Computer Simulation of TiAlN Coatings and Its Analogues on Iron Surface

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Abstract. The strength of various variants of the TiAlN coating and its analogues on the iron surface is studied by using quantum chemistry methods. As a computer model, we consider a system of 5.5 atomic layers, 3 of which imitate the base (metallic iron), and 2.5 layers imitate its coating. The dependence of the coating strength on its chemical composition and the mutual arrangement of atoms of various elements is studied. It follows from the calculations that the strength of the optimal TiAlN coating is almost equal to the strength of the surface of pure iron. The proposed model was used also to study the role of the coating in protecting the iron surface from oxidation. It is shown that the considered coating variants practically do not undergo oxygen corrosion, which is one of the reasons for their high efficiency.

1. Introduction

Technologies for applying nanometer coatings to metal surfaces, including cutting tools and parts of tribotechnical devices, which have appeared in the last two decades, make it possible to protect reliably these surfaces from wear and destruction. These technologies include magnetron sputtering, physical vapour deposition (PVD), and chemical vapour deposition (CVD) [1-3]. One of the challenges arising from the use of these technologies is to find the most effective coating compositions consisting of several chemical elements. Since the number of chemical elements and their combinations can be very large, it is advisable to pre-analyse the various coating options to choose the optimal ones.

For this purpose, it is possible to use modern quantum chemical methods that allow us to study the strength characteristics of such coatings on metals with a high accuracy comparable to the accuracy of instrument measurements. In such studies, it is convenient to compare a large number of variants of the studied objects, which is usually difficult or impossible to do in the case of real samples that are tested in real experiments.

One of the coating options that are currently being actively investigated experimentally and theoretically are TiAlN films and their analogues. A number of publications (see, for example, [4-13]) have shown the high efficiency of such coatings in protecting the iron surface from destruction.

In this paper, a quantum chemical study of the TiAlN coating and its analogues is carried out, possible variants of the distribution of elements in them are considered, conclusions about the strength of such coatings are made, and considerations on the optimal variants of these coatings are presented.
2. Geometry of the TiAlN system on the iron surface

Figure 1 shows one of the possible variants of the distribution of titanium, aluminium, and nitrogen atoms on the surface of iron with the crystallographic axis [011] corresponding to the densest packing of atoms.

Initially, proceeding from general considerations, we prepropose to study the phenomenon of self-organization of such a structure on the iron surface and evaluate its strength properties. The atoms and ions of all three elements Ti, Al, N have individual sizes, which makes it possible to create cell structures with a high density and a period coinciding with the period of the iron crystal lattice. Within the model under study we took into account that the parameters of the iron lattice in the direction [011] are 0.406 and 0.287 nm.

![Figure 1. Atomic structure of the TiAlN compound on the Fe surface [011]. 9 vertically arranged elementary cells of the surface layer are shown. Each cell consists of 6 Fe atoms, 2 Ti atoms, 2 N atoms, and one Al atom.](image)

Let’s consider this situation in more detail. The phenomenologically determined (so-called effective) radii of neutral atoms of Ti, Al, N are: R(Ti) = 0.146 nm, R(Al) = 0.143 nm, R(N) = 0.071 nm (by L. Pauling). These data show that the radii of the titanium and aluminium atoms are close to each other, and the radius of the nitrogen atom is about half as small. Such differences in the size of atoms, alternating in the coating, lead to the fact that the atomic layers are not flat, they have a wavy relief.

When packing (laying) Ti, Al, N atoms on a free and almost flat surface of iron, these atoms, due to the force fields on the iron surface, are grouped into cells. We accept that parameters of these cells in horizontal directions are identical to the corresponding parameters of iron crystal cells. Ultimately, the structure with the lowest possible energy appears on the surface. With a uniform distribution of deposited atoms on the surface of iron cells, groups of these atoms are located above each of the cells, optimally filling their surface. The main principle in forming such a structure, of course, is the minimum of the total energy of the system.

For greater clarity of the process of laying atoms and a better understanding of its results, we divided the entire process into two stages. In the first stage, we consider the laying of neutral Ti, Al, and N atoms. To fill the surface of iron as tightly as possible, atoms with smaller sizes (in this case, nitrogen atoms) must be located between larger atoms (i.e., titanium and aluminium atoms). Figure 1 shows the relative position of the atoms based on this condition.

At the second stage of packing, we should take into account the occurrence of chemical bonds between the packing atoms. The appearance of bonds leads to a decrease in the energy of the system. Due to the different electronegativity of the elements, some of electrons are transferred from the metal.
atoms Ti and Al to the N atoms, and there will be ions Ti$^{2+}$, Al$^{3+}$ and N$^{3-}$ with radically changed radii of 0.078, 0.057 and 0.171 nm, respectively.

Now, on the contrary, radii of metal ions are noticeably smaller than the radius of the nitrogen ion. These changes in atomic dimensions lead to significant compression of the system along the vertical axis: instead of the height of 0.360 nm of the layer of coating atoms, we get a value of 0.306 nm (a decrease of 15%). Note that the compression of the system along the horizontal axes in contrast to the vertical axis does not occur due to the rigid connection of the formed coating with the underlying solid matrix of iron atoms. As a result, such vertically compressed layers have increased strength, providing the overall strength of the coating surface of iron. The results of the above phenomenological assessment of the strength of the system based on data on the sizes of atoms are confirmed below by calculations using quantum chemical methods.

3. Calculations of system strength
To study the strength properties of the TiAlN coating, we estimated the energy required to separate the cells of this fragment into two parts, as shown in figure 2. Such separation can occur under the influence of intensive mechanical or heat effect.

![Figure 2. Separating the coating layer from the protected metal](image)

The separation energy per cell was calculated using the formula:

$$\Delta E = E_1 - (E_2 + E_3),$$  \hspace{1cm} (1)

where $E_1$ is the energy of the cell of the initial system, $E_2$ and $E_3$ are the energies of its two parts formed as a result of the separation. We calculated these values with the help of the ADF software package [14] based on the DFT approximation [15, 16]. In this case, we used the scheme that was applied earlier when calculating the strength of grain boundaries in iron [17-20].

4. Selecting chemical elements and their surface compounds to create the most durable coating on iron
During the calculations, we changed the chemical composition and arrangement of atoms of individual elements in the structure in order to choose the most durable coating. Such changes were made to the composition of elements that would not radically change the structure and properties of the system. In various variants, nitrogen atoms were partially or completely replaced by boron and carbon atoms, which are neighbors of nitrogen in the periodic table. The titanium and nitrogen atoms rearranged in the structure shown in figure 1, suggesting that they could replace each other in their initial positions.

For each of these structures, calculations were performed using the same algorithm. The calculation results are shown in table 1. The elements in each of the chemical formulas presented in the
"composition" column are listed in the following order. First, the elements at the bottom of the flowchart are listed sequentially, and then the elements at the top of the flowchart. For example, in the formula 6Fe+2Ti+N+B+Al, relating to the composition of one of the cell variants, it is assumed that there are 6 Fe atoms in the lower part of the cell, and 2 Ti atoms above. These Ti atoms are located along a sinuous surface (try to imagine this surface in the figure). Above the recesses of this surface there are N atoms and, finally, in the uppermost position there are B and Al atoms.

| Atomic composition | E (total) | E1 (6Fe) | E2 | ΔE |
|--------------------|----------|----------|----|----|
| 6Fe+2Ti+2N+Al      | -97.28   | -54.91   | -37.70 | 4.67 |
| 6Fe+2Ti+2B+Al      | -87.17   | «         | -28.20 | 4.06 |
| 6Fe+2Ti+N+B+Al     | -93.06   | «         | -33.74 | 4.41 |
| 6Fe+2Ti+B+N+Al     | -91.27   | «         | -32.15 | 4.21 |
| 6Fe+2Ti+2C+Al      | -93.86   | «         | -34.74 | 4.21 |
| 6Fe+2Ti+C+B+Al     | -91.12   | «         | -32.10 | 4.11 |
| 6Fe+2Ti+C+N+Al     | -95.26   | «         | -36.05 | 4.30 |
| 6Fe+2Ti+B+C+Al     | -89.95   | «         | -30.90 | 4.14 |
| 6Fe+2Ti+N+C+Al     | -95.85   | «         | -36.31 | 4.63 |
| 6Fe+2Ti+2N+Ti      | -101.62  | «         | -42.21 | 4.50 |
| 6Fe+2Al+2N+Al      | -89.64   | «         | -30.28 | 4.45 |
| 10Fe               | -94.47   | -54.71   | -34.98 | 4.78 |

Within the same model, energy values were calculated for the Fe [011] structure consisting of pure iron. In the case of such a homogeneous system, the relief of the layers is absent. Figure 3 shows the decay of the 5-atomic system into 3- and 2-atomic plane layers. The energy values of 5-, 3-, and 2-atomic flat layers are presented in the 12-th row of table 1. Using these data, we find that the energy of decay of one 5-layer cell of pure iron into 3- and 2-layer cells is 4.78 eV, which is slightly higher (by 2%) than the decay energy of a cell with a TiAlN coating (see the 1-st row of table 1).

Thus, we conclude that the surface strength of pure iron is slightly higher than that of TiAlN-coated iron. However, it should be noted that pure iron, being a chemically active material, corrodes easily in a humid or any other aggressive environment, and must be protected from this environment. In this case, an additional coating is necessary. The TiAlN coating does not need such additional protection, since it is slightly corrosive due to its dense structure.
5. Iron surface protection from oxidation

In this section, we use simple models to assess how effectively the coating options under consideration protect the iron surface from oxidation in an oxygen atmosphere. To do this, we will consider two models that differ in the fact that in the first model oxygen atoms are located directly on the surface of iron (Fig. 4), and in the second one these atoms are located on the coated surface (figure 5). The task is to evaluate the strength of various variants of these configurations.

When simulating a system containing oxygen on the iron surface, we looked for a configuration with minimal energy. This condition corresponds to the position of oxygen atoms above the internodes in the iron. Then the variants of the system decay were considered. The lowest decay energy corresponded to the configuration shown in the right part of figure 4. It is turned out that the appearance of oxygen on the surface of iron leads to a weakening of the bonds between the upper layer of iron atoms and the remaining array. The separation energy calculated in the framework of the presented model and related to one cell of the system was equal to 4.60 eV. In this case, the binding energy between the oxygen layer and the iron surface is 12 eV, which means that this bond is much stronger than the bond between neighboring layers in the iron itself (with $E=5.41$ eV).

![Figure 4. Separating the oxygen layer structure of iron surface](image)

Next, we consider the case when the iron surface has a TiAlN coating. Here, the state with the minimum energy of oxygen atoms corresponds to their position above the aluminum atoms (see figure 5). As a result of searching for the variant with the minimum decay energy of the system, we found the variant shown in the right part of figure 5. In this case, the decay energy per cell, equal to 1.8 eV. We see that this value is significantly less than the 4.60 eV required for the uncoated system to decay. Thus, applying a TiAlN coating to the iron surface dramatically increases the stability of the iron surface against destruction in an oxygen environment.

![Figure 5. Separating the oxygen layer from surface coated by TiAlN layer](image)
6. Conclusions
The calculations have shown that the energy values of different variants of the structure under study with different atomic composition and mutual arrangement of atoms of different elements differ significantly from each other. The range of these changes in the studied cases is from -42.21 eV to -30.28 eV (\(\Delta E = 11.93 \text{ eV}\)). However, the strength of these systems remains stable. It changes by no more than 0.56 eV, which is only 5% of the \(\Delta E\) value. As follows from our calculations, the coating of the composition 2Ti+2N+Al, shown in figure 1, has the highest strength among the coatings studied by us.

Calculations of the strength of the studied structures in an atmosphere containing oxygen showed that the presence of a TiAlN coating on the surface of iron significantly reduces the probability of its oxidation, which is probably one of the main advantages of such coatings.

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