Molecular dynamics simulation of nanoindentation of nickel-titanium crystal

G B Sushko¹, A V Verkhovtsev¹,², A V Yakubovich¹,³ and A V Solov’yov¹,³

¹ Frankfurt Institute for Advanced Studies, Ruth-Moufang-Str. 1, 60438 Frankfurt am Main, Germany
² St. Petersburg State Polytechnic University, Politekhnicheskaya ul. 29, 195251 St. Petersburg, Russia
E-mail: verkhovtsev@fias.uni-frankfurt.de

Abstract. We present the results of molecular dynamics simulations of nanoindentation of a bimetallic nickel-titanium crystal in the austenitic (cubic) B2 phase. By considering three different types of indenters, namely of square, conical and spherical shapes, we observe the dependence of deformations of the crystalline structure on the type of the indenter. Various load-displacement curves are observed for different indenter types. We perform the molecular dynamics simulations of a full indentation cycle, which includes the loading and unloading stages. On the basis of such simulations we evaluate mechanical properties of the material, namely we calculate hardness and reduced Young’s modulus. We observe variation of the calculated parameters depending on the indenter type and discuss the origin of occurring discrepancies.

1. Introduction

Various metallic materials (stainless steels, Co-based alloys, titanium and its alloys, Ni-Ti alloys) are widely used for medical implants in trauma surgery, orthopaedic and dental medicine [1,2]. Successful incorporation of these materials into clinical practice requires that they meet several principal criteria. One of them is the ability of the material to provide sufficient mechanical strength, especially under the cyclic loading conditions, to ensure the durability of medical devices made thereof [2]. Finally, the material should be machinable and formable, thereby, enabling fabrication of devices at an affordable cost.

The deposition of multifunctional bioactive films is an effective way to promote the formation of bone-like layers on the implant surface, prevent toxic ion release, and improve mechanical and tribological characteristics of implants [3]. In order to determine the optimal directions of development and design of nanostructured titanium and titanium based alloys for medical applications, fundamental understanding of the deformation mechanisms and reliable computational models for the virtual, numerical testing of these materials are necessary.

In the present paper we investigate the nanoindentation process of the crystalline nickel-titanium alloy by large-scale molecular dynamics (MD) simulations. To describe interatomic interactions, we utilize the classical Finnis-Sinclair potential. We study the austenitic (B2) face-centered cubic (fcc) phase of the Ni-Ti alloy with equal concentration of nickel and titanium

³ On leave from A.F. Ioffe Physical-Technical Institute, St. Petersburg, Russia
atoms. Three different types of indenters, namely of a square, conical and spherical shapes, are considered in the present study. For each indenter type, we perform MD simulations of a full indentation cycle, which includes the loading and unloading stages. On the basis of such simulations we evaluate mechanical properties of the material, namely we calculate hardness and reduced Young’s modulus. We observe the dependence of the obtained values of the parameters on the type of the indenter and discuss the origin of this dependence.

The study presented is devoted to the modeling of nanoindentation and mechanisms of localized deformation of nanostructured biomaterials, Ni-Ti alloys in particular. The main aim of this study is to investigate the strength and mechanical properties of the films and the substrate/coating systems to be used in implants. Understanding the fracture mechanisms during indentation, scratching and impact testing is critical for understanding of how the film/substrate system will perform in service.

The prime advantage of the nanoindentation procedure is the possibility to test very small material volumes and its applicability to thin film characterization. Generally, the indenter is made of diamond in order to avoid spurious effects of indenter tip deformation. Only single crystal diamond, free of impurities or inclusions is used. The advantages of diamond for nanoindentation come from its exceptional properties of hardness, thermal conductivity and chemical inertness, which surpass any other known material. There are numerous geometries commercially available for the indenter shape such as three-sided pyramids, four-sided pyramids, wedges, cones, cylinders or spheres. The tip end of the indenter can be made sharp, flat, or rounded to a cylindrical or spherical shape. A typical size of the tip is of the order of a few tens of nanometers for the sharpest tips and of a few hundreds of nanometers for the rounded tips. The residual imprint on the sample surface after nanoindentation is on the order of a micrometer diameter even with high force levels and a blunt indenter type with a conical geometry (with a nominal radius of curvature of a few μm) leaving a rather large imprint.

In contrast to traditional hardness testers, the nanoindentation system allows the application of a specified force on the indenter (of the order of μN) while simultaneously monitoring the indenter displacement (of the order of nm) to obtain the applied force-indenter displacement curve as the output (see, e.g., [4, 5]). The experiment follows a predefined loading sequence where the applied force on the indenter displacement as a function of time is specified. Generally, three parts of the loading sequence are distinguished: the loading part where the applied force is increased until a peak value, the holding part where this peak load is maintained for a prescribed amount of time, and finally the unloading part where the applied force is decreased gradually to zero. A nanoindentation experiment lasts generally only for some tens of seconds in order to remain in the high precision domain of the measuring equipment. In experiments the indenter velocity varies between tens of nm/s to μm/s.

2. Numerical simulations of the nanoindentation process

Depending on the purpose of the simulation, different aspects of the nanoindentation procedure are addressed in different numerical models. Every numerical model is adapted to specific requirements, therefore it is hardly possible to compare directly the simulation results issued from different models. In Ref. [6], different numerical models and techniques applied at different length scales of the nanoindentation process are described.

When the numerical frame has to be coupled directly to experiments, most frequently the continuum models are preferred because of their computational efficiency. These models are well adapted to reproduce the overall average response of the material in nanoindentation and to conduct parametric studies concerning parameters which are experimentally difficult to access (e.g. surface roughness, contact geometry etc. [7]). It is worth mentioning the widely used finite element method (FEM) for the simulation of the nanoindentation procedure in the large and moderate indentation depths domain [8]. This method allows one to identify the key
parameters of the nanoindentation process and various material parameters using dimensional analysis together with the continuum numerical models. In order to describe the more complex physics of shallow nanoindentations, where the size-dependent response of the material has to be taken into account, the continuum methods are specially adapted to microscale simulations, using higher order theories in the finite element method [9, 10].

However, when the purpose of investigation is a deeper understanding of the plastic deformations one needs to deal with the models on a smaller scale. The descent to the scales where continuum mechanics is not applicable anymore implies the use of more computationally expensive simulations as they require more information to be included in the model itself. One of the relatively computationally cheap numerical methods uses the discrete dislocation plasticity model which focuses on the plastic deformation of the crystalline material considering only the slip planes without details on the positions of the atoms [11, 12].

When the details of the onset of the plastic deformation and the dislocation activity are in the focus of interest, the numerical models have to descend to the lowest scale: atomistic simulations are conducted. Generally, atomistic models are used for system sizes not larger than 100 nm (around the upper limit of the range of thin film nanoindentations) from which scale on other numerical methods are more adequate to describe the behavior of the material [6]. The atomistic models have the indisputable advantage of identifying the trends concerning the main physical variables of a problem and give important qualitative information for the understanding of experimentally observed complex phenomena, such as the size effects, that cannot be reproduced by coarser models.

The main drawback of purely atomistic models for mechanical applications is that they are computationally expensive. Therefore, generally, they handle length (in the order of tens of nm) and time scales of some ns, i.e. several orders of magnitude smaller than in the experiments. Due to computing power limitations, the speeds of the indenter tip reported in the literature are on an order of $1 - 100 \text{ m/s}$ for most MD simulations of nanoindentation [13, 14]. Even though atomistic calculations are computationally expensive, in the past years the dynamic increase in computational power has allowed the adaptation of atomic level models to interesting mechanical applications [15]. Different approaches based on molecular dynamics addressing the problem of nanoscratching [16] or nanoscale machining [17] have been used for the identification of different wear regimes [18], adhesion [19] and the explication of the tribological phenomenon. Recently, very large systems (up to several million atoms [13, 20]) have become accessible for modeling using parallel computational techniques, but the computational effort, directly related to the enormous quantity of information of atomic level models becomes very large.

3. Modeling the nickel-titanium crystal

In the present study, atomistic simulations of nanoindentation of the Ni-Ti crystal were conducted using molecular dynamics (MD) methods. The geometrical structure of the system of interest was constructed on the basis of experimental crystallographic structures. For the theoretical investigation of the nanoindentation process on the nanoscale, we created a three-dimensional nickel-titanium sample of $260 \text{ Å} \times 260 \text{ Å} \times 260 \text{ Å}$ consisting of about 1 million atoms.

The interaction between the nickel and titanium atoms was modeled using a Finnis-Sinclair-type potential [21], an empirical many-body potential which allows one to describe interatomic interactions in transition-metal materials. The total potential energy $U$ of a system of nickel and titanium atoms, located at positions $\mathbf{r}_i$, can be written as:
\[ U = \sum_{i=1}^{N} \sum_{\substack{j=1 \atop i \neq j}}^{N} A_{\alpha\beta} e^{-p_{\alpha\beta} \left( \frac{r_{ij}}{d_{\alpha\beta}} - 1 \right)} - \left( \sum_{\substack{j=1 \atop i \neq j}}^{N} \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta} \left( \frac{r_{ij}}{d_{\alpha\beta}} - 1 \right)} \right), \]  

(1)

where \((\alpha, \beta = \text{Ni, Ti})\), \(N\) stands for the total number of considered atoms in the system, \(r_{ij}\) is the distance between the \(i^{th}\) and \(j^{th}\) atoms, and \(d_{\alpha\beta}, p_{\alpha\beta}, q_{\alpha\beta}, A_{\alpha\beta}\) and \(\xi_{\alpha\beta}\) are adjustable parameters of the potential. The parameter \(d_{\alpha\beta}\) is the first-neighbor distance, \(\xi_{\alpha\beta}\) results from an effective hopping integral and \(q_{\alpha\beta}\) describes the distance dependence of the hopping integral. In equation (1), the first term on the right-hand side describes a repulsive part of the potential which results from the repulsion between core electron of neighboring atoms, and the second term stands for the attractive density-dependent many-body term. The parameters of the potential were fitted to reproduce the properties (the cohesive energy, lattice parameters, elastic constants and the unrelaxed vacancy formation energy) of the B2 NiTi phase at 0 K. The MD simulations were performed using the parametrization proposed by Liu et al. [22]. Values of the parameters, used in the calculations are as follows: \(d = 2.607 \, \text{Å}, A = 0.3 \, \text{eV}, p = 7.9, \xi = 2.48 \, \text{eV}\) and \(q = 3.0023\) [22]. In order to reduce the computational time, the linked cell method for the short range potential was used (see [23] for details). To use this method, the cutoff distance for the interatomic potential was chosen to be equal to 5.5 Å. In the range between 4.2 and 5.5 Å we used the spline interpolation for attractive and repulsive parts of the potential (see [23] for details). Coefficients of the splines were chosen to correspond to the value and the first derivative of the potential at 4.2 Å and equal to zero at 5.5 Å.

4. Modeling the indenter

We investigated the indentation process using three different shapes of the indenter, namely a square indenter with a cross section of 18 Å \times 18 Å, a conical indenter with the cone angle of 90\(^\circ\), and a spherical indenter of the radius of 70 Å. The indenters were modeled as absolutely rigid bodies constructed from carbon atoms in the fcc lattice with a unit cell size of 1 Å. Such a tight packing of atoms of the indenters was chosen in order to avoid possible penetration of nickel and titanium atoms into the indenter. The inner atoms from the indenters were removed in order to decrease the computational time. Although the tip radius of standard nanoindenters is on the order of tens-hundreds of nanometers, in the present simulations we used the indenters of smaller size because of computational limitations. The deformability of the indenters and the thermal oscillations of their atoms were neglected. The hardness of a diamond is much higher than that of NiTi alloys, therefore the rigid body model for the indenter is fully applicable in the case of a nickel-titanium sample.

The interaction of the indenter with the titanium sample was described using the following repulsive potential:

\[ U = \varepsilon \left( \frac{r_m}{r} \right)^{12} \]

with the following values of the parameters: \(\varepsilon = 0.1 \, \text{eV}\) and \(r_m = 1.5 \, \text{Å}\). The cutoff radius for the Ni-C and Ti-C potential (the linked cell algorithm was used in the calculations) was set to 3 Å.

5. Results and discussion

The molecular dynamic simulations were performed using the MBN Explorer computer package [23], a universal program for structure optimization, simulation of dynamics, and growth processes in various nanosystems [24–28].
Figure 1. (a) Nanoindentation of the sample with a square indenter. Panels (b) and (c) show deformation of the crystalline structure at intermediate, \( \sim 0.6 \) nm, and the largest, 3 nm, penetration depths, respectively. Titanium and nickel atoms are shown by red and blue colors, respectively.

MD simulations of nanoindentation comprise the equilibration and indentation stages. In the equilibration stage, the indenter tip and the crystal surface were positioned \( \sim 0.3 \) nm apart from each other, and the system was simulated with a Langevin thermostat at 30 K for \( \sim 60 \) ps. After equilibration, the atomic positions of the two bottom layers of the crystal were "frozen" in order to fix the system in space. In the indentation stage of the simulations, the process is modeled by moving the indenter approximately 3 nm downward at a constant speed of 40 m/s, and then retracting the tip upwards at a constant speed of 10 m/s. These values correspond to the typical range of velocities which are used nowadays in the MD simulations of nanoindentation.

To describe the loading stage we performed two independent sets of simulations for each type of the indenter with various initial random seeds for Maxwell velocity distributions. The time integration of motion is performed by the velocity-Verlet algorithm [29]. After initial annealing of the crystalline structure at 30 K, the penetration of the indenter into the crystal was simulated in the canonical ensemble using the time integration step of 2 fs and the thermostat damping coefficient of 0.5 ps. The total vertical force acting on the indenter and coordinates of all the atoms in the system were recorded each 20 and 200 fs of the simulation, respectively. Each of the indenters was moved to the maximum indentation depth of approximately 3 nm into the crystal.

Firstly, we consider the simulations performed with the square indenter. The crystalline structure and the structural deformations occurring at various indentation depths are presented in figure 1. Panel (a) shows the penetration of the square indenter into the constructed crystalline sample. Panels (b) and (c) show the deformation of the structure at the indentation depth of 0.6 nm and 3 nm, respectively. The latter case corresponds to the maximal penetration of the indenter into the crystal.

The dependence of the force, exerted on the square indenter by the crystal, on the indentation depth is shown in figure 2. Solid black and blue lines represent two independent sets of simulations of the loading stage. The unloading stage was simulated in the first set of simulations (see black line). At the initial stage of indentation the load-displacement curve has a linear dependence, which means that at this stage the indentation is performed in the linear elastic regime. The dashed red line represents the analytic fit of the loading curve by a linear function.

After the initial stage of the loading, the load-displacement curve reaches the maximum and then fluctuates around a constant value of \( \sim 0.08 \) \( \mu \)N/nm during the further displacement of the indenter. Such a behavior of the curve can be explained by the geometry of the indenter. Due to the constant cross section of the square indenter, its further penetration into the crystal
Figure 2. Dependence of the force acting on the square indenter on the indentation depth. Solid black and blue lines represent two independent sets of simulations of the loading stage. The unloading stage, studied within the first set of simulations, is shown also by the black line. Dashed red line represents the analytic fit to the pressure created by the indenter by a linear function. Green dashed line shows the fit to the initial part of the unloading curve.

Figure 3. Load-displacement curves obtained for the case of the square indenter moving with the constant speed of 10 (black line), 20 (red line) and 40 m/s (blue line). The indenter speed does not affect significantly the force acting on the indenter. The fluctuations are caused by the relaxation of stresses in the system, such as migration of dislocations from the deformed sites.

To evaluate the dependence of the obtained load-displacement curves on the indenter speed, we performed several independent simulations of the process with the square indenter. In the course of simulations the indenter was moving with the constant speed of 10, 20 and 40 m/s for each case study. The results of the comparison are presented in figure 3. Load-displacement curves obtained for the indenter speed of 10, 20 and 40 m/s are shown by the black, red and blue lines, respectively. It is seen that the indenter speed does not affect significantly the shape of the load-displacement curve.

Figure 4 represents the indentation process with a conical indenter. Panel (b) shows the structural deformations which occur in the system at the maximal penetration depth of 3 nm. The dependence of the force acting on the indenter is presented in figure 5. It indicates that the force acting on the indenter gradually increases with the increase of the penetration depth.
In the case of the conical indenter, the obtained load-displacement curves can be fitted with a quadratic function. In this case, there is no elastic regime, and the indentation process enters the plastic regime just after the initial contact of the indenter tip with the sample.

Figure 6 shows a general view of the crystalline structure and the occurring structural deformation during indentation with a conical indenter. The dependence of the force acting on the spherical indenter on the penetration depth is shown in figure 7. In case of the spherical indenter, the elastic regime is not observed since the spherical tip induces plastic deformations even at very small penetration depths. Nevertheless, for the small indentation depths, less than \( \sim 1 \) nm, the obtained load-displacement curves can be fitted quite well by the expression [30]

\[
F = \alpha h^{3/2},
\]  

\[ (3) \]
Figure 6. (a) Nanoindentation of the sample with a spherical indenter. Panels (b) and (c) show deformation of the crystalline structure at intermediate, ~1.2 nm, and the largest, 2.5 nm, penetration depths, respectively. Titanium and nickel atoms are shown by red and blue colors, respectively.

where $F$ is the indenter load, $h$ is the displacement of the indenter, and $\alpha$ is a proportionality factor. The analytic fit of the load-displacement curve by such a power function is shown by the dashed red line in figure 7. Although equation (3) is valid for the elastic indentation regime, we observed that the power function $F \propto h^{3/2}$ is valid also for extended indentation depths. Movement of the spherical indenter at distances exceeding ~1.5 nm leads to the deviation from the $h^{3/2}$ dependence. This deviation can be explained by the fact that the indenter radius becomes comparable with the indentation depth, as well as the finite size of the whole sample. Indeed, at high indentation depths dislocations move to the boundaries of the crystal and the system as a whole expands (see the right panel of figure 6). For the spherical indenter we observed the largest value of the force acting on the indenter. This can be explained by the largest deformations imposed on the system by the spherical indenter as compared to the square and conical ones.

Figure 7. Dependence of the force acting on the spherical indenter on the indentation depth. Solid black and blue lines represent two independent sets of simulations of the loading stage. The unloading stage, studied within the first set of simulations, is shown also by the black line. Dashed red line represents the analytic fit to the pressure created by the indenter by a power function. Green dashed line shows the fit to the initial part of the unloading curve.

In the present study, we used the results of the performed MD simulations to calculate hardness of the material, which is defined as the ratio of the force acting on the indenter divided by the contact area of the indenter. Hardness was calculated at ~1.3 nm of the indenter path.
from the beginning of the simulations for each of the indenters. The corresponding values of hardness are presented in table 1.

Table 1. Hardness of the NiTi alloy calculated for the square, conical and spherical indenters.

| Indenter        | Square | Conical | Spherical |
|-----------------|--------|---------|-----------|
| Hardness (GPa)  | 39     | 24      | 15        |

As it is seen from table 1, the calculated value of hardness depends on the form of the indenter. This can be explained by the fact that for small indenters the channel of stress release from the deformation site associated with dislocations migration is suppressed, while for a large spherical indenter much higher dislocation activity is observed. Indeed, for small indenters it requires substantial relative energy (as compared to the total work done by indenter to deform the material) to activate the dislocation migration, therefore material has extended elastic deformation region, which results in higher values of hardness.

In the present study, we calculated also the reduced Young’s modulus of the material, which is defined as:

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i},$$

(4)

where $E$ and $\nu$ are Young’s modulus and Poisson’s ratio for the sample material, and $E_i$ and $\nu_i$ are the same parameters for the indenter, respectively. In the present calculations the second term in equation (4) can be omitted since we treat the indenter as an infinitely stiff body.

The reduced Young’s modulus can be calculated from the initial part of the unloading curve using the following formula proposed by Oliver and Pharr [30]:

$$\frac{dF}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A},$$

(5)

where $dF/dh$ is the initial slope of the unloading curve and $A$ is the contact area at the initial moment of unloading. One can also apply the aforementioned equation to the initial part of the loading curve of the square indenter, when the indentation proceeds in the elastic regime. The results of calculation of reduced Young’s modulus for the considered nickel-titanium sample are presented in table 2.

Table 2. Reduced Young’s modulus of the bulk NiTi sample, $E_r$, calculated for the square, conical and spherical indenters at the beginning of the unloading stage, as well as the for the square indenter at the initial part of the loading, when the indentation proceeds in the linear elastic regime. See the text for details.

| Indenter | Square (load) | Square | Conical | Spherical |
|----------|---------------|--------|---------|-----------|
| $E_r$ (GPa) | 164           | 125    | 137     | 169       |

As it is seen from table 2, the value calculated for different indenters are about 130 – 170 GPa, which is somewhat larger than reported in experimental measurements for the NiTi B19’ phase. In Ref. [31], the measured values of reduced modulus are about 114 – 140 GPa (with Poisson ratio 0.35). The discrepancies between the results of the present simulations and experimental measurements can be attributed to different phases of the NiTi alloy (B2 in MD simulations
and B19’ in experiments) as well as insufficient accuracy of derivation of the initial slope of the unloading curve, absence of constant force segment in the simulations before unloading, low (∼30 K) temperature of the thermostat in the simulations and higher indentation velocity, as compared to that one used in experiments.

6. Conclusion
In this paper we presented the results of MD simulations of the nanoindentation process of a bimetallic nickel-titanium crystal. We considered the system consisting of approximately 1,000,000 atoms packed in the fcc lattice and studied its interaction with an infinitely stiff indenter of three different shapes, namely the square, conical and spherical ones. In the performed simulations, the indenter was moving with the constant speed of 40 m/s during the loading stage and 10 m/s during the unloading. The maximal penetration depth into the crystal was approximately 3 nm.

We observed the appearance of different deformation regimes depending on the geometry of the indenter. We found that the initial stage of indentation with a square indenter is performed in the linear elastic regime. Later on, the load-displacement curve reaches the maximum and fluctuates around a constant value during the further displacement of the indenter, which is caused by the constant cross section of the square indenter. In case of the conical and spherical indenters we did not observe the elastic regime and the indentation process enters the plastic regime just after the initial contact of the indenter tip with the sample. In both cases, the force, acting on the indenter, gradually increases with the increase of the penetration depth. For the spherical indenter we observed the largest value of the force acting on the indenter. This can be explained by the largest deformations imposed on the system by the spherical indenter as compared to the square and conical ones.

For each type of the indenter we calculated hardness and reduced Young’s modulus. We found that the calculated value of hardness depends on the form of the indenter. This can be explained by the suppression of the channel of stress release from the deformation site associated with dislocations migration for small square and conical indenters, and a much higher dislocation activity for a large spherical indenter. The calculated reduced Young’s modulus also depends slightly on the type of the indenter and corresponds to experimentally measured values for the nickel-titanium crystal.

In our further work, we will investigate the influence of grain boundaries present in the sample on the nanoindentation load-displacement curve. A detailed and comprehensive analysis of the results of MD simulations of nanoindentation will be performed. In particular, we will focus on the processes of phase transitions in the materials under the applied pressure and the associated shape-memory effects.

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