

Kinetics of scale removal from mild steel in sulfuric acid

The kinetics of chemical dissolution of surface metallic oxides on steel sheets (scale removal) in sulfuric acid (5-20 w%) was studied in the temperature range from 70 to 90 °C. It was found that the rate of this process, followed by spectrophotometric determination of Fe^{2+} -concentration in the solution at a given temperature, mainly depends on the concentration of sulfuric acid following the equation: $v_{diss} = k C^n_{H_2SO_4}$. The calculated values of the activation energy ranged between 22 and 25 $kJmol^{-1}$ and slightly depend on the H_2SO_4 -concentration, clearly indicating that the process is under diffusion control. As it was shown the limiting diffusion flux of protons, from the bulk of the solution to the oxide/solution interface, corresponds to the quantity of the protons consumed in the dissolution process ($FeO + 2H^+ = Fe^{2+} + H_2O$). The calculated value of the proton diffusion coefficient (D_{H^+}): $5.8 \cdot 10^{-5}$ for 70°C; $7.78 \cdot 10^{-5}$ for 80°C; $8.3 \cdot 10^{-5}$ for 85°C and $9.3 \cdot 10^{-5} cm^2s^{-1}$ for 90°C are in good agreement with literature data.

INTRODUCTION

Mainly two techniques for scale removal from steel sheets (for automotive industry, shipbuilding and domestic appliances), preceding the further processes of corrosion protection (conversion coatings, plastic coatings etc.), are frequently used: mechanical and chemical [1].

The chemical method is based on the acidic pickling of steel sheets in mineral acids (HCl or H_2SO_4) at elevated temperatures (70-95 °C).

The main stage of pickling is designed to remove corrosion products (mainly metal oxides) formed in the processes of hot rolling or atmospheric corrosion at ambient temperature, in order to achieve a good metal-metal or metal-organic coating adhesion contact.

Therefore, the better understanding of the kinetics and mechanism of the process of scale removal is of special interest, both from theoretical and practical view of point.

EXPERIMENTAL

The experiments were carried out with steel specimens (70x15x3 mm) in sulfuric acid (5, 10, 15 and 20 w %) in temperature range from 70 to 90 °C.

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The rate of the chemical dissolution of Fe(II)-oxides has been followed using spectrophotometry (phenanthroline method) [2, 3]. The steel specimens were treated in 150 cm^3 H_2SO_4 in thermostatic cell at 70, 80, 85 and 90 °C for a maximum time of treatment of 240 s. The solution of H_2SO_4 also contains a commercial corrosion inhibitor for steel "RODINE" (5 cm^3/dm^3) with $\eta_{inh} \approx 96$ %. Under these conditions the rate of the scale removal (v_{diss}) is much greater than the rate of corrosion of the bare steel ($v_{diss} \gg v_{corr}$); due to the fact that the inhibitor can be only adsorbed at the metal surface but not at the metal oxide/solution interface.

RESULTS AND DISCUSSION

Using potentiometric oxido-reduction titration (with Ce(IV)sulfate) of the H_2SO_4 -solution after quantitative dissolution of Fe-oxides, it was shown that mainly Fe(II)-oxides with an average thickness of about 11 μm are present at the steel surface [4].

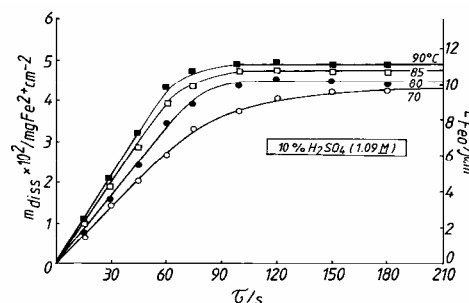
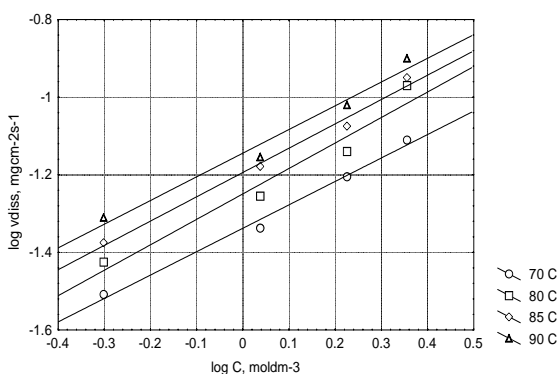


Fig.1. The rate of the chemical dissolution of Fe(II)-oxides on the steel surface in 10 % H_2SO_4

Table I - The rate of chemical dissolution of the surface Fe(II)-oxide in H₂SO₄

C _{H₂SO₄} /% (M)	v _{diss} · 10 ² / mgFe ²⁺ · cm ⁻² · s ⁻¹				v _{cons H⁺} · 10 ⁶ / molcm ⁻² · s ⁻¹				D _{H⁺} · 10 ⁵ / cm ² · s ⁻¹			
	70°C	80°C	85°C	90°C	70°C	80°C	85°C	90°C	70°C	80°C	85°C	90°C
5 (0.50)	3.10	3.76	4.22	4.90	1.11	1.34	1.51	1.76				
10 (1.09)	4.60	5.56	6.62	7.01	1.64	1.98	2.36	2.50	5.80	7.78	8.30	9.30
15 (1.68)	6.24	7.24	8.42	9.55	2.23	2.59	3.01	3.41				
20 (2.265)	7.76	10.72	11.22	12.59	2.77	3.83	4.01	4.51				

Fig. 2. The initial rate of the chemical dissolution of Fe(II)-oxides on the steel surface v.s. concentration of H₂SO₄

As can be seen from Fig. 1 and 2 and Table I, the rate of the chemical dissolution of Fe(II)-oxide (v_{diss}), (given with equation: FeO + 2H⁺ = Fe²⁺ + H₂O) depends both on the concentration of sulfuric acid (C) and temperature. In these cases the limited value of about 5 mg Fe²⁺/cm² has been obtained corresponding to the thickness of Fe(II)-oxide of about 11 μm. This value is in good agreement with some literature data [1,5].

It was also, shown that the limiting time for quantitative dissolution of Fe(II)-oxide (from 60 to 100 s) depends both on the concentration of H₂SO₄ and temperature (Fig. 1). These measurements were performed in un-stirred solutions. In the industrial processes the scale removal lasts even shorter due to the different hydrodynamic conditions (moving of steel sheets in the sulfuric acid).

The initial rate of the oxide dissolution process (linear parts of the m_{diss}/τ-profiles, Fig. 1) regularly depends of the solution temperature and its concentration (Table I).

On the other hand, the activation energy (E_a) of this process (Table II) was calculated from the linear (ln v_{diss}/1/T)-plots (Fig.3) using the Arrhenius equation:

$$v_{diss} = v_o \exp(-E_a/RT) \quad (1)$$

These values are presented in Table II. As it was found, the energy of activation of this process

ranged between 22 and 25 kJmol⁻¹ (Table II); slightly depending on the sulfuric acid concentration and clearly indicates that the process of metallic oxide dissolution is under diffusion control. This process starts at the oxide/solution-interface (interaction between oxide and proton) and continues by diffusion of protons in the oxide pores. The experimental results (Table I) fit fairly well the empirical equation:

$$v_{diss} = k C_{H_2SO_4}^n \quad (mgFe^{2+} \cdot cm^{-2} \cdot s^{-1}) \quad (2)$$

where exponent n ranged between 0.6 and 0.63 and the rate constant k, depending of temperature, ranged between 4.5 · 10⁻² and 7.2 · 10⁻². C_{H₂SO₄} is given in mol dm⁻³.

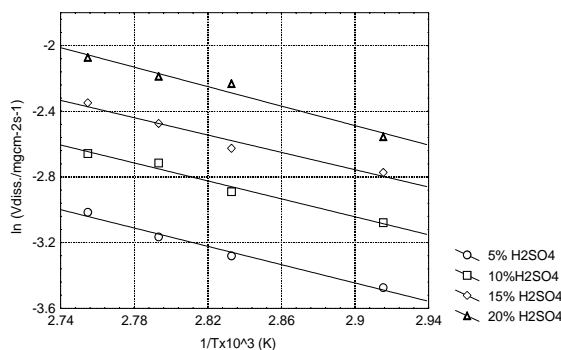


Fig.3. The initial rate of the chemical dissolution of Fe(II)-oxides on the steel surface v.s. temperature

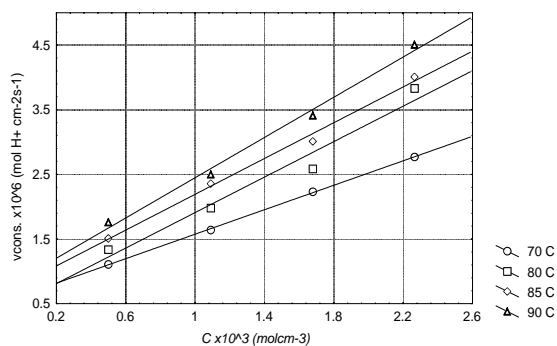
Fig.4. The rate of the proton consumption in the dissolution process of Fe(II)-oxides v.s. concentration of H₂SO₄ (Table I)

Table II. Activation energies of the Fe(II) - oxide dissolution processes in H₂SO₄

CH ₂ SO ₄ /% (M)	Ea/kJmol ⁻¹	vo/mgcm ⁻² s ⁻¹
5 (0.50)	23.20	104.0
10 (1.09)	22.73	123.3
15 (1.68)	21.94	134.0
20 (2.265)	24.66	452.6

It was also shown that the limiting diffusion flux of protons from the bulk of the solution to the oxide/solution interface corresponds to the quantity of the protons consumed in the dissolution process: FeO + 2H⁺ = Fe²⁺ + H₂O; Table I and Fig. 4.

$$v_{cons.H^+} = dif.flux = D_{H^+}(C_{H^+}/\delta) \text{ (molcm}^{-2}\text{s}^{-1}) \quad (3)$$

assuming the value of the Nernst-diffusion layer thickness, for un-stirred solution, $\delta = 0.05$ cm [6].

Using equation 3 and data given in Table I, the value of diffusion coefficient of protons (D_{H^+}) was calculated.

Thus, the following results are obtained: $5.8 \cdot 10^{-5}$ for 70°C; $7.78 \cdot 10^{-5}$ for 80°C; $8.3 \cdot 10^{-5}$ for 85°C and $9.3 \cdot 10^{-5}$ cm²s⁻¹ for 90°C, which are in a good agreement with literature data.

CONCLUSIONS

- The rate of dissolution of surface Fe(II)-oxide (in temperature range from 70-90 °C) followed by spectrophotometric determination of the Fe²⁺-concentration in the solution, is proportional to the H₂SO₄ concentration ($v_{diss} = k C_{H_2SO_4}^n$).

- The activation energy of this process ranged between 22 and 25 kJmol⁻¹ (depending on the H₂SO₄ concentration), and clearly indicates that the process is under diffusion control.
- The limiting diffusion flux of protons, from the bulk of the solution to the oxide/solution interface, exactly corresponds to the quantity of the consumed protons in the dissolution process (FeO + 2H⁺ = Fe²⁺ + H₂O). The calculated values of the diffusion coefficients (D_{H^+}) ($5.8 \cdot 10^{-5}$ for 70°C; $7.78 \cdot 10^{-5}$ for 80°C; $8.3 \cdot 10^{-5}$ for 85°C and $9.3 \cdot 10^{-5}$ cm²s⁻¹ for 90°C) are in good agreement with literature data.

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IZVOD

KINETIKA UKLANJANJA METALNIH OKSIDA SA POVRŠINE ČELIKA U SUMPORNOJ KISELINI

Kinetika uklanjanja metalnih oksida sa površine celika u sumpornoj kiselini (5-20%) je izucavana u temperaturskom intervalu od 70-90 °C. Nadjeno je da brzina ovih procesa na datim temperaturama zavisi uglavnom od koncentracije sumporne kiseline ($v_{diss} = k C_{H_2SO_4}^n$). Izracunate vrednosti aktivacione energije se kreću u intervalu 22-25 kJmol⁻¹ sto jasno ukazuje da su procesi difuziono kontrolisani.