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Oxidation Of Steels And Alloys In Water Vapor

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Introduction. Currently, increasing the corrosion resistance of products made from structural steels, developing resource-saving and controlled technologies, intensifying processes and improving the quality of products are the most important tasks facing the modern engineering industry.

In this regard, an important role is played by the development of technologies for surface hardening of steel products, which would ensure high anti-corrosion properties of parts made of structural steels operating in severe corrosive operating conditions, as well as increasing requirements for their reliability and ensuring the necessary service life.

Objects and methods of research. Are technical hardware; structural steels used in mechanical engineering for the manufacture of parts of various configurations, in particular high-quality low-carbon steels 10 and 20; special medium carbon steels 30, 35 and 45; corrosion properties of compositions of nitride - oxide phases in nitride - oxide coating on steel.

Results and its discussion. In the mechanical engineering industry, to protect steels and powder metallurgy products from atmospheric corrosion, as well as to increase the wear resistance of steel and cast iron products, steam-thermal oxidation has received the greatest practical application, in which diffusion saturation of the surface with oxygen is carried out in water vapor with the formation of a film of oxides.

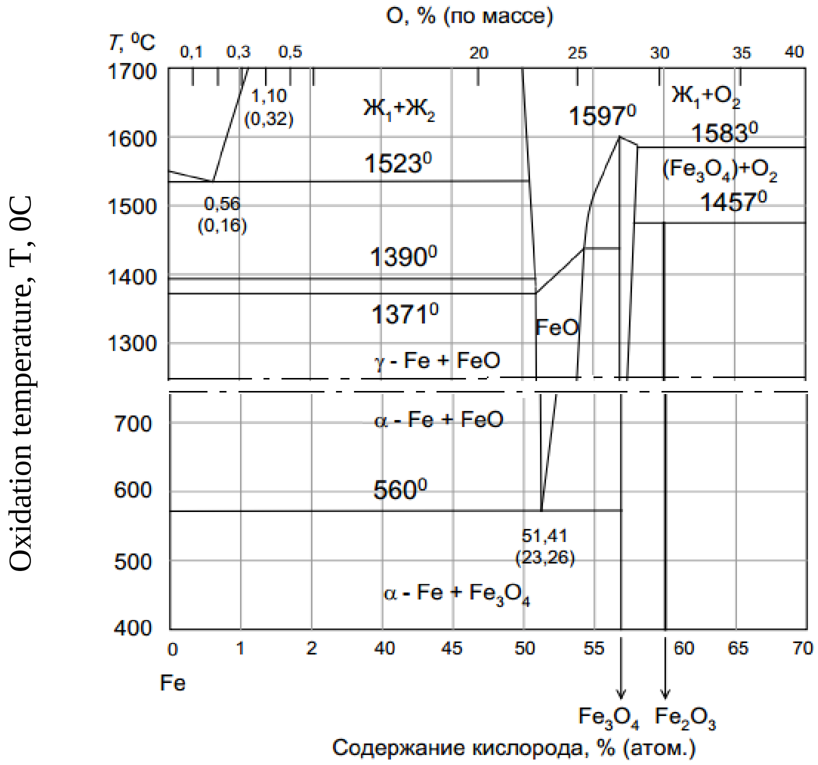
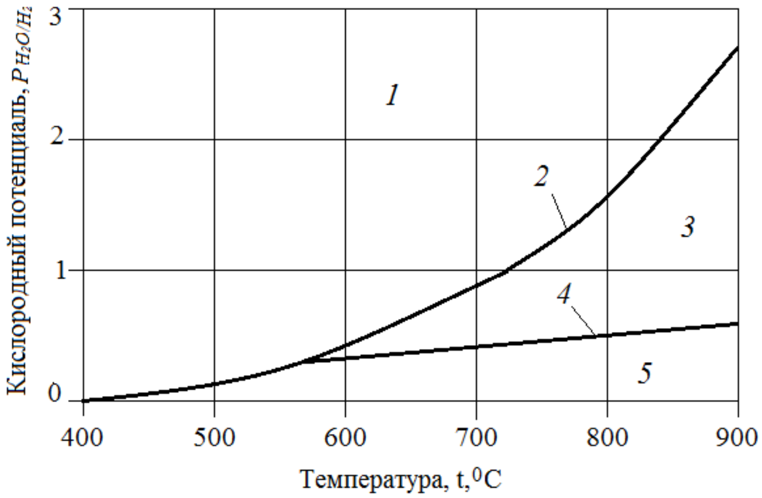


Fig.1.1. Diagram of the state of the iron-oxygen system

In the technically interesting region of the iron-oxygen phase diagram (Fig. 1.1), depending on the oxidation temperature, the following three types of oxides are formed on the iron surface: Fe2O3 (iron oxide - hematite), Fe3O4 (iron oxide - magnetite) and FeO (iron oxide - wustite). Stable hematite has a rhombohedral crystal lattice of the corundum type, and the lattices of γ-Fe2O3 and Fe3O4 are very similar and have spinel-type lattices.

All types of iron oxides differ from each other in the oxygen content in their composition and the types of crystal lattice, which determine their differences in the protective properties of the surface of steels and alloys from atmospheric corrosion.

From a thermodynamic point of view, iron in water vapor constitutes an unstable system, and in pure water vapor on the surface of steel, reactions occur between iron and water vapor, with the formation of hydrogen after the chemical decomposition of the latter. In this case, the chemical effect of iron with water vapor depends on the ratio of the partial pressures of hydrogen and water vapor. When steels are oxidized in water vapor, the process of formation of a surface oxide film occurs in two stages: with the initial formation of a continuous oxide film and a continuous increase in the thickness of the formed film, the continuity and stability of which in the growth stage is determined by the dependence of temperature and pH2O/pH2 ratios (Fig. 1.2).



1 – Fe_3O_4; 2 - $3{\cdot}FeO+H_2O \rightarrow Fe_3O_4+H_2$; 3 – FeO; 4 – $Fe+H_2O \rightarrow FeO+H_2$; 5 - Fe

Rice. 1.2. Equilibrium diagram "Fe-H2O-H2".

In real values of the ratio of the partial pressures of water vapor and hydrogen up to a temperature of 570 0C, iron oxidation reactions with pure water vapor are possible only with the formation of magnetite. At temperatures above 570 0C, iron, oxidizing in water vapor, forms wustite, which, with a decrease in temperature below the eutectoid, undergoes decomposition with the release of magnetite and Feα, the latter, which in an atmosphere of water vapor is oxidized to magnetite according to the following sequential reaction:

$$FeO+H_2O \rightarrow Fe_\alpha+H_2O+Fe_3O_4 \rightarrow Fe_3O_4+H_2 \qquad (1.)$$

The equilibrium diagram “Fe-H2O-H2” (Fig. 1.2) is valid for a pure system, but in real conditions steel contains carbon, impurities and alloying elements in its composition, and water vapor as a saturating medium in its composition contains, in addition to hydrogen, other gaseous substances. Therefore, the data presented in Fig. 1.2 may change to some extent in one direction or another.

Oxide coatings on alloy steels, obtained by oxidation in water vapor at processing temperatures from 400 to 650 0C and for a duration of 1.5-2 hours, have increased corrosion resistance. With increasing temperature and duration of the oxidation process, the total thickness of the oxide coating increases, as a result of which the phase composition and structure of the coating greatly changes, internal stresses in the oxide layer increase and the oxide coating peels off the surface, which negatively affects the corrosion properties of the workpiece.

Works are devoted to a more in-depth study of the properties of the oxide film on structural steels obtained by steam oxidation. Comparing the relative corrosion resistance of oxide coatings of different phase compositions and different thicknesses, the authors of the work confirm that under conditions of atmospheric corrosion, magnetite has the greatest corrosion resistance and wüstite has less resistance. The thin film of Fe2O3 oxide obtained on the surface is formed at temperatures below 400 0C, which differs significantly from the rest, both in structure and in the ratio of lattice parameters, has low adhesion to the main oxide coating and has virtually no effect on the corrosion rate.

The oxide film formed on the surface of carbon steel as a result of complex processing differs from the spontaneously formed film by higher quality, good adhesion to the base metal due to a denser packing of crystals, generally having a more rounded shape, as well as more favorable thermophysical properties.

Currently, the chemical industry has synthesized a large range of phosphonic-based complexons, which are widely used in the national economy. These include hydroxyethylidene diphonic acid (HEDP). It is based on phosphoric acid groups, which make it possible to obtain strong intra-complex bonds with cations of other metals, in particular iron, and ensure the high strength of these complexes.

The content of oxygen in the HEDP molecule allows it to be used for passivation of surfaces made of carbon steel during thermolysis of the HEDP solution at a temperature of 550 0C, i.e. a temperature significantly higher than the temperature of its thermal decomposition, which is about 180 0C (the beginning of thermolysis is about 120 0C).

The film-forming properties of the HEDP complexon are known, which, by forming strong oxide films consisting of magnetite on the steel surface, increase the corrosion resistance of steels in atmospheric and high-temperature conditions.

An analysis of literature sources shows that when oxidizing in water vapor and in vapors of aqueous solutions of complexons, single-phase diffusion oxide coatings consisting of magnetite are achieved; provided they are of sufficient continuity and density, high corrosion properties and wear resistance of the processed steels and alloys are ensured.

Conclusion: Composite coatings formed during nitriding followed by steam oxidation, consisting of a surface oxide and nitride zone with an internal nitriding zone, can provide a wide range of performance characteristics of nitrided products. By creating a nitride-oxide diffusion layer with the development of certain phase components of nitrides and oxides, as well as obtaining their compositions, it is possible to achieve the required corrosion resistance of steel products.

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