Quantum molecular dynamics simulation of structural and thermodynamic properties of NiAl

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Abstract. In this work, structural and thermodynamic properties of a solid and liquid Ni–Al compound are studied using an \textit{ab initio} method of quantum molecular dynamics (QMD). Simulations were carried out in 700–3000 K temperature range at atmospheric pressure. Radial distribution functions are analyzed to determine the presence of Ni–Al chemical bonds. Diffusion coefficients for individual components are also calculated. Another goal of this work is the investigation of the reaction propagation in thermally-initiated Ni–Al foils. For this purpose, we performed QMD simulations of Ni–Al layers in the microcanonical ensemble. An exothermic reaction between the solid Ni–Al layers is observed in our simulations at temperature less than the melting temperatures of the components.

1. Introduction

Ni–Al alloy systems are of high scientific and technological interest as they combine high strength and high-temperature resistance with low weight. Furthermore, the Ni–Al systems are an important subclass of high-density reactive materials (HDRM). These materials undergo a self-sustained exothermic reaction upon initiation through a shock or thermal loading and do not need additional reagents. This property allows to use HDRM as a fuel, welding flux, combustion and detonation initiator. So because of their useful properties and promising applications, the Ni–Al reactive systems have attracted significant attention over the last two decades, both experimental [1–4] and theoretical [5–9].

Determining the structural properties of intermetallic liquids is important for understanding processes like solidification, undercooling, and glass formation. Recently, it was experimentally shown that the metallic liquid of Ni–Al alloy is not a completely random disordered system but has generally the tendency to have a local structural order [10–13]. This phenomenon is widely studied using both classical and quantum molecular dynamics (MD) simulations [14–20]. However, uncertainties still persist in theoretical models of bonding, structure, and thermodynamics of alloys. In particular, the problem of equation of state of compounds under extreme conditions still claims attention of researchers [21, 22].

It is also found in quasielastic neutron scattering (QNS) measurements that the Ni self-diffusion coefficient (SDC) in Ni–Al alloys exhibits a non-linear dependence on the composition with a strong increase on the Al-rich side [11, 23]. It should be mentioned that measurements of the Al SDC remain challenging, therefore, MD simulations can also be of interest in this
case. However, computed dynamic properties of liquid Ni–Al alloys are shown to be strongly dependent on the different implementations of the embedded-atom method (EAM) potentials. Recently, similar non-linear behavior for the Al SDC was demonstrated using quantum molecular dynamics (QMD) calculations [24].

Reaction properties in Ni–Al multilayered systems have received significant attention because of their potential for applied use in both military and industry applications, and because of interesting chemical and physical behavior of the material during the reaction, including melting, diffusion, structural expansion, and phase change. Atomistic simulation can provide a detailed fundamental information about the reaction processes. Until now, the Ni–Al reactive systems have studied with only empirical computational models [5, 6] or classical MD simulations [7–9] employing EAM interatomic potentials for Ni–Al [25,26]. These simulations showed an extremely complex mix of simultaneous physical and chemical processes. Undoubtedly, since first-principle MD simulations possess better predictive capabilities than classical MD [27], QMD calculations of Ni–Al multilayered systems could provide much more valuable and accurate information about the reactive processes. In this work we present QMD simulation of the interdiffusion reactive process in a Ni–Al bilayer system. We also investigate structural properties of NiAl compound in the crystalline and liquid states using QMD simulations to analyze a thermal stability of the crystal, to verify the presence of local short-range order in liquid NiAl and to reproduce a non-linear dependence of SDCs of Ni and Al on the composition.

2. Methods
We use the QMD approach to determine thermodynamic properties of NiAl in the range of temperatures 700–3000 K. This approach can be considered as \textit{ab initio}, e.g. it does not employ any experimental data except for fundamental physical constants, that is why the alternative abbreviation AIMD (\textit{ab initio} molecular dynamics) is also widely known. The electrons are treated within the framework of the finite temperature density functional theory (DFT) while the classical ions move according to Newton’s equations in response to forces from the interaction with other ions and electrons. High accuracy of QMD simulation of structural and thermodynamic properties of metals and compounds was demonstrated in our previous works [28–30].

The well-known Vienna Ab initio Simulation Package [31–34] is applied for performing QMD simulations. This code implements DFT using the plane-wave basis set and several types of pseudopotentials including ultrasoft [35] and projector augmented-wave (PAW) [36]. The Kohn–Sham equations are solved only for valence electrons while inner ones are replaced by an invariable core. Electronic states were occupied according to the Mermin’s finite temperature formulation of DFT [37]. All calculations in this work were performed with PAW pseudopotentials. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [38, 39] corrections was used for the exchange-correlation functional.

We use 10 valence electrons for Ni atom and 3 for Al. The cut-off energy for the plane-wave basis was set to 350 eV. The radius of the invariable core (RCORE) for Ni was 2.3\(a_B\) (1.217 Å) and for Al 1.9\(a_B\) (1.005 Å) with \(a_B\) being the Bohr radius.

All QMD simulations were started from the ideal CsCl-type lattice structure [40] in the canonical ensemble (NVT), except for a calculation of diffusion coefficient of separate components, where a disordered initial state was used. The electronic temperature \(T_e\) was fixed through the Fermi–Dirac distribution and the ionic one \(T_i\) was maintained by the Nosé–Hoover thermostat [41], \(T_e = T_i = T\) was set in all our calculations. Thermodynamic properties of NiAl were computed in a cubic supercell containing 64 atoms of Ni and 64 atoms of Al with periodic boundary conditions.

In all QMD calculations only the \(\Gamma\)-point in the Brillouin zone was used. The time step was set to 2 fs; the system evolved for at least 10000 steps in all calculation.
3. Results

To investigate the presence of a chemical bond, we analyzed radial distribution functions (RDF) \( g(r) \) at \( T = 700 \) and \( 3000 \) K. The lattice constant was chosen so that at a corresponding density the compound was at zero pressure.

Figure 1(a) shows the RDFs for Ni–Ni, Ni–Al, and Al–Al pairs for a NiAl system at \( T = 700 \) K, \( \rho = 5.74 \) g/cm\(^3\). The form of the functions indicates the presence of the long-
range order; therefore, the compound in this case is in the crystalline state. The analysis of the maxima of the RDFs indicates the retention of the original crystal lattice. In figure 1(b) one can see the RDF for the same ion pairs of NiAl at $T = 3000$ K, $\rho = 4.55$ g/cm$^3$. The character of the RDFs under such conditions indicates that only the short-range order is presented; therefore, the state of the compound is disordered. It can also be noted that the maximum of the Ni–Al RDF is significantly higher than the other two ones, that can be considered as evidence of a connection between Ni and Al atoms with a length of $r = 2.4$ Å.

To demonstrate this fact, in figure 2 we show a snapshot of one of the calculated configurations at $T = 3000$ K and $\rho = 4.55$ g/cm$^3$, where the isosurface of the electron density and the Ni–Al bond length of 2.4 Å are shown. The localization of electron density around Ni–Al pairs is clearly seen. It should be noted that the bonds between Ni and Al are short-living: they form and break apart during the simulation. Additional analysis is required to determine the lifetime of the bonds at various conditions.

We also estimated the melting temperature of NiAl. To do this, a number of QMD simulations were performed at increasing temperature from 1500 K to 3000 K, and the mean square displacement (MSD) of both components was analyzed. The corresponding densities were chosen in such a way that the pressure in the system remained zero. As the melting point we took a temperature at which the MSD becomes positive. Figure 3 shows the MSD dependence for three temperatures: 1500 K, 2500 K, 3000 K. It can be seen from the figure that at $T = 2500$ K the MSDs for both Ni and Al begin to rise at $t \gtrsim 6$ ps. At $T = 3000$ K, the system melts.

![Figure 2. A snapshot of one of the calculated configurations at $T = 3000$ K, $\rho = 4.55$ g/cm$^3$. Ni ions (blue spheres), Al (pink) and the isosurface of electron density are shown. Ni–Al bonds with a length of 2.4 Å are marked by thick blue-pink lines.](image)
Figure 3. Dependences of MSD of Ni and Al ions on time at 1500 K ($\rho = 5.5$ g/cm$^3$), 2500 K ($\rho = 5.05$ g/cm$^3$), and 3000 K ($\rho = 4.55$ g/cm$^3$). Blue line corresponds to Ni, red line—to Al.

Figure 4. Dependences of SDCs for Ni and Al in the alloy Ni$_x$Al$_{1-x}$ on the Ni mole fraction at $T = 1795$ K. Blue circles—experimental data [11, 23]. Blue triangles—SDC of Ni [24]; red triangles—SDC of Al [24]. Blue squares—SDC of Ni, this work; red squares—SDC of Al, this work.
just after the start of the simulation. Thus, our estimate of the melting temperature of NiAl is $T = 2500 \text{ K}$, which is approximately 30% higher than the experimental value. This can be explained by the small size of the supercell and insufficient simulation time [28].

For comparison with experimental and other AIMD studies, we analyzed the dependence of the self-diffusion coefficients (SDCs) of Ni and Al on the compound composition. The coefficients were calculated using the formula:

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle.$$  \hspace{1cm} (1)

The simulation in this case was started out from a disordered state at $T = 1795 \text{ K}$ in order to reproduce initial conditions in papers [11, 23]. We performed a number of calculations for $\text{Ni}_x\text{Al}_{1-x}$ systems, where mole fraction $x$ of Ni varied from 0.1 to 0.9. The results of the calculations are shown in figure 4. It is interesting to note that the SDCs at $x > 0.5$ remain constant, approximately the same for both metals (and is about 0.4 $\text{Å}^2/\text{ps}$). At $x < 0.5$, with the decrease of Ni concentration in the melt, the SDCs of both components increase, while the mobility of Al atoms becomes higher than that of Ni. As it is shown in the graph, our dependence of the Ni SDC is in good agreement with the experiment [11] and the AIMD simulation [24]. The self-diffusion of Al is in a satisfactory correlation with the work [24]; the distinctions may be explained by a big error of SDC obtained from noisy data on MSD.

To investigate reactive processes in a Ni–Al bilayer system we use a supercell containing 300 atoms of Ni and 288 atoms of Al. Initially each layer is an ideal face-centered cubic lattice with different parameters: $a_{\text{Ni}} = 3.5 \text{ Å}$ for Ni and $a_{\text{Al}} = 4.375 \text{ Å}$ for Al. The system was equilibrated for 0.5 ps in the NVT ensemble at $T = 800 \text{ K}$. The configuration of particles at the end of the equilibration is shown in figure 5(a): the system is in a crystallized state. Then a long run in the

![Figure 5. Snapshots of NiAl bilayer system. Periodic boundary conditions are used in all directions. Blue circles—Ni atoms, pink circles—Al atoms. (a) 0.5 ps—equilibrated system at $T = 800 \text{ K}$. (b) 4 ps—melting of the aluminum layer and arrangement of Al atoms at the Ni–Al boundary. (c) 20 ps—diffusion of Ni and Al ions and formation of NiAl molecules.](image-url)
Figure 6. Kinetic temperature of NiAl bilayer system. Gray line—original data, red line—
moving average using 50 time steps.

microcanonical NVE ensemble was carried out. As can be seen from figure 5(b), after 4 ps the
aluminum layer melts and a special ordering of atoms on the contact between Ni and Al is formed:
each Al atom is located at the same distance $\approx 2.4\,\text{Å}$ from a corresponding Ni atom. During
the further evolution of the system the diffusion of Ni atoms into the aluminum layer and Al
atoms into the nickel one begins; the formation of NiAl molecules is observed. The configuration
of particles after 20 ps of the simulation is shown in figure 5(c). The formation of molecules
releases additional energy which transforms into the kinetic movement of particles. This effect
can be visualized from the analysis of kinetic temperature of the system: the temperature rises
significantly with time (figure 6). Further analysis of the reaction is possible only at much longer
simulation time which is currently unavailable in QMD simulation [42–44].

4. Conclusions
In this work we have studied thermodynamic and structural properties of the NiAl compound
using QMD. We have analyzed RDFs in the range of temperature 700–3000 K and found the
presence of Ni–Al bonds. We have also observed the localization of electron density around
Ni–Al molecules and a characteristic Ni–Al bond length of approximately $2.4\,\text{Å}$ in a snapshot of
the system. The melting temperature of the NiAl system have been estimated as approximately
2500 K from the time dependence of the MSD of Ni and Al. The SDC of Ni in the Ni$_x$Al$_{1-x}$ alloy
at $T = 1795$ K have turned out to be in good agreement with experiment; the independence
of the SDC on the Ni mole fraction at $x > 0.5$ has been confirmed. Also we have revealed the
diffusion of Ni and Al and the formation of NiAl molecules in the NiAl bilayer at $T = 800$ K;
the initiation of the chemical reaction have been proved by the rising kinetic temperature of the
system.
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