# INTRODUCTION

Most modern structural or functional materials somehow consist some base element and alloying elements. For example, any steel contains an iron-carbon compound where iron is a base element and carbon is an alloying element. It is not necessary to say that steels are very common materials nowadays as construction materials, in medicine or rocket engineering, in nuclear power engineering and so on. The currently used corrosion-resistant and heat-resistant steels are classified according to their structure. Chromium steels of martensitic and ferritic-martensitic classes with small amount of carbon in it (about ), and chromium from 5 to 13% have increased corrosion resistance compared to pure iron. There are quite a lot of methods to protect surface against the corrosive effects of the environment. It can be the coating of varnishes, paints or other metals or it can be the creation of an inert atmosphere, or the oxidation or phosphating of the surface. By alloying the steel with chrome, corrosion-resistant (stainless) steel can be obtained. Such steel has a greater resistance to the corrosive effects of oxygen because the chromium atoms oxidize more strongly than the iron atoms.

It is known that in the presence of oxygen or an oxygen atmosphere, iron is oxidized []. In case where oxygen and iron begin to interact, oxygen "takes" electrons from the iron, thereby oxidizing it. Iron then transform into state. Such compound of iron and oxygen is stable. When there is a more complex system, such as oxygen atmosphere, and surface of clean iron (without other atoms or other compounds), the corrosive effect behavior becomes more complex. Oxygen oxidizes the surface, creating a primary oxide, in this case, since the iron-oxygen compound in the near-surface zone has already been created, the surface becomes passivated, i.e. the surface becomes protective. Strictly speaking frankly speaking, iron does not stop oxidizing, and the process slows down by itself and the diffusion comes into play. Oxygen, diffuses into the material, finds iron atoms under the surface which are not oxidized, thus the oxide grows inside the material. At high temperatures (𝑇> 570 °𝐶) an oxide film is formed containing three basic stable oxides: 𝐹𝑒𝑂 (wustite), 𝐹𝑒3𝑂4 (magnetite) and 𝐹𝑒2𝑂3 (hematite).

As mentioned earlier, alloying with chromium increases corrosion resistance. This is because a stable chromium oxide Cr2O3 is formed on the surface. Additional doping with aluminum allows further increase corrosion resistance []. A stable layer of α-Al2O3 is formed on the surface, rather than Cr2O3.

The studies on the oxidation of ferritic martensitic steels HT9, T91 at a temperature of and an oxygen concentration of 25 wt.% and 2 wt.% (for HT9 steel) and 25 ppb and 2 ppm (for steel T91) were carried out []. After 505 hours of aging in oxygen atmosphere, a stable oxide layer was formed on the samples. Depending on the concentration of oxygen, an oxide layer of different thickness was formed. Concentration of dissolved oxygen plays a main role in oxidation behavior. In the case aging in oxygen atmosphere with a concentration of 25 wt.% (25 ppb) a two-layer oxide was formed consisting of an outer layer of iron-enriched magnetite and an inner layer of chromium oxide consisting of spinel and ferrite. On those samples of steels that were kept in a medium of 2 wt.% (2 ppm), a hematite layer was also formed.

Similar results were obtained in [] where the HCM12A and NF616 steels were oxidized. After aging in an oxygen medium at 500 °C, the outer layer contained only Fe3O4, whereas the inner layer contained a mixture of Fe3O4 and FeCr2O4.

Direct tests of growth and stability of protective coatings require the use of complex equipment and considerable time, as well as significant financial costs. In this regard, methods of analytical and numerical modeling are widely used to evaluate the properties of coatings. One of the possible methods for studying the process of formation and growth of oxide at the atomic level is the use of computer simulation methods. Such methods have a number of advantages over classical experiments. Thus, it is possible to control all the parameters of the system (from the temperature to the charges of individual atoms), it is possible to observe the initial stages of oxidation, as well as the cheapness of research, which is a fundamental factor in modern science.

An experiment on the oxidation of pure iron with different orientations (100, 110, 111) at temperatures 300˚K (≈26 ˚С) and 900˚К (≈620˚С) for 1000 ps (1 ns) was carried out in []. In the early stages of oxidation of Fe with orientations <100>, <110> and <111>, oxygen transport predominates through the interstitial sites, which leads to non-stoichiometric (Fe1-xO) oxides. The authors observed a thickening of the iron lattice when oxygen was transferred into it. As the non-stoichiometry of the oxide increases, the passage of oxygen inside slows down, and the movement of iron cations to the surface increases.

Similar results on the oxidation of pure iron were obtained in []. It is established that the rate of growth of the oxide layer depends logarithmically on over time, and the limiting thickness is from 1 to 2 nm, depending on the orientation of the crystal. The stoichiometry of the oxide layer formed at room temperature indicates the presence of a nonstoichiometric oxide layer consisting of two phases: a FexOy surface layer with y / x ≈ 1.3-1.5 and a bulk layer with y / x ≈ 0.7-0, 8. It was found that this is directly related to the propagation of oxide growth through a thin film.

In paper [] authors carried out a study on the oxidation by water molecules of the surface of pure fcc-Fe and Fe-Cr systems. The calculations were performed using DFT methods, and as a consequence, the cell size was small. The modeling temperature was 561 ˚K (≈ 287 ˚С). The total simulation time was 1 ps. The surface structure of the Fe-Cr system differs from the structures of the pure iron system because of the high concentration of O, OH and H2O around the chromium atoms, which indicates a strong Cr-O bond. On the surface of the Fe-Cr system, an increase in the concentration of chromium atoms and also of oxygen atoms was observed, indicating that the film becomes protective.

# methodology

In accordance with the existing problem, the task is: "How does oxygen interact with iron with alloying additives?". This task should be divided into subtasks:

1. Molecular-static modeling of the interaction of oxygen with iron. This simulation allows us to calculate the binding energies of various alloying elements with oxygen and iron, as well as dissociation energy of oxygen molecules upon approach to the surface, and observe the passage of individual oxygen atoms along the iron lattice. Such a simulation allows one to find the configuration of an atomic system with a minimum energy at 0˚K;
2. Molecular-dynamic modeling of the formation and growth of oxide films. Such a method will allow to study the evolution of oxide growth at a certain temperature on the surface of iron.

The modeling of the dissociation of oxygen molecules over the surface was carried out by a «pulling» method, i.e. An oxygen molecule O2 was created above the surface of iron with a size of 30x30x38 Å at a distance ≈6 Å. At each step of the simulation, the lower atom of the molecule shifted in the direction of decreasing the z axis by a distance of 0.1 Å, after which the energy of the system was minimized. Thus, one of the atoms "stretched" to the surface, the second atom "pulled" to the first. For simulation, the ReaxFF potential with Fe / O support was used [].

To simulate the passage of oxygen along the iron lattice an oxygen atom O was created over the surface of iron with dimensions 30x30x38 Å at a distance of 2 Å. Before each step of minimizing the energy of the system, the atom shifted down along the z axis by a distance of 0.1 Å. The same potential was used for modeling, as in the previous case.

For calculations on the oxidation of the surface, we used the molecular dynamics method with the Verlet algorithm with a step of 1 fs. For simulated systems, a cell was created that was filled with atoms, then a certain number of atoms were removed, thereby creating a surface, above the surface there was a vacuum. In the cell, along the x and y axes, periodic boundaries were established to simulate an infinite surface. The lower 2 layers along the z axis were fixed, so an imitation of the existence of a "bulk" (an infinite material below the surface) was provided. Every 4 ps above the surface oxygen molecules were created and after that they were given some initial impulses randomly directed in space and having quantities generated in accordance with the Boltzmann distribution at the modeling temperature. Strictly speaking, in the model used, the oxygen density is much higher than in reality, but since oxygen molecules interact with the surface of the iron strictly individually, the use of high concentrations of oxygen in the gas phase is simply a way to accelerate the kinetics of oxidation, practically without affecting the physics of the process.

For calculations, the ReaxFF potential was used which made it possible to model systems with the presence of *Fe/Cr/O/Al* []. The simulation temperature was 650 °C. To maintain the temperature and the initial heating of the system, the Berendsen thermostat was used. The total simulation time was 200 ps.

To process the obtained results, the Ovito program was used, which allows to work with the output formats of the LAMMPS molecular dynamics package.

# RESULTS AND DISCUSSIONS

## Oxygen molecule dissociation

First of all, calculations were made of the dependence of the energy of the oxygen molecule on the distance to the free surface of the iron crystallite of the (001) type. Since the oxygen molecule can have different orientations, the calculations used molecules with three different orientations relative to the surface: diagonal, horizontal and vertical. All other orientations are all possible combinations of the orientations indicated above.

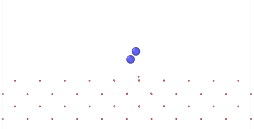


Fig - Oxygen molecule during approaching to the surface. Iron atoms are red, oxygen atoms are blue.

When the surface is reached by molecule it dissociates and then incorporated into the iron crystallite, which is accompanied by a sharp decrease of energy of the system. With the further passage of the oxygen atom (which has already lost the second atom near the surface), a periodic change in energy is observed, due to the displacement of the matrix atoms near the trajectory of the oxygen atom. Oxygen moves along the line which connect octahedral positions.

It should be noted that the results obtained in this paper are in good agreement with similar studies carried out using the density functional method with the approximation of local electron density (LDA). As can be seen from Fig, regardless of the method used, the oxygen molecule, as a result of interaction with the metal surface, dissociates to form two oxygen atoms.

|  |  |
| --- | --- |
| a | b |

a – 2,98 Å, b – 1,97 Å

Fig - Interaction of the surface of iron with an oxygen molecule at various distances

TODO: About MS

# OXIDATION OF THE SURFACE

The oxygen molecules entering the cell move chaotically in the free space until they collide with the surface of the metal. In rare cases, the reflection of molecules from the surface is observed, but as a rule, quite effective capture of molecules occurs. Although iron is the main component of corrosion-resistant steels, the latter also contain a significant amount of chromium. Therefore, in this work, the influence of the chromium and aluminum content (as a possible alloying agent in the near-surface zone) in steel on the efficiency of oxidation of the metal was studied.

The picture of the adsorption of oxygen atoms is qualitatively as follows: in a collision with the surface, the oxygen molecules dissociate into atomic oxygen, and after that the oxygen ions accumulate predominantly in the near-surface layers of the metal. According to the results, first the oxygen atoms fill the octahedral voids in the iron lattice, forming structures like wustite (FeO). However, when oxygen is filled with several near-surface monolayers of iron, two clearly effects are observed. First of all, in two or three upper monolayers of iron, the crystalline order is disturbed and the surface looks more amorphous (Fig).

|  |  |
| --- | --- |
| a | b |
| c | |

Fig - System segment at the beginning of the simulation (a), after 200 ps (b) where red is the iron atoms, blue - oxygen, yellow - chromium, green - aluminum and charge distribution (c), in which atoms of larger radius - iron, smaller - oxygen and alloying elements (the smallest) color is responsible for charge, white is a neutral charge, positively charged atoms have a blue hue, negatively charged ones are red.

It should be noted that due to the growth of the film and the redistribution of charges, the near-surface layers have some potential difference, which can accelerate the capture of oxygen from the atmosphere (Fig c).

Some of the iron atoms are extruded above the surface and serve as centers for efficient capture of oxygen molecules. In the case where there are alloying additives that increase corrosion resistance (chromium and / or aluminum), they slow down the growth of the oxide by something. With the accumulation of oxygen at a greater depth below the surface, a visible transformation of the structure of the material takes place: the monolayers of the iron are expanded and separated by layers of oxygen (Fig).



Fig - The concentration of oxygen in the near-surface zone at different times.

It can be seen that at the beginning the surface was at 134 Å, just at this level, the surface oxidation began. After 20 ps of simulation, oxygen penetrated deep into the material (Fig black line) by several angstroms, forming a concentration peak in the near-surface zone. During the subsequent modeling, this peak first grew, which indicated an increase in concentration (Fig red and blue lines), and after 200 ps it was divided into 2 separated peaks. Firstly, it means that the oxide is grown, at least two atomic layers, and secondly, the fact that oxygen thus pushes the iron lattice plane. A modification of the near-surface layers can be seeing, which visually look like the displacement of the surface level upwards (Fig to the right) with respect to the reference level.

Oxygen, getting to the surface and penetrating deep into the octahedral position, the consequence of this is the growth of wustite (Fig).

|  |  |
| --- | --- |
| a | b |
| c |
| d |

a - structural analysis, b - pure iron, c - wustite, d - magnetite

Fig - Comparison of structural analysis data of near-surface layers of the pure iron system with reference structures.

In the upper layers into which oxygen entered, during the simulation a visible transformation of the structure began with a transition from pure iron to an oxide structure with a noticeably greater distance between the nearest neighbors on the iron sublattice. The change in the structure develops gradually with time and the more oxygen enters the near-surface layers, the stronger the radial distribution function of the atoms g (r) changes. When there are alloying additives in the system, the picture of the structural analysis looks like this (Fig).

|  |  |
| --- | --- |
| a | b |
| c | d |

a - Fe-13 at.% Cr system, b - Fe-30 at.% Cr system, c - Fe-30 at.% Cr-5 at.% Al system, d - all structures together with respect to magnetite structure

Fig - Structural analysis of near-surface layers in comparison with reference structures for various systems.

It can be seen that the qualitative picture of the structure change is analogous to that observed for the oxidation of pure iron. However, in the presence of chromium and / or aluminum, the structure changes more slowly (in particular, the first peak of the RFD for the iron-chromium-oxygen atmosphere lies to the left of the analogous first peak in the iron-oxygen atmosphere structure). In other words, the presence of chromium inhibits the growth kinetics of the oxide layer, the presence of an increased concentration of chromium further increases the oxidation resistance. The addition of 5 at.% Aluminum to the already existing 30 at.% Chromium, influences very much on kinetics. This phenomenon of suppressing the rate of growth of the oxide film has been studied in more detail. The Fig shows the results of the change in oxide thickness depending on the simulation time.



Fig - Comparison of approximations of oxide film thickness for iron systems without chromium, with chromium and with chromium and aluminum.

Note the fact that with 13 at.% chromium in the system, the film grows more slowly. The nature of growth is similar. At the beginning, up to 100 ps, there is an intensive growth of oxide and after that, slowing growth and reaching the "plateau". With 30 at.% chromium, the film grows more slowly (at 200 ps the film thickness is less by ≈1.5 times). Although the character of the oxidation does not change, the presence of 5 at.% aluminum further slows down the growth rate of the film compared to the iron system with 30 at.% chromium.

# Disscussion

Molecular dynamic simulation demonstrated a high efficiency of capture of oxygen from the gas phase by pure iron. The Fe-12 at.% Cr alloy demonstrates inhibition of oxidation. However, in both cases only a few surface atomic layers of metal are effectively converted to oxide, after which the oxide growth begins to slow down. The influence of chromium is mainly reduced to a slowing down of the formation of the primary oxide film and a decrease in its thickness. The crystal structure of the primary oxide is not magnetite, but much more near wustite (FeO). The increase in the chromium concentration up to 30 at.% and the addition of aluminum further slows down the growth of the film. The structure of the near-surface layers is almost the same as in the case of 13 at.% chromium.

The alloying of iron with chromium and aluminum does not change the structure of the oxide film. The rate of growth of the oxide film slows down with increasing concentration of alloying elements.

It is shown that the slowing down of the growth of the oxide film with increasing concentration of alloying elements is associated with the suppression of the diffusion mobility of oxygen in iron due to the interaction of oxygen with the alloying elements.