Molecular dynamics for Ti-Ni dimer adsorbed on pristine and defective graphene

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Abstract. Motivated by the oxidation and corrosion processes of the nitinol alloy that has been used in biological applications, we show initial first principles calculations for the interaction of the Ti-Ni dimer, the simplest nitinol alloy, with a graphene layer, (gl). We have selected the graphene layer for the interaction, because our results can be compared with similar results for the interaction of many substances with a graphitic system as the gl. The results of several relaxations of the system Ti-Ni-gl shows that the dimer has been adsorbed to the gl. Temperatures of 300, 800, 1100 and 1300 K are not enough to desorb the dimer from the gl, these results are obtained from the molecular dynamics for those temperatures. The metallic character of the system is obtained from the density of states and projected density of states. Similar results are obtained for the interaction of the dimer when there are one or two carbon vacancies on the gl.

1. Introduction
The aim of the project behind this study is the explanation from first principles for the oxidation and corrosion of the nitinol alloy [1], a very attractive and useful material for several applications. Because the simplest nitinol composition is formed with one Ni and one Ti atom, we use the dimer Ti-Ni as the initial system to be studied. We explore the response of the dimer when it is approached to a graphitic material, in this case a piece of pristine and defective gl. Several initial orientations of the dimer respect to the gl have been studied. After the adsorption process of the dimer on the pristine and defective gl is confirmed in general, also, with one and two vacancies, we have selected the system with two closer vacancies to study the effect of temperature on the possible desorption of the dimer, from the gl, by means of molecular dynamics for different temperatures. The results given here can be used as reference when a bigger nitinol system or with different composition, could interact with a bigger graphitic system.

2. Nitinol
Nitinol is a metal alloy of nickel and titanium, with the elements present in nearly equal atomic percentages. The principal characteristics of this material are a). The shape memory effect, that can be seen when it is deformed at a given temperature, remains in its deformed state and shape if the external force is removed and finally can recover its initial undeformed shape if it is heated above its transformation temperature. b) Superelasticity of the alloy, that can be described as the ability of this material to undergo large deformations and recover the initial shape once the external force is removed. The shape memory effect has been seen also in Cu-Zn and gold-cadmium alloys

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[2]. With these quality's there are many practical applications, such as those in biomedicine, using also, the biocompatibility with the human beam [3].

3. Computer method

The computer simulations for the system Ti-Ni-gl were done with Quantum espresso computer package [4], because the electronic-structure calculations can be done with this free software, using pseudopotentials, useful also, to reduce the computer time calculations. The software is based on DFT (density-functional theory), plane waves, and pseudopotentials. We have designed an optimized a graphene layer with 32 carbon atoms, some of them are illustrated in figure 1. Our system is periodic with 25 a.u. between parallel graphene layers and 18.684 a.u. for the supercell parameter of the system. This is the distance between closer Ti-Ni dimers, between two adjacent supercells. Also, a layer with one and two adjacent carbon vacancies are considered with the Ti-Ni dimer in different initial configurations (see figure 1). The cell parameter for graphene is 4.6710 a.u. We used norm conserving pseudopotentials in the calculations, C.pbe-hgh.UPF, Ni.starls-pbe-sp-mt_gigapaw.UPF and Ti.upf.

![Figure 1. Points where the Ti-Ni dimer is placed, perpendicularly above the graphene layer (A, B, C) and parallel to the graphene layer (D). Both cases were considered, Ni or Ti closer to the graphene layer. The results shown in this work are for Ti closer to the gl, because the Ti-Ni dimer is adsorbed closer to the gl than the other case, when the Ni atom in the dimer, is closer to the gl. The energy curves in function of the distance between the dimer and the gl, for orientations A, B, C and D, have a similar behavior as those obtained previously [7], for the adsorption of molecular hydrogen on graphene.](image)

4. Calculations

For the dimer Ti-Ni we obtained 4.18 a.u. for the interatomic distance. This is approximately 8.96 % bigger than the reported by Kai [5]. They show that for different DFT (density functional theory) theoretical calculations, the Ti-Ni bond lengths is between 201 and 207 pm, but they don’t give any experimental value for that distance. Experimental diatomic bond lengths for Ti with H, O and Cl are respectively 1.785, 1.62 and 2.265 Å [8].

For each one of the orientations of the Ti-Ni dimer, as given in figure 1, we made several static calculations putting the dimer at different distances above the frozen coordinates of the gl but maintaining always 4.18 a.u. as the interatomic distance for the dimer. A minimal energy was obtained from the plot of the energy values as a function of the distance of the dimer to the graphene plane for all the studied configurations. The next step in the sequence of calculations was the relaxation process of the entire system. This is the distance between closer Ti-Ni dimers, between two adjacent supercells. Also, a layer with one and two adjacent carbon vacancies are considered with the Ti-Ni dimer in different initial configurations (see figure 1). The cell parameter for graphene is 4.6710 a.u. We used norm conserving pseudopotentials in the calculations, C.pbe-hgh.UPF, Ni.starls-pbe-sp-mt_gigapaw.UPF and Ti.upf.

5. Results and discussion for the graphene layer with two closer carbon vacancies.

Figure 2 shows the final configuration of the relaxation of the system Ti-Ni-gl. when the Ti atom points closer to the center of the double vacancy gl. The distance Ti-Ni is 4.3206 a.u., a little bigger than the calculated equilibrium distance for the dimer, 4.18 a.u. Ti atom makes bonds with lengths 3.9305 or 3.9306 a.u. with four carbon atoms around the double vacancy. Because the approach of the dimer in the relaxation occurs along the perpendicular line to the gl, this final configuration is of high symmetry. We used as initial state in the molecular dynamics study the configuration of figure 2. Four different sequences of molecular dynamics have done, for room temperature 300, 800, 1100 and 1300 K. The purpose of these is to see if the dimer is broken or desorbed from the graphitic surface at a certain temperature. These have been very consuming time calculations. The results are in figure 3.
The red curve is the result for room temperature. As can be seen the energy has oscillations in an interval no longer than 0.02 Ry. The dimer remains attached to the gl. This is shown in figure 4. The dimer moves always above the defective gl, changing the orientation of the dimer. The symmetry is broken because distances from the Ti atom to the carbon atoms changes a little, as both panels of the figure suggests. The curves for 800 and 1300 K (green and violet curves), have bigger oscillations, but around step number 600 both curves get closer to the room temperature curve. The oscillations are bigger for 1300 than for 800 K, as could be expected. These results say that due to the temperature, there are oscillations in the adsorption energy such as in the forces between the dimer and the gl. The more intriguing result is for 1100 K. As has been said before, the four molecular dynamics processes begin from the same state, so we can see the effect only of the temperature. With the tendency of the energy in the last steps for 1100 K, this curve could be closer to the room temperature curve. By this reason, molecular dynamics study continues up to date.

Figure 2. Final relaxed configuration for Ti-Ni dimer adsorbed above a pair of closer carbon vacancies on the graphene layer. This is the initial configuration for the molecular dynamics of the system. The distance Ti-Ni is 4.3206 a.u. Ti atom makes bonds with four carbon atoms around the double vacancy. The distance Ti-C is close to 3.93 a.u.

Figure 3. Energy (Ry) as a function of the step number for the molecular dynamics of the Ti-Ni dimer adsorbed on the graphene layer with two closer carbon vacancies.
Figure 4. Molecular dynamics configuration of the system Ti-Ni-gl with the same vacancies as in figure 2, for temperature $T = 300$ K, after 1268 relaxation steps. The distance Ti-Ni is 4.4297 a.u. Ti atom makes bonds with four carbon atoms around the double vacancy. The distance Ti-C is between 3.8419 and 4.0068 a.u.

In a similar way, figures 5, 6 and 7 gives the configurations for temperatures 800, 1100 and 1300 K. The increase in temperature facilitates a greater movement of the Ti-Ni dimer on the graphene sheet. This is deduced comparing the distances between all the atoms.

Figure 5. Molecular dynamics configuration of the system Ti-Ni-gl with the same vacancies as in figure 2, for temperature $T = 800$ K, after relaxation 867 steps. The distance Ti-Ni is 4.5013 a.u. Ti atom makes bonds with four carbon atoms around the double vacancy. The distance Ti-C is between 3.87 and 4.14 a.u.

Figure 6. Molecular dynamics configuration of the system Ti-Ni-graphene layer with the same vacancies as in figure 2, for temperature $T = 1100$ K, after 501 steps. The distance Ti-Ni is 4.6011 a.u. Ti atom makes bonds with four carbon atoms around the double vacancy but also Ni atom makes bonds with two carbon atoms. The distance Ti-C is between 3.71 and 4.03 a.u. The distance Ni-C is close to 4.03 a.u.

Figure 7. Molecular dynamics configuration of the system Ti-Ni-graphene layer with the same vacancies as in figure 2, for temperature $T = 1300$ K, after 972 steps. The distance Ti-Ni is 4.8710 a.u. Ti atom makes bonds with four carbon atoms around the double vacancy. The distance Ti-C is between 3.74 and 4.23 a.u.
To obtain the density of states (DOS) and the projected density of states (PDOS), for the final configuration of figure 2, we have considered 150 K points along the high symmetry path Γ-K-M-Γ of the reciprocal lattice of the system and made first, a self-consistent calculation (scf), next, the DOS calculation was done using the 91 electronic bands obtained in the previous calculation and the last calculation was to obtain the PDOS. Figure 8 shows that the system is metallic because both results, DOS and PDOS are nonzero around the fermi level (E = 0 eV). On the contrary there are occupied levels up to energies close to 3.12 eV.

![Figure 8. DOS (left panel) and PDOS (right panel) for the equilibrium configuration shown in figure 2.](image)

The PDOS file, besides the first column, the energy E(eV), has four more: DOS with spin up, DOS with spin down, PDOS with spin up and PDOS with spin down, those are plotted respectively with curves of color red, green, blue and violet. This result means that DOS with spin up and DOS with spin down have the same values. The same occurs for PDOS with spin up and PDOS with spin down. By this reason it appears only green and violet curves. This agrees whit the numerical values of the PDOS file. The last picks in the PDOS results are around the energy 2.691eV, with values 4.43 and 2.57 (states/energy).

The Lowdin charges obtained for the equilibrium relaxed configuration shown in figure 2 are in Table 1. The valence charge is 4.0, 12.0 and 19.0 for C, Ti and Ni atoms, respectively, while the Pauling electronegativity is respectively, 2.55, 1.54 and 1.9 for C, Ti and Ni atoms. The total charge of Ti has been reduced to 11.0656. Then, Ti donates a total charge of 0.9344, 0.6932 of one electron charge goes to the four C atoms making bond with Ti, and a charge of 0.2193 is transferred to the other carbon atoms of the graphene layer. Only 0.0219 of one electron charge is received by Ni atom. These results agree with the fact that C (Ti) atom has the larger (smaller) electronegativity of the atoms involved in the Ti-Ni-gl studied system. On the other side, Ni has a relatively small change in total charge, in principle expected, because is farer from the graphene layer and because the distance Ti-Ni is 4.3206 a.u., a little more than the equilibrium calculated distance, given before, 4.18 a.u.

Table 1. Lowdin charge and total polarization for C, Ti and Ni atoms for the configuration of figure 2. The data for C atoms is very nearly the same for the four C atoms around the double vacancy, due to the high symmetry of that configuration.

|        | s    | p    | d    |
|--------|------|------|------|
| C: total charge | 4.1733 | 1.0627 | 3.1106 | 0.0 |
| spin up | 2.0868 | 0.5314 | 1.5554 | 0.0 |
| spin down | 2.0866 | 0.5313 | 1.5552 | 0.0 |
| polarization | 0.0002 | 0.0000 | 0.0002 | 0.0 |
| Ti: total charge | 11.0656 | 2.5392 | 5.9381 | 2.5883 |
| spin up | 5.5329 | 1.2696 | 2.9691 | 1.2942 |
| spin down | 5.5327 | 1.2696 | 2.9691 | 1.2941 |
6. Conclusions

Sequences of different kind of calculations shows that the desorption of the Ti-Ni dimer on pristine and defective graphene with one or two vacancies doesn’t occur at lest up to temperatures of 1300 K. Perhaps some little changes could be seen for the adsorption of the dimer on a site with only one carbon vacancy. Still, metallic behavior is expected for that case, this will be reported latter. One next step in the sequence of calculations that are under consideration, is the study of a thin nitinol nanoribbon (4 to 6 layers) above the same graphitic layer as in this work. This will be reported elsewhere.

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