Analysis of Irradiation Induced Defect Clusterization for Zr-1%Nb Alloy Using Atomistic Simulation

M. R. Basaadat*, M. Payami, S. Sheikhi

Physics and Accelerators Research School, Nuclear Science and Technology Research Institute, AEOI, B. O. Box: 1439951113, Tehran, Iran.

ABSTRACT

Nuclear-grade zirconium alloys' properties are very similar to those of pure zirconium (Zr) because in most cases they contain more than 95% of Zr atoms. They have extensive applications in the nuclear industry, especially in fuel cladding. In this work, for the atomic simulations, we have used an ADP model interatomic potential. The calculated lattice properties of Zr-1%Nb show a very good agreement with experiments. Investigation of the possibility of a di-vacancy formation showed that it is possible only for the first and second nearest neighbor positions. It shows that at zero pressure, the Nb atoms in the alloy tend to join and create Nb clusters. However, under external pressure, the Nb clusters become less stable, tending to decay into smaller ones.

Keywords: Zirconium-Niobium alloy; Defect, Di-vacancy; Niobium Clusters; Pressure.

1. Introductions

Low neutron-capture cross-section, high water corrosion resistance, and appropriate mechanical properties of zirconium and its alloys with niobium make them suitable materials to be used in the core and fuel cladding components of water-cooled nuclear reactors [1-4]. Since these components are subject to continuous irradiation with energetic particles, the study of the effects of crystal defects on the properties of these components is a very pertinent subject in nuclear materials research.

One of the properties that are highly sensitive to crystal defects is the mechanical properties.

According to available data, there are three phases for zirconium crystalline state: α-phase (<863 °C), β-phase (> 863°C), and ω-phase (under 2-7 GPa ambient pressure) [5-6]. Due to the very low concentration of Nb impurities in Zr-Nb alloys, their lattice properties are largely determined by the zirconium impurities. It is well-known that the low-Nb content is important to prevent these alloys from corrosion and hydrogenation[7]. Zr-1%Nb has a hexagonal close-packed (HCP) structure at low temperatures with a homogeneous distribution of Niobium atoms. Vacancies and other defects are

formed when energetic particles collide with the atoms in the Zr-Nb alloy. Especially, under irradiation, the Nb atoms may join together to make Nb-clusters. The macroscopic properties of the Zr-Nb alloy are highly dependent on the micro-structural evolution of atoms as well as on other parameters such as temperature and pressure. Extensive research has already been conducted on the properties of zirconium-niobium alloys. For example, the evolution of mechanical properties with defects has been studied by some of the present authors[8-9]; the vacancy formation and self-interstitial clusterization under irradiation for pure zirconium have been studied by Maxwell and coworkers[10]; the mechanical properties of zirconium alloys and zirconium hydrides were studied by Weck and his coworkers[11]; according to Singh and colleagues, the fracture behavior of bi-crystalline zirconium-niobium alloys was examined with different niobium percentages[12]. Additional studies on the properties of Zr-Nb alloy and similar materials can be found in the literature [13-20].

Despite these extensive studies, there remain a lot of open questions that are important and worthstudying. In this work, we have studied the clusterization effect of Nb atoms in Zr-1%Nb under irradiation and the possibility of void formation from joining single-atom vacancies. In the first step, the lattice properties, vacancy formation energy (VFE), and self-interstitial formation energy (SIFE) of pure zirconium have been investigated. In the next step, the di-vacancy binding energy has been calculated to check the possibility of joining the vacancies to produce a vacancy cluster. To perceive the stability of those clusters, the impurity formation energies (IFE) of niobium clusters have been calculated in the next step. Finally, the effect of pressure on the stability of niobium clusters has been investigated.

Here is the organizational structure of the paper.The second section is devoted to theories and computational details; the results have been discussed in the third section, and we conclude this study in the final section.

2. Theories and Computational Details

The study of different defect production in Zr-1%Nb alloy was carried out by using the molecular static (MS) engine of LAMMPS code packages [21]. The interatomic potential used for the Zr–Nb binary system was an angular-dependent potential (ADP) [22]. This kind of interatomic model potential has been mostly used for metals and metal alloys and it is a generalization of an embedded-atom model (EAM) potential that includes both dipole and quadrupole distortions of the local environment of an atom which has been shown to reproduce a wide range of properties [8]. The convergency of the size dependence of the simulation box for the calculation of impurity formation energy has been achieved for 2592 atoms in a $3\times3\times3$ supercell composed of the unit cell with 96 atoms. In addition to checking the validity of this test, the chemical potential of nickel was also determined. This study has been conducted at a temperature of zero. For the optimization of the geometries, the conjugate gradient (CG) method has been used so that the forces on atoms vanish and the residual stress on the box is of the order of 0.1 Kbar.

3. Results and Discussion
Lattice Structure Properties

Applying the CG method, the lattice parameters of pure-Zr have been obtained as a=3.188, and c=5.206 Å in very good agreement with experiments (3.232, 5.149 Å [23]). Each unit cell for Zr-1%Nb contains 96 atoms (95 Zr and 1 Nb atoms) with HCP structure, and the equilibrium lattice parameters for this unit cell are determined as 12.856 and 15.360 Å (Fig 1). Vacancy and self-interstitial formation energies for pure Zr crystal have also been obtained as 1.90, 2.76 eV

respectively, which are consistent with experimental values (> 1eV [24]) and DFT (2.75 eV [25]). According to this data, the Frenkel pair (FP) formation energy (FPFE), which is defined as the sum of VFE and SIFE, is determined as 4.66 eV. Even though the vacancy formation happens at low temperatures or low-energy irradiation conditions, the high value for FPFE indicates that the formation of FP is not possible with only increasing the temperature, and it needs external high-energy irradiation sources.
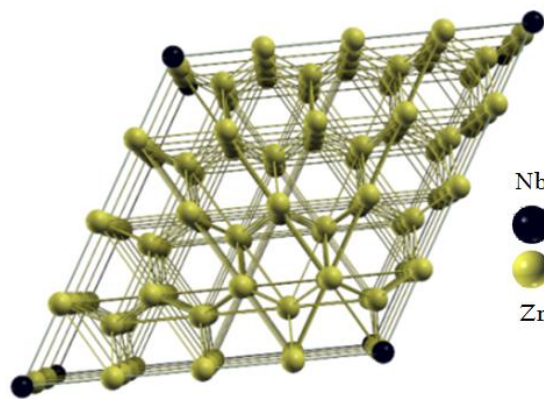

Fig. 1. Zr-1%Nb alloy structures at low temperatures.

Di-vacancy Binding Energy

In this section, in order to study the clusterization of vacancies, the binding energies of two vacancies located at different positions have been calculated. The binding energy for a vacancy cluster is defined as the difference between two separate vacancy formation energies and a di-vacancy cluster formation energy [26]:

$$E^b(V_2) = 2E^f(V_1) - E^f(V_2) = 2E(V_1) - E(V_2) - E(bulk) \qquad (1)$$

where $E(V_1)$, $E(V_2)$, and $E(bulk)$ are the energies of the system with one, two, and without any vacancies respectively. The positive value for the binding energy indicates that the interaction between two vacancies is attractive, leading to the formation of a di-vacancy. On the other hand, the negative value implies that the two vacancies in the structure would not join to make the cluster.

In Fig 2, we have specified five nearest neighbor lattice positions; the reference atom at the origin (V) and the 5 different nearest neighbors are indicated by N1 to N5. For each nearest neighbor, the formation energy has been calculated. The results show that the binding energies for "N1" and "N2" positions (1st and 2nd nearest neighbors) were positive and others were negative. In other words, if the second single-atom vacancy is located at the 1st and 2nd nearest neighbors, the di-vacancy formation is energetically possible.
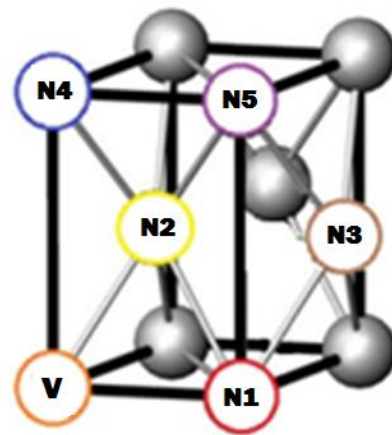

Fig. 2. The first (V) and second vacancy positions (N1 to N5) in the HCP zirconium structure; N1 to N5 refer to 1st to 5th nearest neighbor structure positions.

The Nb-Cluster stability

In this section, the formation energies of Nb-clusters with the different numbers of constituent niobium atoms have been calculated. Six kinds of clusters with 1, 2, 3, 4, 8, and 9 niobium atoms have been considered. The structure with 1 Nb atom (Nb_1 cluster) is the same as that in homogeneous Zr-1%Nb alloy. For Nb_2 cluster, two Nb atoms with minimum distance, like a dumbbell was considered. Nb_3 cluster was the only one with minimum interatomic distances having a minimum area. Nb_4 cluster was composed of four nearest neighbor Nb atoms having minimum possible volume. Nb_8 cluster was modeled by replacing 8 nearest neighbor atoms in pure zirconium lattice, and finally, the Nb_9 cluster was modeled by a

body-centered cubic (BCC) structure embedded inside the HCP zirconium structure (figure 3).

The formation energy of an Nb_n cluster inside a zirconium structure is defined by:

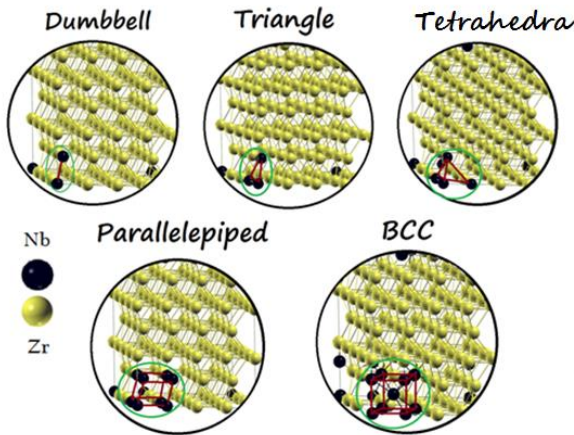$$E_{Imp}{}^f = E_{H+Imp}(N) - nE_i - \frac{N-n}{N}E_P(N) \qquad (2)$$

Fig. 3. Nb_n clusters with different sizes inside the zirconium structure.

Where $E_{imp}{}^f$ is Impurity Formation Energy (IFE), E_{H+imp} is the energy of the system with impurity, E_i is the chemical potential of the impurity atom and E_p is the energy of the perfect system with N atoms. n is the number of Nb constituent atoms of the cluster. The calculated results of IFE for the above-mentioned five cluster is shown in figure 4.
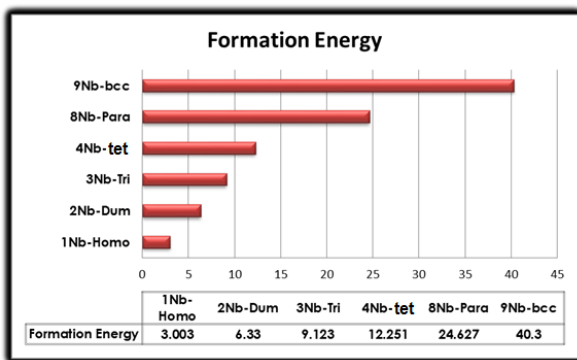

Fig. 4. IFE for clusters with the different numbers of Nb atoms.

The results show that the IFE increases with n. Inspecting the IFE values show that Nb_9 has the highest value among all other clusters. To find this most favored Nb cluster size, for the binding energies (BE) [1] and formation volumes we use the following relations [25]:

$$E_{Bind} = E_{xy}^f - (E_x^f + E_y^f) \qquad (3)$$

$$V_f = (V' - V)/N_{Imp} \qquad (4)$$

Where E_{Bind} is binding energy, $E_{XY}{}^f$ is the formation energy of the cluster, and E_x^f, E_Y^f are the formation energy of two elements that make the cluster. V_f, V, and V' are the formation volume, and structure volume without Nb and with Nb respectively. N_{imp} is the number of Nb (as impurity) in the structure. The above formulas can be generalized to the general case of homogeneously distributed $n_1Nb_x + n_2Nb_y + n_3Nb_z + \cdots$ clusters with the constraint $n_1x + n_2y + n_3z + \cdots = n$ and with n as the total number of Nb atoms in the simulation box. For example, if we consider as $n = 9$ to be the total Nb atoms in the box, one of the possible configurations is obtained for the combination $(n_1 = 0, x = 0, n_2 = 3, y = 3)$. Using the above-mentioned relations, the BEs and formation volumes of the Nb clusters were calculated for a subset of possible configurations and the results are tabulated in Table 1. The positive value for the BE means that the cluster fragments tend to attract each other, while for the negative values, they tend to repel each other.

Inspecting the values in Table 1, the most important conclusion is that the Nb atoms tend to combine into clusters than stay in atomized forms. Since the binding energies of the two configurations are compared to those of the first-row configuration in Table 1, the reference energy is zero.Secondly, because of the highest BE value

Table 1. Binding Energy [in eV] and formation volume [in Å^3] per one Nb atom in clusters.

| Configurations	BE (eV)	Cluster Type	Formation volume (Å^3)
$9Nb_1$	0.000	Homo	-5.100
$1Nb_1+4Nb_2$	0.324	Dumbbell	-4.840
$3Nb_3$	0.114	Triangle	-4.524
$1Nb_1+2Nb_4$	0.239	Tetrahedral	-4.363
$1Nb_1+1Nb_8$	0.603	Parallelepiped	-4.640
$1Nb_9$	13.273	BCC	17.300

for the Nb_9 configuration, one concludes that the fate of Nb atoms in the alloy is to gather to form large Nb clusters with BCC structure, which in turn will degrade the mechanical properties of the alloy. Moreover, comparing the BE for other configurations we conclude thatthe Nb_3 clusters may decay into Nb_2 clusters but the reverse process is rare. It is interesting to note that the large Nb clusters embedded within the HCP zirconium structure take the BCC structure. Regarding the formation volume, the negative sign implies a volume decrease compared to pure zirconium crystal.

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volume decrease compared to pure zirconium crystal.

The effect of pressure on Nb-cluster stability

In this section, the effect of pressure on the stability of 33the Nb cluster has been studied. To this end, we have simulated the system under external pressures from 1 to 6 Gpa with 1 Gpa step. The results of binding energies are shown in figure 5. Inspecting the values in figure 5, we see that because of the negative values for the BE, all clusters of different sizes tend to decay into smaller size ones. Because of the large variation for the Nb_9 BCC configuration, we have not included it in figure 5, but its BE changes from 13.273 (for P=0) to about -13 eV/atom (for P=6 Gpa). Experimentally, the swelling of the fuel inside the cladding applies pressures on the contact areas, and one may set up a spectroscopic experiment to verify the existence of smaller size Nb clusters in the contact regions than in other regions.
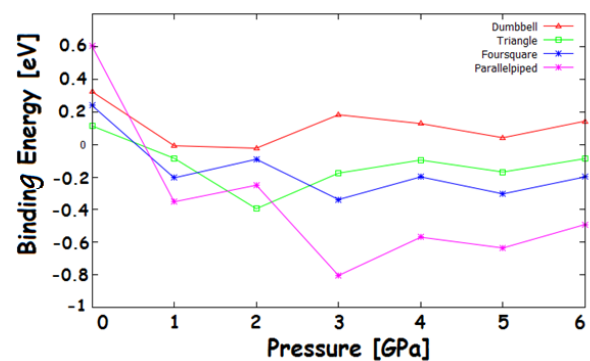
Fig. 5. BE for 2, 3, 4 and 8-Nb clusters in eV.

4. Conclusion

In this study, using a ADP model interatomic potential, the lattice properties of Zr-1%Nb alloy were studied and the results obtained showed very good agreement with experiments. In the next step, the di-vacancy formation from two separate single-atom vacancies has been investigated and it was shown that the di-vacancy formation is possible for only the 1st and 2nd nearest neighbor positions. In the third step, the stabilities of Nb clusters were studied and the results showed that at zero external pressure the Nb atoms in cluster forms were more stable than in the atomized state. On the other hand, it was shown that under external pressure, the Nb clusters become less stable, tending to decay into smaller ones, which may be experimentally verified by spectroscopic study of the fuel cladding with swelled fuel at contact regions. Last but not least, it is necessary to repeat the whole procedure for each value of the Nb percentage in order to see how they affect the properties. In Ref. [8], the authors have already investigated some properties for different values of Nb concentrations.

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