Protection of steels subjected to various types of thermal treatment

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Abstract. Thermal treatment of steels has a certain effect on the corrosion rate of carbon steels. Phase changes in alloys during thermal treatment result in internal stresses, a change in metal potential, and hence an increase in corrosion rate. The use of inhibitors is one of the most effective ways to combat metal corrosion in various aggressive environments. Inhibitors are substances that can slow down or stop chemical processes in small quantities. The purpose of the work is to establish the influence of various types of thermal treatment of steels on the protective capacity of corrosion inhibitors. Similar studies are hardly found in the literature.

1. Introduction
Provision of the specified corrosion resistance and corrosion-mechanical strength of metal structures should be carried out at all stages of production, starting from the stage of design and development of a rational manufacturing process. In many ways, the corrosion resistance of the equipment depends on a correct choice of a manufacturing technology and sequence of various technological operations.

Various methods of production of workpieces and machine parts, methods of metal surface treatment, non-uniformity of its structure determine the level of thermodynamic instability of metal and as a consequence its corrosive behavior during operation. At the same time, thermodynamic instability of metal is mainly determined by the level of residual stresses accumulated during treatment [1-7].

Residual stresses appear mainly due to either strengthening of local areas of the metal surface as a result of plastic deformation, or to thermal cycle action during heat treatment and welding accompanied by phase and structural transformations [8-16]. The main purpose of corrosion inhibitors is to reduce the aggressiveness of electrolytic media, as well as to prevent active contact of the metal surface with the environment. This is achieved by dosing the inhibitor into the corrosion medium, whereupon an adsorption film is formed on the metal which limits the contact area of the surface with the corrosion medium and can serve as a reliable barrier to the corrosion processes. It is necessary that the inhibitor is soluble in an aggressive environment and adsorbs well on both the pure metal surface and oxide films. In addition, corrosion inhibitors should be compatible with other reagents used in various processes [17-20].

When selecting metal corrosion inhibitors, the potential of the metal in the electrolyte is important. If the metal surface is charged positively, it promotes the adsorption of anions, which can lead to accelerated corrosion. Only anionic shielding additives can have a moderating effect under these conditions, and cationic-type moderators are not applicable.
If the metal surface is negatively charged, it facilitates adsorption of cations which are capable of inhibiting corrosion due to increased overvoltage of cathode and anode processes as well as surface shielding.

If the metal surface is not charged, it contributes to a higher adsorption of molecular (uncharged) particles, which can slow corrosion of the metal as a result of mechanical shielding of its surface or (depending on the dipole moment) the creation of an energy barrier.

Thus, a problem can be formulated. Thermal treatment of steels (e.g. annealing or normalisation) results in changes in metal structure, changes in hardness and strength, and changes in metal surface potential in corrosive media. This contributes to thermodynamic instability, and therefore to accelerating or slowing the corrosion rate of metals.

It would be logical to assume that the potential of the metal surface after thermal treatment will significantly affect the adsorption of the corrosion inhibitor and hence the protective effect.

2. Materials and methods

37Cr4 steel samples were used for testing. The following steps were taken to prepare the samples:
- samples were cleaned from traces of past tests, ground to metallic gloss;
- the samples were heat treated (annealing, normalised) in the furnace at 801 °C;
- the scale formed by the heat treatment was removed;
- hardness and electrode potential of the control, annealed and normalized sample were measured.

Measurement results are shown in tables 1 and 2.

| Treatment type   | Surface potential, E, mV (CSE) |
|------------------|--------------------------------|
| Annealing        | minus 0.33                     |
| Normalization    | minus 0.36                     |

Table 1. Electrode potential is model.

| Treatment type   | Hardness of samples, HRC |
|------------------|--------------------------|
| Annealing        | 36.2                     |
| Annealing        | 44.8                     |

Table 2. Hardness of samples.

Analysis of corrosion rate of samples and determination of inhibitor effectiveness were carried out according to GOST 9.502-82.

Essence of gravimetric method consists in determination of weight loss of metal samples during their stay in tested medium. In the gravimetric method, the corrosion rate is characterized by a mass index \( K_m \), (g/(m² · h)).

Corrosion rate \( K_m \) is calculated by formula:

\[
K_m = \frac{m_1 - m_2}{S \cdot t},
\]

where \( m_1 \) is the weight of the sample before the test, g; \( m_2 \) is the weight of the sample after the test, g; \( S \) is surface area, m²; \( t \) is test time in hours.

The tests were carried out in 500 ml cylindrical flasks filled with 3 % NaCl. The samples were placed inside the containers so that they were on the same level, did not touch each other and the vessel walls. At least 5 samples per experiment were used. The samples were previously ground, degreased and weighed on analytical scales to an accuracy of 0.1 mg. The exposure time of the samples was 6 hours. The solution was actively mixed on a magnetic stirrer. As a corrosion inhibitor, a water-soluble RIC-207 reagent from UTTP LLC (Ufa) was used, which was added at concentrations of 10 and 20 g/t.
3. Experimental part
The test results are shown in table 3.

**Table 3.** Results of gravimetric tests.

| Treatment type | Corrosion rate, g/(m² h) | 3 % aqueous solution NaCl |
|----------------|--------------------------|---------------------------|
| Annealing      | 0.795                    |                           |
| Normalization  | 0.822                    |                           |
| 3 % aqueous solution NaCl corrosion inhibitor (10 g/t) |
| Annealing      | 0.213                    |                           |
| Normalization  | 0.190                    |                           |
| 3 % aqueous solution NaCl corrosion inhibitor (20 g/t) |
| Annealing      | 0.101                    |                           |
| Normalization  | 0.111                    |                           |

Further, the obtained data were statistically processed in accordance with GOST 9.502-82 and the protective capacity of the corrosion inhibitor was determined with a confidence interval.

**Table 4.** Corrosion inhibitor protective capacity at different dosages.

| Treatment type | Corrosion rate without inhibitor, g/(m² h) | Corrosion rate with inhibitor, g/(m² h) | Protective effect, % |
|----------------|--------------------------------------------|-----------------------------------------|----------------------|
| Annealing      | 0.795                                      | 0.213                                   | 73.20 ± 0.148        |
| Normalization  | 0.822                                      | 0.190                                   | 76.88 ± 0.107        |
| Inhibitor dosage 10 g/t |
| Annealing      | 0.795                                      | 0.101                                   | 87.29 ± 0.056        |
| Normalization  | 0.822                                      | 0.111                                   | 86.49 ± 0.054        |
| Inhibitor dosage 20 g/t |

It follows that the corrosion rate of the samples in the medium depends on the type of heat treatment and the concentration of the inhibitor. The higher the inhibitor concentration, the lower the corrosion rate.

It is shown that, despite the different corrosion rates of the samples, the protective effect of the corrosion inhibitor remained virtually unchanged. That is, when choosing an inhibitor, it is necessary to pay attention not only to its effectiveness, but also to the rate of corrosion of the samples. Samples for corrosion tests shall be treated as well as elements of the present metal structures.

4. Conclusion
Studies have been carried out on the effect of thermal treatment of 37Cr4 steel on the protective capacity of the corrosion inhibitor. After thermal treatment (annealing of 2 kind and normalization), the electrode potential of the surface of the samples and their hardness changed. It has been suggested that this may affect the adsorption capacity of the inhibitor.

Studies have shown that both thermal treatment and dosing of the inhibitor significantly affect the corrosion rate of steel. The inhibitor concentration is primarily affected. However, the protective effect was about 75% at 10 g/t and 87% at 20 g/t. That is, at different corrosion rates, the efficiency of the inhibitor is the same.

Since in laboratories, witness samples are often used without thermal treatment, or after plastic deformation there is a risk of obtaining either an overestimated or an understated corrosion rate than on actual equipment.

Therefore, it is recommended to treat all the samples used in laboratory studies for corrosion tests as well as elements of real metal structures.
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