial system configuration is selected. (b) A series of penalty function is applied until the system is relaxed to the new local minima in (c) and (d). This image was written after Kushima *et al.* work [12].

The NEB method is one of the most popular methods capable of determining minimum energy paths between two stable atomic configurations. The method provides reaction pathways and reaction coordinates of a solid-state reaction such as chemical reaction and atomic diffusion, among others. The NEB method uses a set of intermediate atomic configurations distributed along a reaction path. These configurations are called *images* that are used to build the reaction path connecting the optimized initial and final atomic configurations. The images are interconnected with fictitious elastic springs to assure that all the intermediate atomic configurations of the path are continuous. The force acting on image *i* is

$$\vec{F}_i = \vec{F}_i^{Spring}\big|_\parallel + \vec{F}_i^{True}\big|_\perp, \tag{1}$$

Where, $\vec{F}_i^{True}\big|_\perp$ is the PES gradient perpendicular to the tangent $\hat{T}_i$

$$\vec{F}_i^{True}\big|_\perp = \nabla V(\vec{R}_i) - \nabla V(\vec{R}_i) \cdot \hat{T}_i, \tag{2}$$

and $\vec{F}_i^{Spring}\big|_\parallel$ is the spring force parallel to the tangent $\hat{T}_i$ to an image

$$\vec{F}_i^{Spring}\big|_\parallel = k\left[(\vec{R}_{i+1} - \vec{R}_i) - (\vec{R}_i - \vec{R}_{i-1})\right] \cdot \hat{T}_i \hat{T}_i, \tag{3}$$

The tangent $\hat{T}_i$ is given by

$$\hat{T}_i = \frac{\vec{R}_{i+1} - \vec{R}_{i-1}}{|\vec{R}_{i+1} - \vec{R}_{i-1}|}, \tag{4}$$

where $\vec{R}_i$ represent the image i. Each intermediate atomic configuration is fully relaxed until the norm of the force orthogonal to the path less than the force cut-off, then the NEB process stops. The last set of image is considered a resemblance of the minimum energy reaction path. Approximately, the image with highest energy image is considered to be the transition state configuration. The ABC method and the NEB method can list all possible neighboring states and determine their activation energy among the states. The information about neighboring states and activation energies can be used as inputs to the Kinetic Monte Carlo (KMC) method.

The KMC method is widely employed for simulating time evolution of many process such as atomistic diffusion [4], creep in a nanocrystal [10], void nucleation [16]. Typically the method is applied when the transition rates among states are known. The method uses neighboring states from ABC method and corresponding transition rates from NEB method. The KMC algorithm applied in this work is called the rejection-free method which can be summarized as follows:

1) Set the initial evolution time, t=0;

2) Choose an initial state k.

3) List of all N_k possible transition rates r_{ki} in the system from state k into a generic state i.

4) Calculate cumulative function $R_{ki} = \sum_{j=1}^{i} r_{kj}$ for $i = 1, \dots, N_k$, The total rate is $Q_k = R_{k,N_k}$

5) Get a random number $u_1 \in (0, 1]$.

6) Find the event to carry out i by finding the i that satisfies following condition

$$R_{k,i-1} < u_1 Q_k \le R_{k,i}. \tag{5}$$

7) After the update to the new state and given that $u_2 \in (0, 1]$, the time evolution in latest step Δt is written as

$$\Delta t = -\ln(u_2) / Q_k. \tag{6}$$

After repeating step 3) – 7) for several iterations, a simple summation over time intervals yields the solid-state reaction time. The KMC method uses transition rates of all neighboring states as inputs. Here, the KMC calculation has been designed based on On-the-fly scheme which keeps any neighbor information of each KMC step independent of the other steps. Thus, oure so-called OKMC is memoryless. We applied all the above computational schemes in this work, and provide more details regarding parametric set-ups in the next section.

COMPUTATIONAL DETAILS AND PROCEDURE

Our cubic simulation cell is made from $2 \times 2 \times 2$ FCC supercell using lattice parameter a = 3.524 Å. The lattice parameter relaxation has been performed prior to diffusion calculations. The periodic boundary conditions are applied to all directions. The Embedded Atom Method (EAM) potential of Ni-Al system from Pun and Mishin [17] has been used alongside with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) packages [18] for all total energy calculations.

We employ the ABC method to sampling a possible diffusion process. A series of activation and relaxation steps occurs until the system climbing out of a local minimum into other neighboring states. The

activation penalty parameters, the strength (W) and the spatial extent (σ) of the activation, used in the activation procedure are 2.17 and 0.64 respectively. All transitions obtained from ABC method are determined their energy barriers (E_a) by the NEB method. In the relaxation step, the force on an image in an NEB calculation is less than 0.1eV/ Å. The transition rate, k of the reaction is given by

$$k = k_0 \exp[-E_a/k_B T], \qquad (7)$$

where k_0 is assumed to be 10^{13}s^{-1}, k_B is Boltzmann constant and T is the temperature. Then all the rates from every neighbor state can be used as inputs to an OKMC simulation for simulating the structure and time evolution.

The tracer diffusion coefficient of solute Al in Ni host, D_{Al} can be obtained from OKMC simulation by tracking displacement of an Al atom at every OKMC step. The tracer diffusion can be extracted from the OKMC simulation using following expression [19-20].

The tracer diffusion coefficient of solute Al in Ni host, D_{Al} can be obtained from OKMC simulation by tracking displacement of an Al atom at every OKMC step. The tracer diffusion can be extracted from the OKMC simulation using following expression [19-20]

$$D^* = \lim_{t \to \infty} \frac{1}{6t} \langle \sum_{t=0}^{\infty} [\vec{r}(t+\Delta t) - \vec{r}(t)]^2 \rangle, \qquad (8)$$

where t is simulation time and $\vec{r}(t+\Delta t) - \vec{r}(t)$ is the change in position at the OKMC step.

Our vacancy concentration in term of atomic fraction is 3.13×10^{-2}. This concentration level is much higher than the real vacancy concentration that often appears to be in rang of 10^{-6} to 10^{-2} at the temperature range from 900 K to 1700 K. The tracer diffusion coefficient can be scaled to make it comparable with actual experiment data by using the following expression [20].

$$D = \frac{C_{\text{Vac,real}}}{C_{\text{Vac}}^*} D^*, \qquad (9)$$

where C_{Vac}^* is a vacancy concentration of the simulation box which equal to 0.03125 fractional unit and $C_{\text{Vac,real}}$ is a real vacancy concentration from the expression $C_{\text{real,vacancy}} = exp(\Delta G_{\text{real,vacancy}} / k_B T)$ [21]. The term $\Delta G_{\text{real,vacancy}}$ is the Gibbs free

energy of vacancy formation, k_B is the Boltzmann constant and T is temperature. The Gibbs free energy of vacancy formation is obtained from the expression $\Delta G_{\text{real,vacancy}} = H_0 - A(T/T_m)^2$ where for nickel H_0 and A is 1.04 and 0.45 respectively [21][22]. The real concentration appears to be 3.77×10^{-6}, $7.14 \times 10^{-5}, 6.13 \times 10^{-4}$, 3.27×10^{-3}, and 1.29×10^{-2} at the temperatures 900K, 1100K, 1300K, 1500K and 1700K respectively.

Test simulation runs are performed on the desktop workstation, specification detail: CPUs: Intel® Core™ i7-6700 3.40GHz × 4 cores, 32 GB of Memory (RAM), 1024 GB local disk space. The operating system is Ubuntu 14.04 LTS 64-bit. Simulation runs at larger amount of time steps are performed at the supercomputer hosted by National e-Science Infrastructure Consortium, Thailand.

Results and discussion

An initial investigation on neighboring states has been examined. The simulation cell for this investigation contains 32 FCC Ni atoms. A vacant site is made by removing a Ni atom from the bulk in order to promote atomic mobility. The neighboring states founded in the ABC method were a state that a vacancy simply exchanges its position to the nearest neighbor atoms. This mechanism agrees with the previous report from Balluffi *at al.* [11]. The neighboring states are illustrated in Figure 2. The vacancy site in an initial state (shown in Figure 2(a)) moves to right-front, bottom-front and top-front directions resulting in neighboring states shown in (b), (c) and (d) respectively.

The NEB method was used to determine the transition state configuration and the activation barrier from an initial state such as shown in Figure 2 (a), to an adjacent state shown in Figure 2 (b). The resultant activation energy of this hopping process is illustrated in Figure 3. Here, the highest energy configuration from the last set of connected configuration (or *image*) is considered to be a transition state, while its energy

approximately represents the activation energy of the process. As shown in the figures, the activation energy of this process is about 1.65 eV. The transition structure of a general hopping process appears to be the state that the hopping atom is approximately in the middle position along the hopping path.
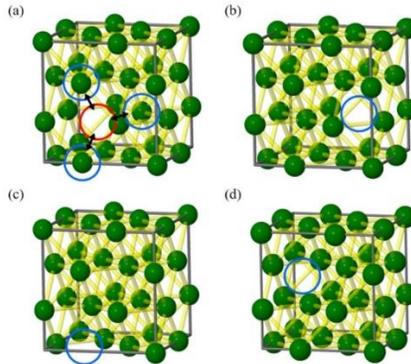

Figure 2. The vacancy site in an initial state (a) and the observed neighboring states (b), (c) and (d) investigated by the ABC method.
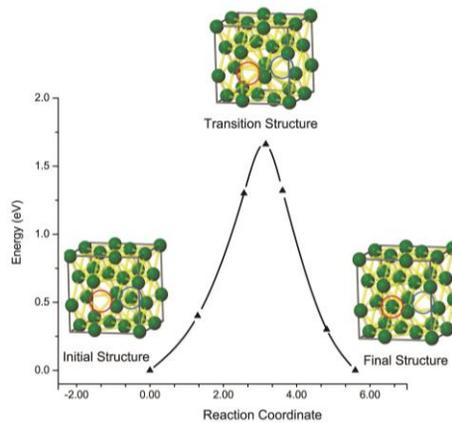

Figure 3. The typical reaction progress of a hopping process from current state and its neighbor state.

It is well known that adding an alloying element, such as aluminum, to a Ni matrix affects the diffusion due to the difference in local atomic environment surrounding the hopping atom. A variance in local atomic environment includes distinct positions between a diffusion-assisted vacancy and a hoping Al solute atom. In calculation of the tracer diffusion of a solute Al in a Ni matrix, a simulation cell containing an Al atom, 30 Ni atoms and a vacancy, equivalent to 3.23%Al ($Ni_{96.77}Al_{3.23}$), has been constructed. This concentration serves as our low concentration limit. A vacant site has been made by removing a Ni atom from the bulk. A simulation cell is illustrated in Figure 4.

In every OKMC steps, we track the position of an Al atom in order to calculate the displacement of solute the Al in the Ni host and the corresponding time evolution. The calculation was performed using 100 OKMC steps at the temperature levels of 900K, 1100K, 1300K, 1500K and 1700K. The tracer diffusion coefficients, D_{Al}^* and D_{Al} are plotted in Figure 5 as a function of inverse temperatures and compared with a

set of experimental data from Gust *et al.* [14], Alision *et al.* [13] and Swalin *et al.* [15]including results from another KMC calculation technique [4]
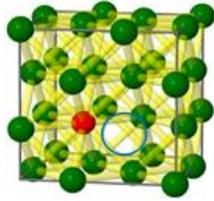

Figure 4. The OKMC simulation cell, representing a low concentration limit, consisting of an Al atom, 30 Ni atoms and a vacancy site.

The diffusion prefactor (D_0) and the effective activation energy (Q_{Al}) have been calculated from the simulated data by fitting to the Arrhenius equation $D = D_0 \exp(-Q_{Al}/k_B T)$. Our calculated diffusion prefactor (D_0) and the effective activation energy (Q_{Al}) are 4.89×10^{-4} m^2/s and 2.92 eV respectively. Table 1 tabulates a few diffusion prefactors (D_0) and the effective activation energies (Q_{Al}) obtained from available experimental and simulated data, along with our results. It should be noted that our diffusion prefactor (D_0) is in the same order of magnitude with experimental obtained D_0's of dilute Ni-Al systems, and it is in a good agreement with other KMC results. However, our effective activation energy (Q_{Al}) is slightly higher than experimental values, but still comparable with the KMC results of Ni-Al systems of compositions Ni$_{95}$Al$_5$ and Ni$_{90}$Al$_{10}$ from Alfonso *et al.[22]*

Figure 5. Tracer diffusion coefficient of Al in Ni host, D^*_{Al} in 900K, 1300K, 1700K compare with experimental data from Gust *et al.[14]*, Alision *et al.* [13], Swalin *et al.* [15] including other KMC calculation technique from Alfonso *et al.* [4]

Table 1. The simulation results and available experimentally measured diffusion prefactor $\boldsymbol{D_0}$ and effective activation energies $\boldsymbol{Q_{Al}}$ for solute Al in Ni host

	$\boldsymbol{D_0}$ (m^2/s)	$\boldsymbol{Q_{Al}}$ (eV)	T(K)
This work (ABC+OKMC), Ni$_{96.77}$ Al$_{3.23}$	4.89×10^{-4}	2.92	900-1700
Alfonso (KMC, 2015), Ni$_{95}$Al$_5$	6.25×10^{-5}	2.81	1000-1700
Alfonso (KMC, 2015), Ni$_{90}$Al$_{10}$	1.30×10^{-4}	2.96	1000-1700
Alfonso (KMC, 2015), Dilute	6.35×10^{-5}	2.73	900-1700
Gust (1981), Dilute	$(1.0 \pm 3.4) \times 10^{-4}$	2.7 ± 0.14	914-1212
Swalin (1956), Dilute	$(1.9 \pm 1.4) \times 10^{-4}$	2.78 ± 0.04	1357-1538
Allison (1959), Dilute	1.1×10^{-4}	2.58	1072-1200

Conclusion

Diffusion kinetics plays central roles in materials deformation at long timescales. Indebted to the small time-step integration, classical molecular dynamics fall short at predicting such long-time scale behaviors. The compounded computational method (ABC NEB and OKMC), designed to circumvent this issue, has been shown to make some progress over molecular dynamics simulations. In this work, we have demonstrated the predictability of these compounded computational methods when applying to the diffusion problem of aluminum hoping in a nickel matrix at a low-concentration Ni-Al alloy. The obtained tracer diffusion coefficient is key imperative to the interdiffusion, self-diffusion, and other kinetic mechanisms in Ni-Al alloys. At the low-concentration limit, our simulation framework not only yields a reasonable diffusion prefactor of aluminum in a nickel bulk, but also a representative effective activation energy. Furthermore, it should be noted that since the

developed computational workflow allows for all-atom relaxations, it should be transferable to other studies of more complex kinetics in materials.

References

[1] Kaledin, M. et al., 2004. "Normal Mode Analysis Using the Driven Molecular Dynamics Method. Ii. An Application to Biological Macromolecules". **The Journal of Chemical Physics.** 121: 5646-5653.

[2] Pollock, T. M.; Tin, S., 2006. "Nickel-Based Superalloys for Advanced Turbine Engines: Chemistry, Microstructure, and Properties". **Journal of propulsion and power.** 22: 361-374.

[3] Reed, R. C. 2008. **The Superalloys: Fundamentals and Applications.** Cambridge university press.

[4] Alfonso, D. R.; Tafen, D. N., 2015. "Simulation of Atomic Diffusion in the Fcc Nial System: A Kinetic Monte Carlo Study". **The Journal of Physical Chemistry C.** 119: 11809-11817.

[5] Németh, A. A. N. et al., 2017. "Environmentally-Assisted Grain Boundary Attack as a Mechanism of Embrittlement in a Nickel-Based Superalloy". **Acta Materialia.** 126: 361-371.

[6] Henkelman, G. et al., 2000. "A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths". **The Journal of Chemical Physics.** 113: 9901-9904.

[7] Voter, A. F., 2007. "Introduction to the Kinetic Monte Carlo Method". **Radiation effects in solids.** 1-23.

[8] Fan, Y. et al., 2010. "Unfaulting Mechanism of Trapped Self-Interstitial Atom Clusters in Bcc Fe: A Kinetic Study Based on the Potential Energy Landscape". **Physical Review B.** 81: 104102.

[9] Fan, Y. et al., 2014. "Autonomous Basin Climbing Method with Sampling of Multiple Transition Pathways: Application to Anisotropic Diffusion of Point Defects in Hcp Zr". **Journal of Physics: Condensed Matter.** 26: 365402.

[10] Lau, T. T. et al., 2010. "Atomistic Simulation of Creep in a Nanocrystal". **Physical review letters.** 104: 175501.

[11] Balluffi, R. W. et al. 2005. **Kinetics of Materials.** John Wiley & Sons.

[12] Kushima, A. et al., 2009. "Computing the Viscosity of Supercooled Liquids". **The Journal of Chemical Physics.** 130: 224504.

[13] Allison, H. W.; Samelson, H., 1959. "Diffusion of Aluminum, Magnesium, Silicon, and Zirconium in Nickel". **Journal of Applied Physics.** 30: 1419-1424.

[14] Gust, W. et al., 1981. "Impurity Diffusion of Al in Ni Single Crystals Studied by Secondary Ion Mass Spectrometry (Sims)". **Physica status solidi (a).** 64: 187-194.

[15] Swalin, R.; Martin, A., 1956. "Solute Diffusion in Nickel-Base Substitutional Solid Solutions". **J. metals.** 8.

[16] Fan, Y. et al., 2011. "Mechanism of Void Nucleation and Growth in Bcc Fe: Atomistic Simulations at Experimental Time Scales". **Physical review letters.** 106: 125501.

[17] Purja Pun, G. P.; Mishin, Y., 2009. "Development of an Interatomic Potential for the Ni-Al System". **Philosophical Magazine.** 89: 3245-3267.

[18] Plimpton, S., 1995. "Fast Parallel Algorithms for Short-Range Molecular Dynamics". **Journal of computational physics.** 117: 1-19.

[19] Lindan, P.; Gillan, M., 1991. "A Molecular Dynamics Study of the Thermal Conductivity of Caf2 and Uo2". **Journal of Physics: Condensed Matter.** 3: 3929.

[20] Shewmon, P., Diffusion in Solids, 203 P. McGraw-Hill, New York: 1963.

[21] Kraftmakher, Y., 1996. "On Equilibrium Point Defects in Metals". **Philosophical Magazine A.** 74: 811-820.

[22] Alfonso, D. R.; Tafen, D. N., 2014. "Simulation of Diffusion in Fcc Nife Binary Alloys Using Kinetic Monte Carlo Method". **The Journal of Physical Chemistry C.** 118: 22221-22228.