Molecular Dynamics Simulation of Nanoindentation of Nb-Zr Alloys with Different Zr Content

Junzhao Ren 1, Hongyan Wu 1,*, Lu Wang 2, Zhehang Fan 3, Yanzhao Qiu 1, Lu Yu 1 and Enxi Shi 1

1 Department of Physics, Institute of Advanced Materials and Flexible Electronics (IAMFE), Nanjing University of Information Science and Technology, Nanjing 210044, China
2 Jiangsu Key Laboratory for Optoelectronic Detection of Atmosphere and Ocean, Nanjing University of Information Science & Technology, Nanjing 210044, China
3 School of Teacher Education, Nanjing University of Information Science and Technology, Nanjing 210044, China

* Correspondence: wuhy2009@nuist.edu.cn

Abstract: To understand the nanomechanical behaviors of the Nb-based alloys with Zr addition at room/high temperature, the molecular dynamics simulations of nanoindentation are conducted. In this work, the load-unload displacement curve, hardness, and dislocation characteristics of Nb-Zr alloys with varying Zr content ranging from 0 to 5 wt.% are studied. The simulation results are found to closely agree with the experimental one at 1 wt.%, therefore showing the reliability of the simulation. Moreover, considering distinct responses of alloys to different service temperature, the high-temperature nanoindentation are performed. The effects of Zr addition on the mechanical deformation under both temperatures are compared. The same phenomenon is found such that the optimum concentration range yielding the greatest hardness is 1–3 wt.%. The elastic modulus of NbZr alloy improves with elevated concentration at room temperature, while the hardness at higher temperature exhibits the opposite trend. This is attributed to the higher amplitude of atomic vibrations at high temperatures, which is more likely to deviate atoms from their equilibrium positions and weaken the pinning effect under external loading. Therefore, we believe that our studies on the nanomechanical mechanisms of materials at room/high temperature will provide an effective way for the alloying optimization design.

Keywords: nanoindentation; molecular dynamic simulation; Nb-Zr alloy; mechanical properties

1. Introduction

Niobium (Nb) as a kind of typical noble metal material has attractive mechanical properties, which have been widely used in nuclear power plants to improve the strength of the material at the service temperature [1]. Whether it is the load-bearing behavior in biomechanics or the creep behavior at high temperatures, the changing nature of the mechanical processes accompanying the microstructure evolution at the atomic scale is an important basis for guiding the modification of materials. Similarly, another important aspect of niobium metal is the strength change at a high temperature. To solve the above problems, one of the effective methods is adding alloying elements into metals for optimization. Zirconium (Zr) is also well-known for its attractive mechanical properties and good biocompatibility. Moreover, the addition of Zr decreases the critical stress for sliding deformation and Zr is considered a neutral element for increasing the β-stabilizing effect of the Nb element to grain refinement and a more homogeneous structure to improve its mechanical properties [2,3]. Although there are many methods to test the mechanical properties of materials, such as tension, bending, torsion, shear, scratch, and indentation [4–7], it is still a great challenge to observe the nucleation, propagation of dislocations, and the evolution of defect structures at the nanoscale. The molecular dynamics (MD) simulation has been used as an effective tool to analyze the mechanical properties of materials and
study the deformation processes at the atomic scale. There are almost no literature reports on the investigation of the effect of Zr content on the mechanical properties of Nb metals and explanation of its micromechanical deformation mechanisms from microstructure evolution at the atomic scale. In view of this, it is necessary to study the characteristics of Nb-Zr alloy with various Zr content. Moreover, considering distinct responses of alloys to different service temperature [8,9], mechanical properties at different temperatures are also needed to be researched.

Molecular dynamics simulations have been extensively used to investigate the deformation process of alloys or composites at the atomic level [10–12], since they can be provided with the ability to observe detailed atomic behavior directly. Li et al. [10] systematically investigated the Zr-Cu metallic glass with pre-oxidized surfaces by MD simulation. According to the simulation, the diffusion bonded metallic glasses possess enhanced mechanical strength and ductility that generally do not exist in nano-glasses and their bulk metallic glass counterparts. Wu et al. [11] studied the effects of Zr concentration on the strengthening and mechanicals of Cu alloyed with Zr using molecular dynamics simulations. Results showed that the increase of Zr concentration results in an increase in structural stabilization and Young’s modulus of Cu-Zr systems decreases with increasing Zr concentration. The mechanical strength of Cu-Zr systems reaches its maximum value, 1.13 times that of the pure Cu counterpart at 5% Zr concentration. Lu et al. [12] used MD nanoindentation to study the deformation behaviors of single crystal Zr for four different surface orientations. Two different potentials were adopted for comparison to reveal the influence of stable and unstable stacking fault energy on dislocation behaviors under nanoindentation. Point defects are also an important consideration in the nanoindentation process. Guan et al. [13] proposed that understanding the effects of various elements on the formation of defects, including the orientation of interstitial atoms at different positions, is conducive to material design. Anisotropic relaxation can enhance the lattice distortion effect, thus affecting the movement of point defects.

The simulation, especially the actual high-temperature nanoindentation, is difficult to achieve in the current experiment. In this work, we performed the molecular dynamics simulations of nanoindentation of Zr addition into Nb. By adding different content elements, the nanoindentation process under the influence of temperature, and its nano-mechanical deformation and dislocation distribution characteristics are investigated. The potential function could be determined by fitting it with the experimental results. The effects of Zr concentration within 0–5 wt.% range on the elastic modulus and hardness were discussed. The propagation of dislocations and defect structures during the nano-deformation process could be analyzed from the atom configurations. In view of this, we discussed the effect of the high temperature on the mechanical deformation of the Nb-Zr alloy with different Zr content. It is of great guiding significance to study the generation of surface mechanical defects of alloy materials in harsh environments, which in turn causes changes in the overall mechanical behavior. Thus, we believe that our study of the mechanical mechanism of materials from the evolution of microstructure and dislocation structure will provide an effective way for optimizing the alloying design.

2. Simulation Methods

2.1. Molecular Dynamics Simulation of Nanoindentation

Figure 1 shows a general three-dimensional MD model of Nb-Zr alloy for nanoindentation, which was constructed to simulate the nanoindentation process with various Zr content. Nb atoms were randomly replaced by Zr atoms in different proportions (0–5 wt.%). The body of the simulation model is the Nb-Zr substrate with a virtual spherical indenter whose radius is above 40 Å. The substrate has a volume of 60 a0 × 60 a0 × 60 a0, where a0 is the lattice constant of Niobium (a0 = 0.330 nm). The whole simulation model contained 432,000 atoms. The three crystal orientations of the workpiece were x-[1 0 0], y-[0 1 0], and z-[0 0 1]. The initial distance between the indenter and the original substrate’s upper surface was set as 10 Å along the y-direction, and perpendicular loading was applied along
the y-direction to the substrate during the nanoindentation process. The Nb-Zr alloy atoms contained three kinds of atoms: Newtonian atoms, thermostat atoms, and boundary atoms. Newtonian atoms interact with the indenter and the movement of atoms in this region is governed purely by the forces on them, with no constraints. The motion of the Newtonian layer obeyed classical Newton’s second law. The thermostat layer was set to absorb heat dissipation of Newtonian atoms and kept thermal equilibrium. The boundary layer was fixed as a barrier to prevent the substrate from translating or moving along the y-direction during the nanoindentation simulation.

Figure 1. Three-dimensional MD model of Nb-Zr alloy for nanoindentation with Zr atoms colored purple.

2.2. MD Simulation Setup

In this work, the Large-scale atomic/molecular massively parallel simulator (LAMMPS) [14] was used to perform a series of MD simulations. Ovito [15] was used to visualize and analyze the atomistic simulation data. The periodic boundary conditions were used in the x and y directions and non-periodic boundary conditions in the z-direction. The integration time step of 1 femtosecond (fs) was set. The systems were subject to a 10 picosecond (ps) simulation time to perform energy minimization. In the first stage, initial velocities of the atoms were assigned according to the Maxwell–Boltzmann distribution. Following initialization, the extensive canonical ensemble (constant number of particles, volume, and temperature (NVT)) was adopted to maintain the system temperature at 296 K. The virtual indenter moved toward the substrate at a rate of 0.0005 Å/fs until reaching an indentation depth (the real penetration depth) of 20 Å, and then the indenter was pulled back to its original position at the same velocity. The nanoindentation simulation was performed in the microcanonical ensemble (constant number of particles, volume, and energy (NVE)). Then, the temperature was reset to 1470 K with other conditions remaining unchanged. Nanoindentation simulations with different concentrations of Zr within the range of 0–5 wt.% were carried out both at room temperature and high temperature.

2.3. Potential Energy Function

In the present study, the interatomic potential for Zr-Nb system based on the form of Angular-Dependent Potential (ADP) [16] was applied. For the ADP the total potential energy U is given by the following formula:

\[
U = \sum_{i>j} \varphi_{ij} (\mathbf{r}_{ij}) + \sum_i F_i (\mathbf{p}_i) + \frac{1}{2} \sum_{i,k} (\mu_i^k)^2 \\
+ \frac{1}{2} \sum_{i,j,l} \left( \lambda_{ij}^l \right)^2 - \frac{1}{6} \sum_i \mathbf{v}_i^2,
\]  

(1)
where

$$\bar{p}_i = \sum_{j \neq i} \rho(r_{ij}), \mu_i^k = \sum_{j \neq i} \mu_{ab}(r_{ij})r_{ij}^k,$$
$$\lambda_i^{kl} = \sum_{j \neq i} \lambda_{ab}(r_{ij})r_{ij}^kr_{ij}^l, \nu_i = \sum_k \lambda_i^{kl},$$

(2)

Here, indices $i$ and $j$ enumerate atoms, while superscripts $k,l = 1, 2$ and 3 refer to the Cartesian components of vectors and tensors. Indices $a$ and $b$ denote the element types of atoms. The first term in Equation (1) represents pair interactions between atoms via a pair potential $\varphi$. The summation is over all $j$-th neighbors of the $i$-th atom within the cut-off distance $r_{cut} = 6.2$. The second term $F$ is the embedding energy that is a function of the total electron density $\rho$. The two first terms in Equation (1) give a principal contribution to the system energy. Additional $\mu$ and $\lambda$ terms introduce non-central interactions through the dipole vectors and quadrupole tensors. They are intended to penalize deviations of the local environment from the cubic symmetry.

The indentation simulation is performed using the built-in “fix indent” command of LAMMPS. The Newton layer interacts with the indenter and the movement of atoms in this region is governed purely by the forces on them, with no constraints. The force exerted by the spherical indenter on each atom in the Nb-Zr alloy is described by:

$$F(r) = -K(r - R)^2,$$

(3)

2.4. Theory Analysis Method of Nanoindentation

The load vs. indentation depth curves are obtained from the nanoindentation simulations performed in LAMMPS. The Oliver–Pharr method [17] based on contact mechanics, is used to analyze the quantitative information, such as the hardness values from the P–h curve in our simulations. The nanoindentation hardness $H$ can be defined as follows:

$$H = \frac{P_{\text{max}}}{A_c},$$

(4)

where $P_{\text{max}}$ is the maximum indentation load on the indenter, $A_c$ is the contact area between the indenter and the surface of the sample given by

$$A_c = \pi h (2R - h),$$

(5)

where $h$ and $R$ denote the indentation depth and the radius of the spherical indenter.

The elastic modulus $E$ can be calculated by the following equation,

$$\frac{1}{E_r} = \frac{(1 - v^2)}{E} + \frac{(1 - v_i^2)}{E_i},$$

(6)

where $v$ and $v_i$ are the Poisson’s ratio of the backing material and the indenter, respectively, $E_i$ is the elastic modulus of the indenter and $E_r$ is the reduced elastic modulus. In this paper, the indenter was a virtual indenter and considered a rigid body, the value of $E_i$ is infinite and the value of $v_i$ is 0. Thus, the equation can be simplified as

$$E = E_r \left(1 - v^2\right),$$

(7)

The value of $E_r$ is given by the following equation,

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S_{\text{max}}}{\sqrt{A}},$$

(8)

where $S_{\text{max}}$ is the slope at the maximum load during unloading and $A$ is the corresponding contact area.
3. Results and Discussions

3.1. Elastic Modulus and Hardness at Room Temperature

Nanoindentation is a well-established technique to investigate the time-dependent deformation behavior and mechanical properties of a small sample of material. Nanoindentation by MD simulation makes it possible to characterize the nucleation and growth of dislocations at an atomic scale. During the loading process, the force applied to the indenter gradually increases as the indenter moves deeper into the sample. Figure 2 shows the load-displacement curves for nanoindentation under various Zr content by simulation. The load vs. displacement curve should match the solution of elastic contact mechanics developed by Hertz [18] before any sudden drop in the load curve. The point where the sudden load drop occurs is often referred to as the yield point in the nanoindentation. One phenomenon that is sometimes observed in experiments is a sudden displacement burst of the indenter represented as a plateau in the load vs. displacement curve which is often referred to as pop-in behavior. If the force follows a 3/2 power rule with indenter depth before the yield point, the loading is considered elastic. The load and unload force vs. depth curve will be identical in the elastic region. Both experiments [19–21] and MD simulations [22–24] observed the nucleation of the dislocations at the yield point, which associates the elastic-plastic transition with pop-in. However, nanoindentation experiments [25] also show that there may be some plasticity or nucleation of the dislocation before the pop-in during indentation, i.e., while the material still displays elastic-like behavior. The nanoindentation mechanical properties could also largely be affected by the components of the materials. Therefore, the hardness value obtained by experiment and simulation will be necessary to study the effect of Zr content on the mechanical properties.

![Figure 2. Load–displacement curves for nanoindentation under various Zr content by simulation.](image)

According to Equations (4)–(8), material properties about hardness $H$, reduced elastic modulus $E_r$, and elastic modulus $E$ with the change in Zr content from the nanoindentation simulation were calculated as shown in Table 1. With the increment of Zr content, the Nb-Zr alloy shows larger hardness than the pure Nb material within 4 wt.% range. In addition, the content of 1 wt.% Zr seems to be the inflection point of the hardness of Nb-Zr materials which is in agreement with the trend of that obtained from the experiment. The hardness of 1.06 wt.% (approximately 1 wt.%) was also acquired by the nanoindentation experiment with a value of 13.23 GPa. By comparison, the hardness with 1 wt.% Zr addition of simulation result is very close to that in the experiment, with a relative error of 3.08%, therefore showing the reliability of the simulation and the rational use of the potential function.
Table 1. Material properties obtained from nanoindentation simulation of Nb-Zr under various Zr contents at 296 K.

<table>
<thead>
<tr>
<th>Zr Content (wt.%)</th>
<th>Hardness (GPa)</th>
<th>Reduced Elastic Modulus $E_r$ (GPa)</th>
<th>Elastic Modulus $E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.09</td>
<td>89.44</td>
<td>78.33</td>
</tr>
<tr>
<td>1</td>
<td>13.65/13.23 *</td>
<td>95.60</td>
<td>83.73</td>
</tr>
<tr>
<td>2</td>
<td>13.63</td>
<td>100.88</td>
<td>88.36</td>
</tr>
<tr>
<td>3</td>
<td>13.32</td>
<td>114.34</td>
<td>100.15</td>
</tr>
<tr>
<td>4</td>
<td>11.93</td>
<td>124.36</td>
<td>108.92</td>
</tr>
<tr>
<td>5</td>
<td>12.36</td>
<td>136.13</td>
<td>119.23</td>
</tr>
</tbody>
</table>

* Hardness value is acquired by experiment.

3.2. Structural and Nanoindentation Transformations

To further investigate the effect of the content on the mechanical response during the nanoindentation process, an atomic-scale displacement analysis was performed. Figure 3 shows the distribution of the atomic displacement in the y-direction of the top view and the cross-section in the [100] direction of the Nb-Zr alloy at different indentation depths of 0.5, 1.5, and 2.0 nm for different Zr content ranging from 0 to 5 wt.%. The atomic deformation becomes more pronounced as the depth increases. For Nb-Zr alloys with different Zr content, there is no clear or unique pattern of the pile-up arrangement around the crater, which means the Nb-Zr alloys are isotropic.

![Figure 3. Snapshots of displacements in the y-direction of various Zr content (0–5 wt.% from left to right) under different depths (a–c); (a) 0.5 nm, (b) 1.5 nm and (c) 2.0 nm. The top diagram shows the cross-section snapshot in the [100] direction, and the bottom diagram shows the top view snapshot.](image)

Snapshots of the instantaneous microstructure defects at different indentation depths at 1 wt.% Zr content are shown in Figure 4a1–a3. This finding presented here are based both on the MD simulation snapshots and the observation of the animations of the indentation process. Perfect BCC Nb atoms were not shown here to display the damaged structures more intuitively. Figure 4a1 shows that at the penetration depth of 1.0 nm, the substrate...
was in its initial deformation stage, and a few defects were generated and distributed from beneath the indenter. As shown in Figure 4a2,a3, the number of defect atoms increased with an increase in penetration depth. Dislocation is a special atomic configuration, also known as a line defect, which occurs in crystalline materials only. Dislocations are conducive to improving the mechanical strength of materials and thus are especially important in materials science. The Dislocation Extraction Algorithm (DXA) was used to extract the dislocation lines during the indentation step. Figure 4b1–b3 are the internal dislocation line at different indentation depths and corresponds to the points shown in Figure 4a1–a3. The dislocations were found in the indentation contact area. According to Figure 4b1–b3, 1/2<111> dislocation played the main role in the process of indentation. A few <100> dislocation lines can also be found in some steps, which then disappeared and did not recur for a while.

To investigate the influence of Zr content on atomic configurations during indentation, the atomic snapshots of the substrate under various content at the indentation depth of 1.0, 1.5, and 2.0 nm were selected, shown in Figure 5. It displays the instantaneous atomic configurations of various Zr content among which Figure 5a–e represents as 0 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% respectively. To be clear, atoms in perfect BCC configuration were removed. Except for boundary atoms shown in white, atoms inside the substrate are colored according to CNA, as HCP atoms (green), BCC atoms (yellow) and the other atoms (blue). (b1–b3) The DXA is used to assign dislocation, as 1/2<111> (green), <100> (purple) and <110> dislocation (blue).

To investigate the influence of Zr content on atomic configurations during indentation, the atomic snapshots of the substrate under various content at the indentation depth of 1.0, 1.5, and 2.0 nm were selected, shown in Figure 5. It displays the instantaneous atomic configurations of various Zr content among which Figure 5a–e represents as 0 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.% respectively. To be clear, atoms in perfect BCC configuration were removed. Except for boundary atoms shown in white, atoms inside the substrate are colored according to CNA, as HCP atoms (green), BCC atoms (yellow) and the other atoms (blue). With the penetration of the indenter, dislocation loops began to be formed. For alloys with different Zr concentrations, the positions of the dislocation loops did not form in the same position. However, they did not expand along a particular orientation and did not make dislocated atoms pile up.
Figure 5. Instantaneous atomic configurations of various Zr content (a–e) under different depths (1.0–2.0 nm), respectively. (a) 0 wt.%, (b) 2 wt.% (c) 3 wt.%, (d) 4 wt.% and (e) 5 wt.%. Except for boundary atoms shown in white, atoms inside the substrate are colored according to CNA, as HCP atoms (green), BCC atoms (yellow), and the other atoms (blue).

Figure 6 displays the dislocation line evolutions under 1.5 nm and 2.0 nm corresponding with that of Figure 5. Figure 7 shows the dislocation density of five different Zr content of Nb-Zr alloys with the indentation depth Figure 7a and the number of defects under various Zr content Figure 7b during the indentation process. According to Figures 6 and 7a, it is noted that with the increase of Zr content, the total dislocations show an overall upward trend. Meanwhile, as depicted, there was a small discrepancy in the numbers of defective atoms, before the indentation, under various content. We can clearly find that when the indentation depth is about 1.4 nm, a new type of dislocation line <100> dislocation appears for 3 wt.% Zr content, shown in pink. The emergence of new dislocation lines increases the length of the total dislocation line to a certain extent, and the box volume is basically unchanged, resulting in a sudden increase in the total dislocation density at this indentation depth. As the indenter penetrated the substrate, the number of defective atoms increased. During the initial stage (before the indentation depth of 0.5 nm), the substrate material went through elastic deformation, and the number of defective atoms increased moderately. After having arrived at the penetration depth of 0.5 nm, the number of defective atoms increased rapidly, which corresponded to the dislocation nucleation that occurred during the indentation.
Figure 6. Dislocation line evolutions of five different Zr content in Figure 5a–e under different depths. (a1–a2) 0 wt.%, (b1–b2) 2 wt.% (c1–c2) 3 wt.%, (d1–d2) 4 wt.% and (e1–e2) 5 wt.%, with subscripts 1, 2 standing for 1.5 nm and 2.0 nm, respectively.

Figure 7. Plotting of the dislocation density and defective atoms number variations of five different Zr content of Nb-Zr alloys during indentation at 296 K. (a) Dislocation density and (b) Number of defective atoms variations.

3.3. Sensitivity of Nanoindentation to the Temperature

Figure 8 displays the load-displacement curves for nanoindentation of Nb-Zr alloy with varying Zr content by simulation under 1470 K. Material properties about hardness \( H \), reduced elastic modulus \( E \), and elastic modulus \( E \) under various Zr content from the nanoindentation simulation were calculated as shown in Table 2.

Figure 9 shows a comparison of the micro-hardness at room temperature (296 K) and high temperature (1470 K) for different Zr content from which it can be seen that the hardness of other Nb-Zr alloys with Zr addition decreases at high temperature compared to room temperature. This result may be due to the following reasons. According to the theory of statistical thermodynamics [26], the kinetic energy of all atoms of the system is related to the temperature as follows:

\[
E_k = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 = \frac{3}{2} Nk_B T, \tag{9}
\]

where \( E_k \), \( N \), and \( T \) are the total energy, the total number of atoms, and the thermodynamic temperature of the system, respectively; \( k_B \) is the Boltzmann constant. It can be seen from Equation (9) that when \( T \) is low, \( E_k \) is relatively small, and the amplitude of atomic vibration is relatively small; on the contrary, when \( T \) is higher, \( E_k \) is large, and the amplitude of atomic vibration at its equilibrium position is larger. Under the action of external
loading, the Nb and Zr atoms of the samples are more likely to deviate from their inherent equilibrium positions.

Figure 8. Load–displacement curves for nanoindentation of Nb-Zr Alloy with various Zr content by simulation under 1470 K.

Table 2. Material properties obtained from nanoindentation simulation of Nb-Zr with varying Zr content at 1470 K.

<table>
<thead>
<tr>
<th>Zr Content (wt.%)</th>
<th>Hardness (GPa)</th>
<th>Reduced Elastic Modulus $E_r$(GPa)</th>
<th>Elastic Modulus $E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.12</td>
<td>138.02</td>
<td>120.88</td>
</tr>
<tr>
<td>1</td>
<td>12.45</td>
<td>120.66</td>
<td>105.67</td>
</tr>
<tr>
<td>2</td>
<td>13.40</td>
<td>143.65</td>
<td>125.81</td>
</tr>
<tr>
<td>3</td>
<td>11.84</td>
<td>141.87</td>
<td>124.26</td>
</tr>
<tr>
<td>4</td>
<td>11.38</td>
<td>149.81</td>
<td>131.21</td>
</tr>
<tr>
<td>5</td>
<td>9.79</td>
<td>106.03</td>
<td>92.87</td>
</tr>
</tbody>
</table>

Figure 9. Hardness at room temperature (296 K) and high temperature (1470 K) for different Zr content.
Figure 10a,b compares the effect of increasing Zr content on elastic modulus at room and elevated temperatures. As can be observed, both of the moduli, namely elastic modulus and reduced elastic modulus, increase with increasing the Zr content from 1 to 4 wt.% regardless of the temperature. Further increase in Zr content, however, adversely affects both the moduli at elevated temperature of 1470 K. Similar results of adding Zr have been reported for AlCrZr alloy [27] and of Zr-Nb alloy [28,29]. However, the addition of more than 4% of Zr content negatively affects the moduli therefore allowing us to conclude that only a specific amount of Zr is beneficial for raising the moduli at elevated temperatures, which in the present study is found to be 4%. Figure 11 shows the dislocation density of five different Zr content of Nb-Zr alloys with the indentation depth. According to Figure 11, it is not difficult to find a similar conclusion as in room temperature that with the increase of Zr content, the total dislocations show an overall upward trend. Figure 12 displays the dislocation line evolutions of five different Zr content under different depths during the indentation process at 1470 K, among them 0–5 wt.% Zr content Nb-Zr alloy with subscripts 1, 2 standing for 1.5 nm (Figure 12a1–f1) and 2.0 nm (Figure 12a2–f2), respectively. At the high temperature, the heat energy as input provides sufficient energy to deviate the atoms from the lattice equilibrium position so that the pinning effect is weakened, the dislocations are increased in value, the dislocation density is increased, and the hardness is reduced. Therefore, at high temperatures, the atomic deviation caused by thermal energy dominates, and the dislocation increment is caused by the atomic deviation. While at room temperature, there is not enough energy as input, the atoms vibrate near the lattice position, and the indenter provides external force to make some atoms deviate from the equilibrium position, causing lattice distortion and multiplication of dislocations. However, the energy provided by the indenter alone cannot make the impurity atoms completely deviate from the lattice position they occupy, so the impurity atoms will hinder the movement of dislocations, which will strengthen the material and increase the hardness.

![Figure 10](image_url)

**Figure 10.** Comparison of reduced elastic modulus and elastic modulus between room temperature (296 K) and high temperature (1470 K) for different Zr content. (a) room temperature; (b) high temperature.
4. Conclusions

In this work, three-dimensional MD simulations were conducted to investigate the nanoindentation response of Nb-Zr alloy with a varying Zr content under room/high temperature using an ADP potential. We obtained the load-displacement curves from simulations of nanoindentation under different content. The hardness of the Nb-Zr alloy system was calculated and investigated. The hardness value obtained by simulation and experiment at 1 wt.% Zr content is relatively close with a relative error of 3.08%, showing reliability of the simulation. The highest hardness of NbZr alloy is within the 1–3 wt.% concentration range during the room/high-temperature nanoindentation, while other than that the hardness has an obvious decreasing trend. In addition, the 1 wt.% content seems to be the inflection point of the hardness of Nb-Zr materials which is in agreement with the trend of that obtained from the experiment. Furthermore, atom configurations were retrieved to investigate the evolution of defects during penetrating process. Then the elastic moduli of NbZr alloy are obtained and are found increasing with elevated concentration at room temperature while the hardness at high temperatures exhibit an opposite trend. This can be attributed to the higher amplitude of atomic vibrations at higher temperatures, which is more likely to deviate atoms from their equilibrium positions and weaken the pinning effect under external loading. Our study of the nano-mechanical mechanisms of NbZr alloys with varying Zr content under different temperatures will provide an effective way for optimizing the alloying design.
Author Contributions: Conceptualization, J.R.; methodology, J.R. and L.W.; validation, Z.F., L.Y. and E.S.; formal analysis, Y.Q.; investigation, J.R.; writing—original draft preparation, J.R.; writing—review and editing, H.W.; visualization, Z.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

5. Yue, Y.; Wang, R.; Ma, D.Q.; Tian, J.F.; Zhang, X.Y.; Jing, Q.; Ma, M.Z.; Liu, R.P. Fatigue behavior of a Zr-based bulk metallic glass under uniaxial tension–tension and three-point bending loading mode. Intermetallics 2015, 60, 86–91. [CrossRef]
19. Montagnon, A.; Audurier, V.; Tomas, C. Influence of pre-existing dislocations on the pop-in phenomenon during nanoindentation in MgO. Acta Mater. 2013, 61, 4778–4786. [CrossRef]


