AN INVESTIGATION OF DISSOLUTION OF ALLOY STEELS IN WEAK SOLUTIONS OF HYDROCHLORIC ACID IN THE PRESENCE OF INHIBITORS

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At present there is sufficient research in the corrosion of alloy steels. Usually the research of corrosion of alloy steels was carried out by studying the the kinetics of the dissolution (1), determination of the rate of corrosion in circulating currents (2) and the effect of alloy additives on the dissolution of steels (3 and 4).

The aim of our work was investigation of selective dissolution of alloy steels in mineral acids, and the effect of inhibitors of this process.

Stainless austenit steel 1X18H 10T and ferrite steel E-1 756 were selected as the object of research.

The spectral method developed by us (5) was used to investigate selective corrosion of alloy steels; to verify the correctness of spectral findings corrosive tests on the loss of weight were also carried out simultaneously.

Procedure :

Corrosive tests were conducted in circulating currents of 4% solution of hydrochloric acid by means of measuring the loss in the weight of the samples. Weight measurements were carried out on an analytical balance of the ADN-200 type every half an hour for 2–4 hours. At the same time samples of the solution amounting to 10 ml were selected. These samples were subjected to spectral analysis.

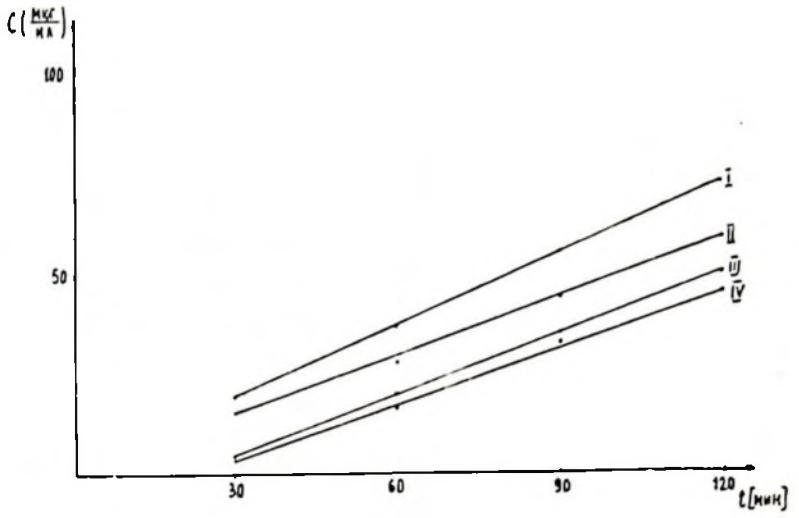


Fig. 1 represents the kinetic curves of the growth in the concentration of cations versus time for both types of steels obtained by the weight and spectral methods. The spectral curve was obtained by the addition of the concentration of all the cations in the corresponding experimental point. The curves thus obtained are sufficiently near to each other within the error limits of the experiment. This is confirmed by the data in table 1 where the corresponding deviations are given.

TABLE 1
Deviation of the results of the Spectral and Weight Measurements

Sl. No.	Type of Steel	1x18H10T E(%)	EN–756 E(%)
1		11	11
2		8	13
3		4	11
4		8	11

Where the serial No. indicates the number of the experiment.

As there were four samples in the current vessel it is possible to use the results of these four measurement in each experimental point to calculate the reproductability of the corrosion tests by loss of weight.

The results of the calculations are summed up in table 2.

TABLE II
Reproducibility of Weight Measurements

Sl. No.	Type of Steel	1x18H10T E(%)	EN–756 E(%)
1		6	4
2		6	3
3		3	3
4		6	4

To find out the effect of the pouring of the solution out of the vessel in order to perform the spectral determinations the error arising here was calculated.

The following considerations were used. The total volume of the solution in all the tests was one and the same viz , V = 750 ml.

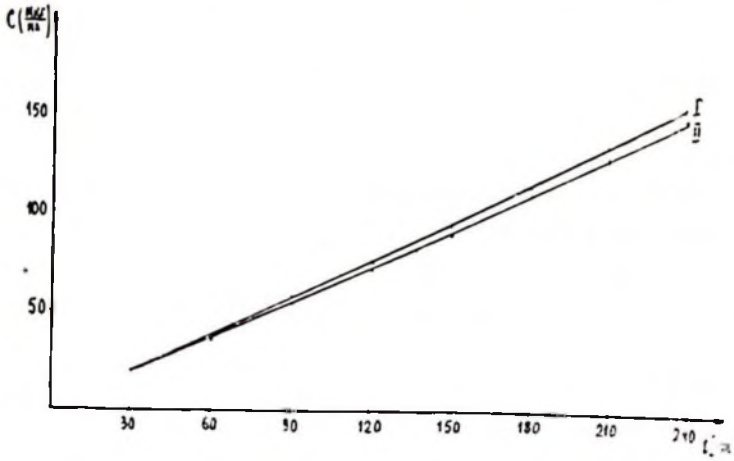
Let us indicate the volume of test 1 as ΔV_1; test 2 ΔV_2 etc. (it was maintained constant and was equal to 10 ml.), the concentration of the cations at the moment of the taking of the first sample as c_1, second section as $-c_2$ etc.

Then after taking the first sample the total volume of the solution becomes less by $V-\Delta V$, while the total weight of the cations by $C_1V-C_1\ \Delta V_1$. The concentration after the pouring out of the selected sample will be:

$$C_1 = \frac{C_1V-C_1\Delta V_1}{V-\Delta V_1}$$

After the second pouring we obtain:

$$C_2 = \frac{C_1V-C_1\Delta V_1-C_2\Delta V_2}{V-\Delta V_1-V_2}$$



On the basis of the obtained data a graph was constructed (fig. 2) taking into account the pouring of the solution and without it. The difference was very small, the maximum error not exceeding 5.0%. This error is not systematic as during the research allowance is made for the pouring of the solution.

Investigation of selective corrosion :

While studying selective corrosion it may be interesting to clarify the question whether the dissolution of all the cations of metal X is the same in accordance with the loss in weight or selectiveness takes place. To this end the graphs of selective corrosion obtained by the method of spectral analysis and the assumed corrosion were compared. The latter had been reduced to 1% of the elementary composition.

While constructing the calculated graph it was assumed that the outcome of cations into the solution was proportional to its percentage content in the elementary composition. Taking the weight losses for alloy steel as $-\Delta pi$ and the volume of the circulating current as $-V_i$ the concentration or the solution by the end of the tests will be $\frac{\Delta_{pi}}{V_i}$. Dividing this magnitude by 100 in each experimental point we shall have the calculated curve reduced to 1% of the elementary composition and obtain by the weight method. On the other hand the concentrations of all the components obtained by spectral analysis and divided by the percentage content in the elementary composition will have also been reduced to 1% of the elementary composition.

The above considerations may be reflected in the following correlation :

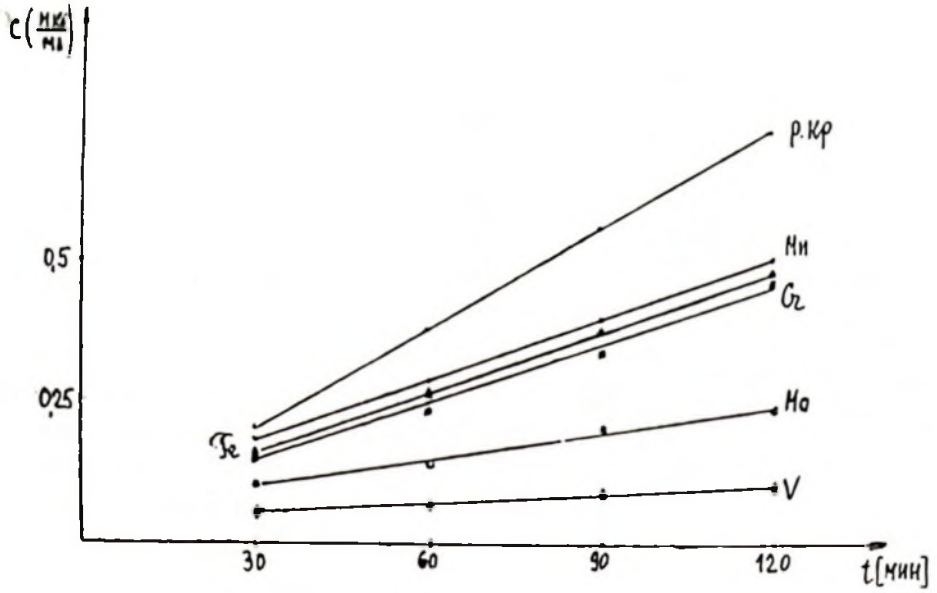
$$\frac{C_{fe}}{A_{fe}} = \frac{C_{cr}}{A_{cr}} = \frac{C_{ni}}{A_{ni}} = \frac{\Delta pi}{100i}$$

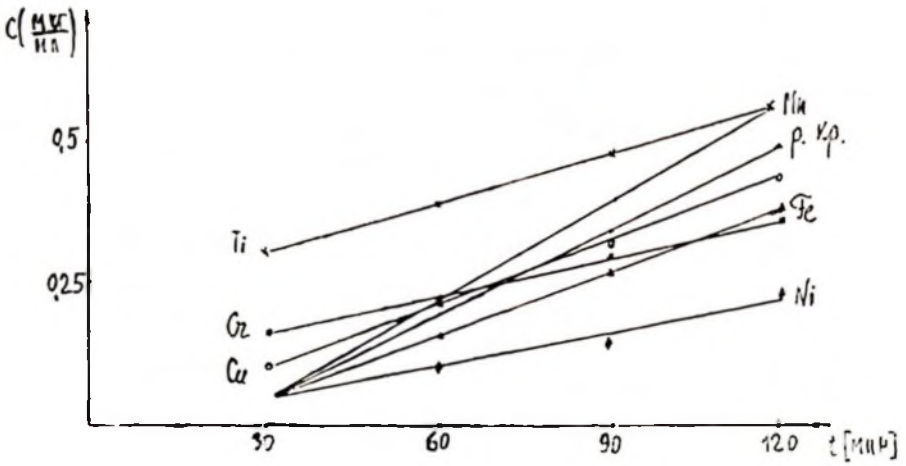
in each experimental point where C_{fe}, C_{cr}, C_{ni},..... .....denotes the concentations of the cations in the corresponding experimental point while A_{fe}, A_{cr}, A_{ni}, ... denotes the percentage content of the component in the cations in the alloy, while a deviation from this equation to either side will be evidence of the selectiveness of corrosion. On the other hand this enables representing all the curves in one figure as the range of deviations decreases. Such curves obtained by the weight and spectral methods are represented for steels 1×18H10T and EI–756 in figures 3a and b.

An analysis of the results obtained showed the selectiveness was characteristic of the both types of steels, being particularly prominent in the case of steel EI–756 : the closest to the calculated curve are the lines of Fe, Cr, and Mn. The experimental curves or MO and V are located much lower than the calculated curve. This circumstance may speak for a much slower outcome of these cations into the solution than it was expected. The reasons for this may be the different chemical resistivities of the metals as well as the effect of various (for example carbide) phases in which they can enter.

The curves for the concentration of all the cations obtained by the method of spectral analysis were subsequently transformed into the rate of corrosion.

The concentration of the corresponding cation C_i expressed in MKG÷ML was multiplied by





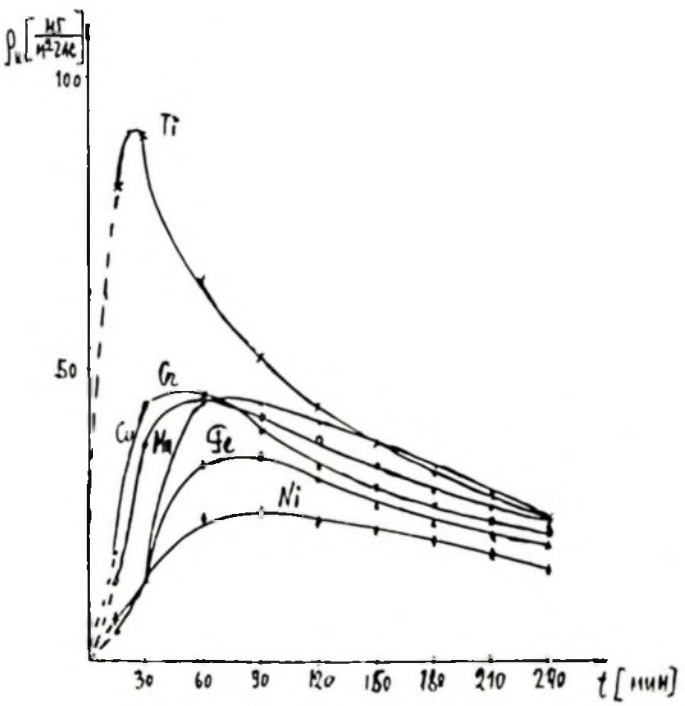
the volume of the solution V_1 taking account of the pouring. As a result the weight losses by cations $\Delta pi = CVi$ (MG) were obtained. Dividing the weight losses Δpi by the surface of all the samples S (M^2) and the corresponding time at which the concentration (T) was determined, the rate of corrosion $pi = \Delta pi \div ST$ was obtained. The results thus processed are represented in graphs (fig. 4 a and b.)

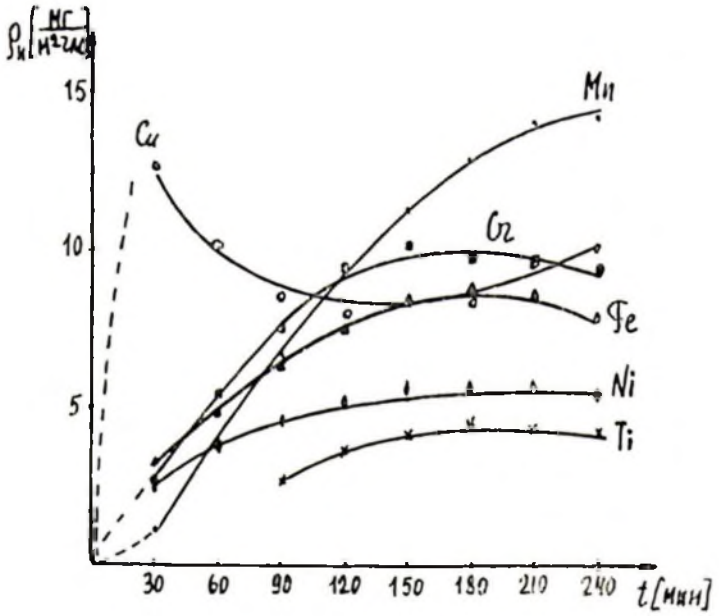
For steel 1X18H10T the curves of the rate of corrosion have clearly expressed maximums for all the elements, each maximum located at different time intervals. The shape of the obtained curves is also different : if for Ti there is a sharp maximum at T=30 minutes, for Fe and Ni it is considerably weaker.

It is of interest to note that beginning with T=30 minutes, for Fe and Ni it is considerably weaker.

It is of interest to note that beginning with T = 90 – 120 minutes the curves approach each other and then go almost parallel with the time axis. Thus, the rate of corrosion stabilizes. For steel E1–756 maximums for all the elements are located at the beginning of the graphs at T=30 minutes with a subsequent abatement after which the rate of corrosion for MO and V is considerably less than for other elements.

The effect of inhibitor on the rate of corrosion element-wise was also considered. Catapin A was used as inhibitor. The introduction of inhibitor drastically changes the shape of the





obtained curves (figs. 4c. and d). If for steel 1×18H10Г the rate of corrosion increases with time, increasing to the largest extent in the case of Mn, Fe, and Cr and subsequently stabilises, in the case steel E1–756 a more complicated shape of the curves is characterised. The maximums for this are located at the beginning of the graphs for all elements with a subsequent abatement to 150 minutes after which the rate of corrosion again increases.

On the basis of the obtained data graphs (figures 5a and b) were constructed of the dependence of the inhibitor effect on the time for both types of steel.

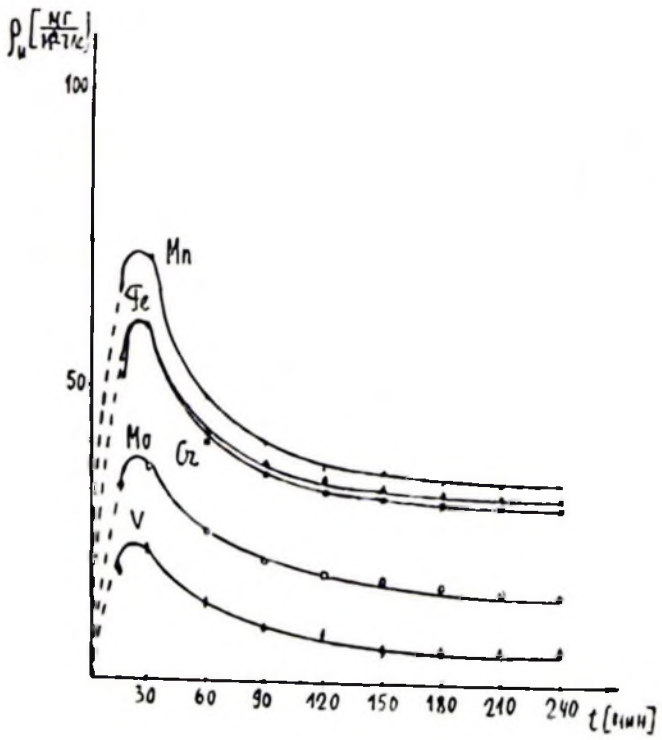
In the case of steel 1×18A10T the inhibitor effect has the maximum for all elements located at different time intervals; for Ni the maximum is at T=30 minutes. for Mn and Cr at T=60 minutes, for Fe and Cu maximum is at T=90 minutes to 120 minutes. The greatest inhibitor effect is in the case of Mn and Cr ∽ 15 and finally in the case of Fe, Cu and Ni (8; 4. 5;6 respectively). For steel E1–756 the inhibitor effect also depends on the time like in the case of steel 1×18H10T though the maximums in this case are more washed out and lie within the range of 30–90 minutes. It is necessary to point out that for steel E–756 the inhibitor effect is less than for steel 1X18H10T: the greatest for the element Cr ∽ 10, the least for the elements Fe and Mn (7 and 5 respectively).

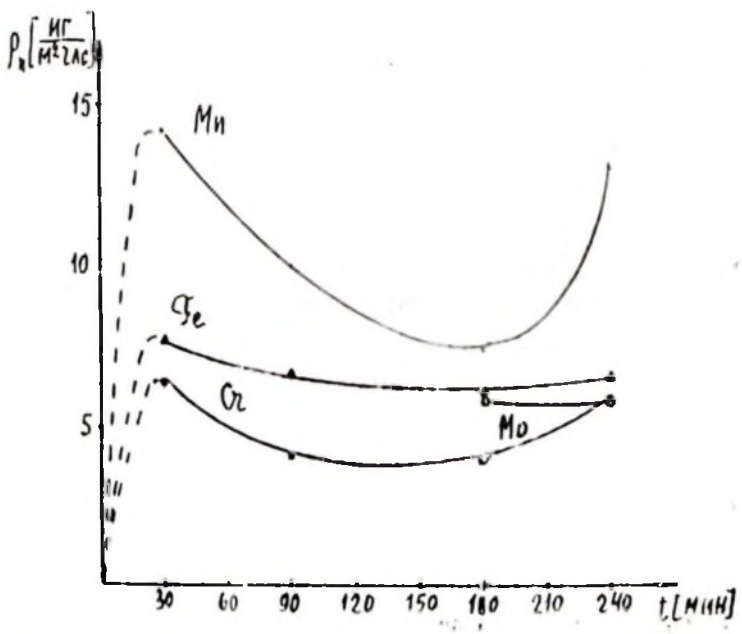
Conclusions:

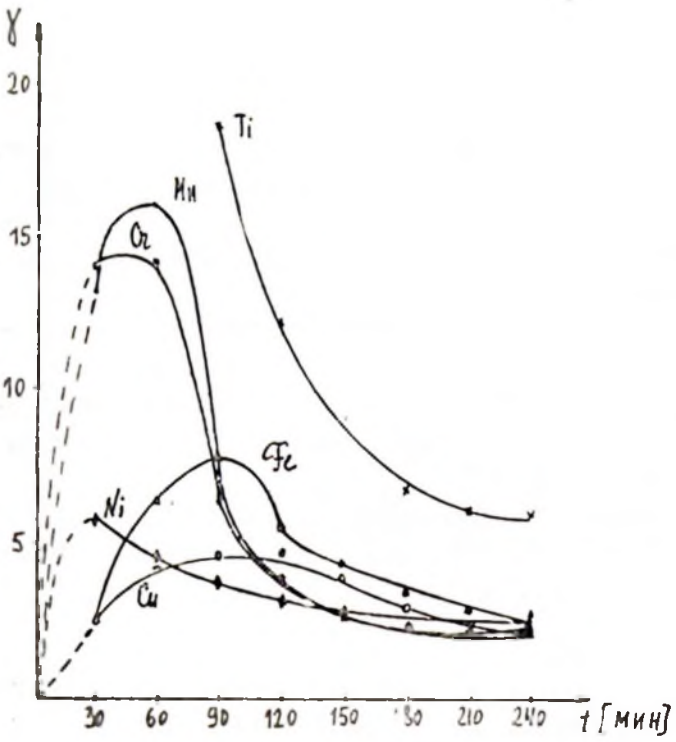
1. The use of the spectral method of investigation of selective corrosion enables to conduct analysis for all components.

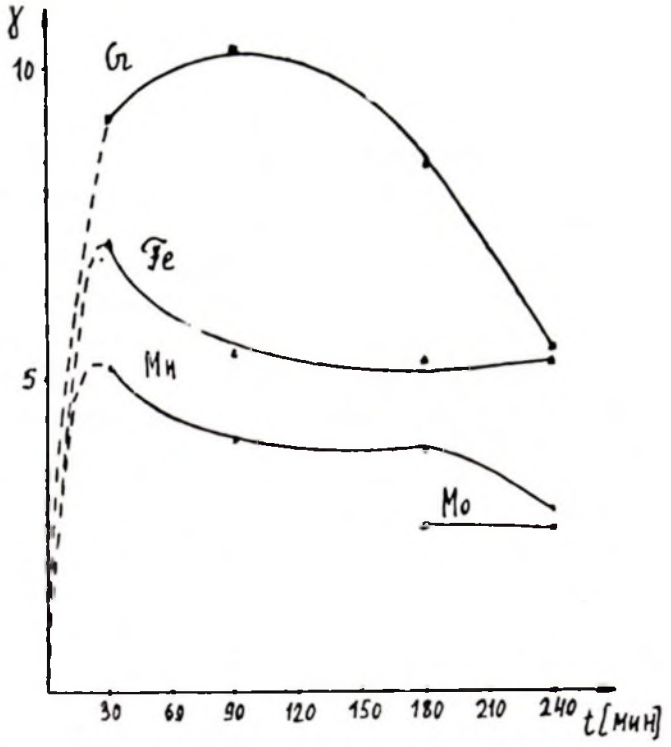
2. Measurements with the use of both the methods viz., by wieght and spectral methods produced the same results within the error limit of the experiment.

3. The hypothesis on the outcome of cations into the solution proportionally to its percentage content in the elementary composition has not been experimentally proved for both types of steel.









4. It was established that the rate of corrosion was dependent in a complicated way on the time for both types of steel while for all the components a maximum was observed within the range of 30–120 minutes, the rate of corrosion subsequently becoming stabilized.

5. The inhibitor effect also depends on the time, the curves having maximums within the range of 30–90 minutes.

6. The inhibitor used in our research as unequal inhibiting effect on the outcome of cations from steels 1×18H10T and E1–756.

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