STUDY OF THE OXIDATION OF IRON BY NITRIC OXIDE I.

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RESUMEN. Se determina por Espectrometría de Masa y Espectrometría Mössbauer que la oxidación del Fe por el NO se realiza en dos pasos:

$$8NO + 3Fe \longrightarrow Fe_3O_4 + 4N_2O.$$

$$4N_2O + 3Fe \longrightarrow Fe_3O_4 + 4N_2$$

Se calcula el orden de reacción y la energía de activación del primer paso de la oxidación a través del estudio de la disminución de la presión total de la fase gaseosa, y se propone un mecanismo del proceso.

ABSTRACT: It is found by mass spectrometry and Mössbauer Spectrometry that the oxidation of Fe by NO takes place in two steps:

$$8NO + 3Fe \longrightarrow Fe_3O_4 + 4N_2O.$$

$$4N_2O + 3Fe \longrightarrow Fe_3O_4 + 4N_2$$

The order of the reaction and the energy of activation of the first stage is calculated measuring the decrease pressure of mechanism for the process is postulated.

INTRODUCTION

The corrosion of iron and steel can be retarded by the action of compounds that contain NO–functional groups.[1,2] In this connection it was stated that a covering of a metal surface by NO protect this surface.[3] The action of NO with metals was studied by Sachtler[4] and Terenin and Roev.[5] But specially importants results were obtained by Blyholder and Allen and Poilings and Eischens.[2] They investigated the action of NO over Ni and Fe by IR spectrometry and concluded that the NO decomposes in these metals when it is chemisorbed, and the oxygen produced in the decomposition oxidize the metals and form a superficial oxide. They did not confirm what kind of oxide was formed but proposed[2] the following reaction to describe the decomposition.

$$2NO + Fe \longrightarrow 2\ (FeO)_{ad} + N_2$$

Onchi and Farnsworth[7] studied the chemisorption of NO at low pressures in Ni, and Otto and Shelef[8] studied the adsorption isotherms of NO over Fe_2O_3 and Fe_3O_4. One of the authors and Büttner[9] studied by Mass spectrometry and electron diffraction the action of NO over evaporated iron films, and concluded that the NO oxidize the Fe to Fe_3O (or γFe_2O_3) and reduce itself to N_2O and N_2 remaining after the attack NO sorbed over the oxide formed.

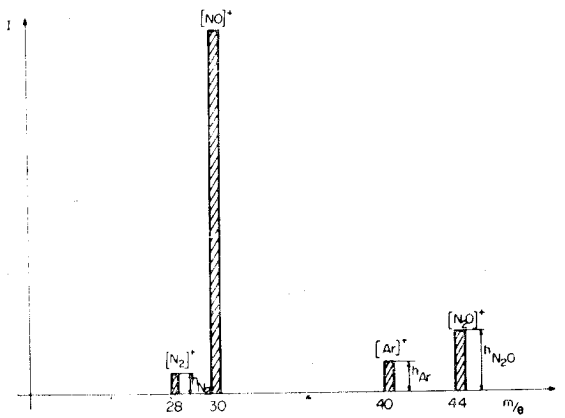
The purpose of the present paper is to define the mechanism of the oxidation of Fe by NO, and to determine the products of the oxidation by Mössbouer spectroscopy.

EXPERIMENTAL PART

Mass spectrometric study of the oxidation in fresh iron surface.

A high vacuum system constructed to evaporate metals in the reaction chamber was coupled to a mass spectrometer HITACHI RMU-6D. The method used to follow the interaction of the NO with the created in the evaporation films consisted in taking out samples from the reaction chamber trough its connection with the mass spectrometer and measure these samples taked at different times using the spectrometer. A complete description is given elsewhere.[9]

And standard mass specter was as follow (Fig. 1) where the A_r was introduced in the reaction chamber as a standard.



The parameters that we take as representatives are

$$\alpha_{N2O} = \frac{h_{N2O}}{h_{Ar}} \text{ and } \alpha_{N_2} = \frac{h_{N2O}}{h_{Ar}}$$

Where h_{N2O} , h_{N_2} , and h_{Ar} are the heights of peaks in the mass specter.

Kinetic of the first stage reaction of NO with Fe powders.

The experiments corresponding to this part of the work were performed in a reaction vessel evacuated by a vacuum system consisting of a rotation vacuum pump, an oil diffusion pump, a trap and ionization and Pirani manometers. The reaction vessel was coupled to an oil and mercury *U* manometers to measure the pressure of the NO in the reaction vessel.

The reactor was of the closed type[10], and the iron powder was dispersed at the bottom of the reactor in the form of a thin layer as in this form we can obtain really significatives results.[11] As we expect a change in the quantity of moles in the course of the reaction, the process was followed by measuring the total pressure "*p*" at different times.[11]

Mössbauer study of the products of the reaction

Ten micron foils of Fe were used in these experiments. They were oxidized in a vertical quariz tube evacuated by a symple vacuum system that can obtain $\sim 10^{-5}$ Torr.

The Mössbauer spectra of the ten micron foils were taken in a constant acceleration instrument. It consisted basically of:

1. An electromechanical drive.
2. A NaI (Tl) scintillation detector with a single channel analyser for the selection of the 14.4 Kev ray pulses.
3. A 256 channel analyser.
4. A source of Co^{57} diffused into Cr.

The collimation was provided by a lead shield. An "Al" filter was used in front of the counter to substract the 6.5 Kev X–Rays, and the background radiation.

All the reagents used were of analytical grade and the iron used in all these case was of 99.0% purity.

RESULTS

Mass spectrometric analysis of the products of the reaction.

The action of NO over evaporated iron films was followed at 150, 250 and 300°C 15 Torr pressure (Figs. 2 and 3).

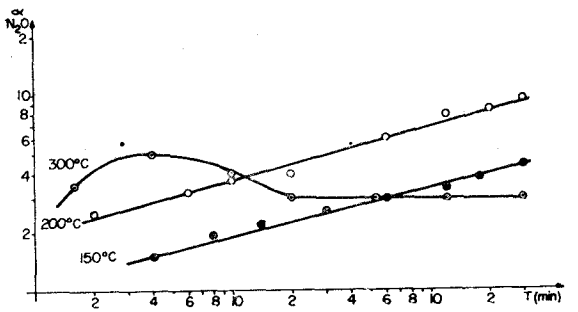


Fig. 2

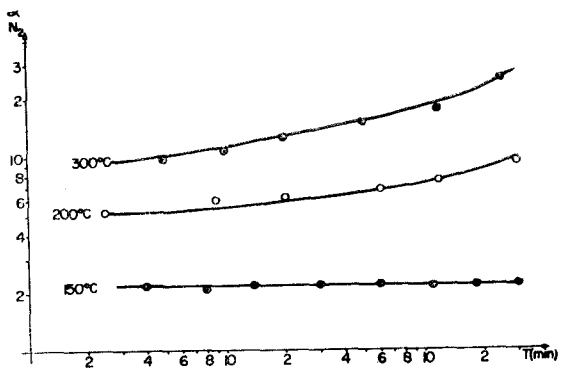


Fig. 3

The parameter α_{N_2O} and α_{N_2} are plotted in log paper versus time.

Kinetics of the first stage reaction of NO with Fe.

The total pressure was measured at differents times. As this parameter is not

representative of the course of the reaction, for reasons that we will explain later we plot the parameter:

$$\alpha = RT\left(\frac{P}{2P-P_0} - 1\right)$$

where P_0 is the initial total pressure. This parameter was measured at differents times at 130, 140, 150, 160, 180 and 200°C at $P_0 = 20$ Torr.

A lineal dependence was obtained. See figure 4.

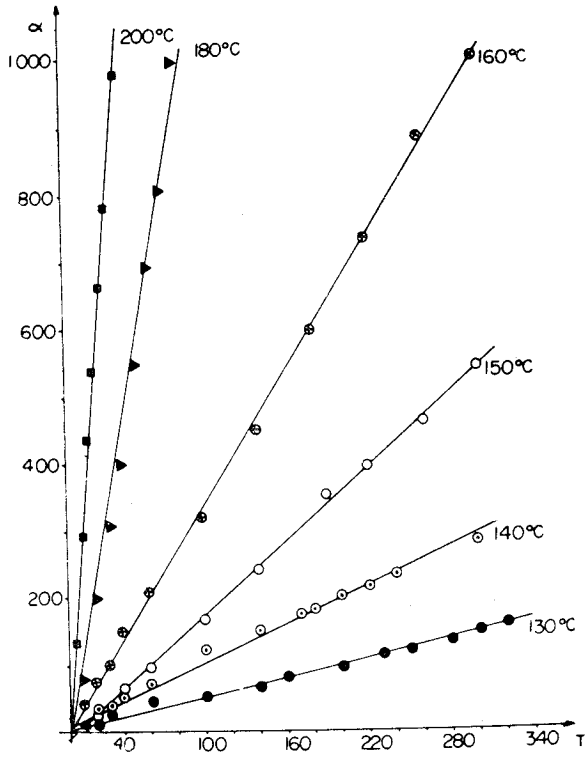


Fig. 4

Mössbauer spectra.

We obtained the heigh velocity Mössbauer spectra of standars of Fe, FeO, Fe_2O_3, Fe_3O_4 and with the same conditions, were measured the spectra of the foils treated

with NO at 500, 600°C by 6 hours and at 700°C by 3 hours all at 20 Torr of pressure. (Figs. 5-7).

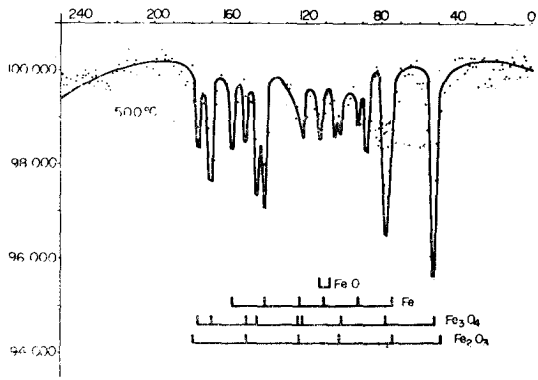


Fig. 5

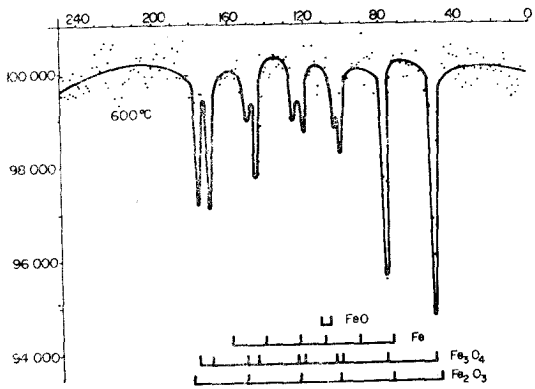


Fig. 6

DISCUSSION

From the mass spectrometric data can be seen that the reaction in her first stage only produces N_2O by the reaction:

$$8NO + 3Fe \longrightarrow Fe_3O_4 + 4N_2O \uparrow \qquad (1)$$

because at 150°C we did'nt see an increasement of the relation,

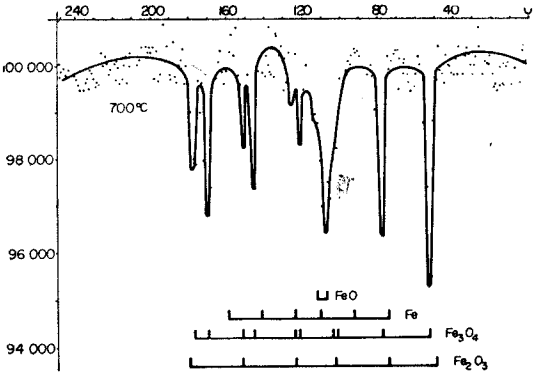


Fig. 7

However at 300°C we can see a quick increase of the peak of N_Z and a decrease of the peak of N_2O which indicates that the production of N_2 is caused by the decomposition of the N_2O by the reaction:

$$4N_2O + 3Fe \longrightarrow Fe_3O_4 + 4N_2. \qquad (2)$$

Therefore the process consist of two consecutive reaction of oxidation of iron.

From the manometric data we can give an explanation of the mechanism of the first stage reaction that is the most interesting part of the process.

The total pressure in this stage is:

$$P = P_{NO} + P_{N_2O} \qquad (3)$$

but by (1):

$$P_{NO} = P_o - 2P_{N_2O} \qquad (4)$$

in this form if we put (3) in (4) we obtain:

$$2P = P_o + P_{NO} \qquad (5)$$

therefore:

$$2P - P_o = P_{NO} \qquad (6)$$

and:

$$C_{NO} = \frac{2P - P_o}{RT} \qquad (7)$$

We know that:

$$\frac{dC_{NO}}{dt} = -K\,(C_{NO})^n \tag{3}$$

And as our results are consistent with the equation:

$$\frac{1}{C_{NO}} - \frac{1}{C_{NO}} = Kt \tag{9}$$

obtained using $n = 2$. Sustituting (7) into (9) we obtain:

$$\frac{RT}{2P - P_0} - \frac{RT}{P_0} = Kt \tag{10}$$

and

$$\frac{RT}{P_0}\left(\frac{P_0}{2P - P_0} - 1\right) = Kt \rightarrow \boxed{\alpha = K P_0 t} \tag{11}$$

In this form we obtained a lineal relation when we plotted versus time α, we concluded that the reaction is of the second order in her first step. Now we can make an Arrhenius plot (Fig. 8) and calculate the activation energy that resulted equal to 20 ± 1 kcal/mol.

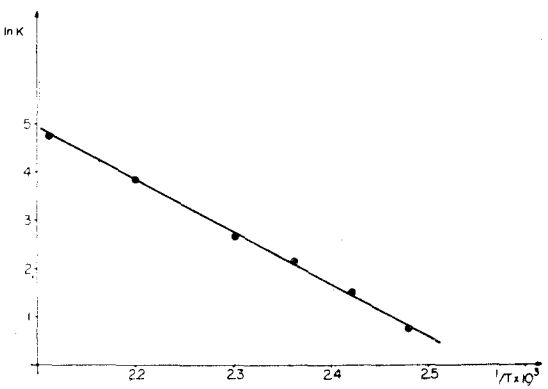


Fig. 8

At this stage we can propose the following mechanism:

$$\left.\begin{array}{ll} 1. & (NO)_{gas} \rightleftarrows (O)_{ad} + (N_2O)_{ad} \\ 2. & 2(NO)_{ad} \longrightarrow (O)_{ad} + (N_2O)_{ad} \\ 3. & 4(O)_{ad} + 3Fe \longrightarrow Fe_3O_4 \\ 4. & (N_2O)_{ad} \rightleftarrows (N_2O)_{gas}\,. \end{array}\right\} \qquad (12)$$

All the species are adsorbed on the oxide formed in the reaction.[9]

If the second process is determining the total velocity of the reaction:

$$\frac{d(C_{NO})ad}{d\,t} = -\,Kr\ [(C_{NO})ad]^2 \qquad (13)$$

but as:

$$(C_{NO})_{ad} = K_a\,(C_{NO})_{gas} \qquad (14)$$

$$K_a \frac{d(C_{NO})_{gas}}{d\,t} = -\,K_r\,(K_a)^2\,[(C_{NO})_{gas}]^2$$

we obtain the equation:

$$K_a \frac{d\,C_{NO}}{d\,t} = -\,K_r\,K_a\,(C_{NO})^2 = -\,K\,(C_{NO})^2 \qquad (15)$$

that fits our experimental results.

The Mössbauer data gives conclusive evidence that the oxide produced is Fe_3O_4, this is clear from the spectra of figures 5 and 6. In the specter of figure 5 we can see "Fe" that did not react with the NO. In the case of the specter of figure 6 there is not Fe visible. In these two spectra we can not see the signals of the Fe_2O_3. The specter at 700°C (Fig. 7) shows the formation of FeO, and if we analyse the width of the peak of FeO, we can conclude that is very near to the stequiometric composition[12, 13].

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