KINETIC OF NITRIDING PROCESS OF FERROMANGANESE ALLOY

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ABSTRACT

This article concerns with the study of some kinetics aspects of the reaction between nitrogen and low carbon ferromanganese (LC-FeMn). Nitriding process of fine low carbon ferromanganese was carried out at temperature range 973 K – 1223 K, under nitrogen and hydrogen gas pressure 15-19 bar. and at time range up to 480 min. Sample weight was 35 gm, nitrided in cylindrical chamber with inner diameter 34 mm and length 1200 mm. The change in nitrogen pressure was taken as an indication for nitrogen pickup. The weight gain i.e. nitrogen pickup in kilograms per surface area (m^2) was determined with time at different temperatures. Nitriding rate constants were calculated and the activation energy of nitriding process was derived from Arrhenius equation. The nitriding rate constant was found to be increase by increasing temperature of the reaction. The activation energy of nitriding process of fine low carbon ferromanganese at time range up to 28800 sec. is around 140 K J/mol. It was found that the rate controlling step of the nitriding process of LC-FeMn is the diffusion mechanism.

1 INTRODUCTION

The study of Mn-N system is a subject of interest nowadays. This is due to the fact that nitrogen addition began to be widely used as an alloying element to replace nickel in austenitic steels. As manganese is added to molten steel in the form of ferromanganese, several authors described different methods for nitriding of ferromanganese or metallic manganese. However few of them dealt with the fundamental issues such as its reaction rate, thermodynamics, and diffusion kinetics in the solid state.

Manganese can be nitrided in the solid state by nitrogen gas, producing Mn_4N and Mn_2N based on the studies carried out by Jin-Zhu et al [1]. However, the kinetics of the reaction studied was limited to a temperature of 1163 K.

Many techniques for nitriding ferroalloys were described in the literature [2-9]. Ammonia gas can be used to nitride ferromanganese in liquid state [4] or in the solid finely divided form [5]. Also, ferromanganese can be nitrided by using nitrogen gas .The rate of reaction between nitrogen gas and manganese in fine ferromanganese was found to be dependent on the surface area and the reaction temperature [5,8]. At the same time, a recent study [11] showed that the maximum content of nitrogen contained in nitrided ferromanganese of high and medium carbon content depends mainly on the temperature of the nitriding process, the nitrogen pressure and its carbon content.

The aim of this study is to evaluate the activation energy of nitriding process of fine low carbon ferromanganese in the solid state at different temperatures to confirm the rate determining step of the process.

2 EXPERIMENTAL

Nitriding process was carried out using fine low-carbon ferromanganese with size -3mm. The nitriding process was carried out at four different temperatures; 973 K, 1023 K, 1123 K, & 1223 K , using 0.035 kg sample of these fines contained in alumina boat. The apparatus used in nitriding is given in Fig. 1. It, mainly, consists of two parts. The first part is gas purification system to eliminate oxygen and humidity from gases to be introduced in the second one (nitriding system). The nitriding system consists of an electric resistant tube furnace with maximum temperature 1473 K and a heat resisting steel reaction tube with endings from both sides by valves for inlet and outlet of the gas. The reaction tube has inner diameter 34mm, and length 1200 mm. A pressure gauge is connected to the inlet side. Nitrogen gas together with hydrogen gas constitutes the source of nitrogen for the nitriding process. The nitriding gas, nitrogen and hydrogen with pressure 10 and 2 bars respectively, at room temperature was injected into the reaction tube at 573 K after flushing it by hydrogen, to prevent oxidation of the alloy. The temperature is then gradually raised to the selected reaction temperature. About 1500 – 2100 seconds is needed to reach the required temperature. The reading of the pressure gauge was taken after 300, 900, 1800, 3600, 7200, 14400 , 21600 and 28800 seconds for each of the four selected temperatures. By the end of the experiment, the nitriding system was flushed by hydrogen and left to cool under hydrogen atmosphere. The boat with the sample, after cooling, was detached from the furnace and was grinded then analyzed to determine its nitrogen content using Kjheldal method.

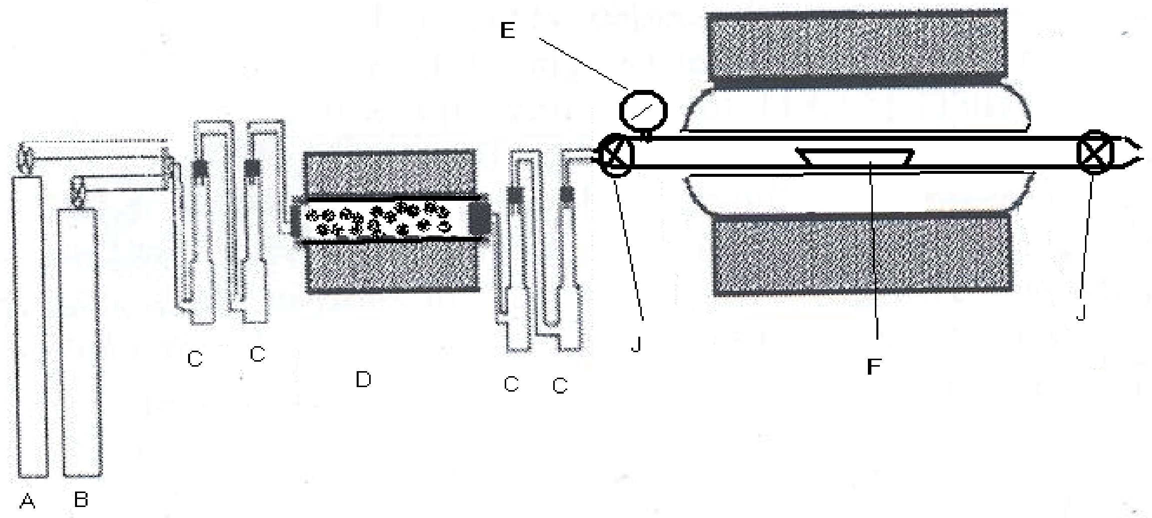

Figure 1: Schematic diagram of nitriding apparatus

With:

A: H_2 gas cylinder	B: N_2 gas cylinder
C : Dryers	D: Tube furnace with cupper turnings
J : Valves	E: Pressure gauge
F : Boat containing sample	

3 RESULTS & DISCUSSIONS

At the first stage of nitriding process i.e. the transfer of nitrogen molecules from the gas phase (N_2 and H_2) to solid ferromanganese occurs in the following steps: (1) transport of nitrogen in the gas phase and adsorption of molecules at the solid surface through a diffusion boundary layer; (2) change of physical adsorption into chemical adsorption and therefore chemical reaction takes place at the surface, and the concentration of nitrogen atoms set up on the surface. This depends on the partial pressure; (3) transfer of nitrogen atoms from the surface and its diffusion inside the particles. Each of these steps has its own specific kinetics that contributes to the global rate of nitriding reaction. By definition, the slowest step determines the rate of the total process. It has been shown that the diffusion in the solid state is the step that controls the process [12]

The determination of chemical composition of the fine ferromanganese used was found to contain 1%C, 80% Mn and 0.01%Si. Its sieve analysis is given in table (1). The surface area of 0.035 kg alloy fines was found to be about 0.10034 m^2.

Based on the dimensions of the reaction tube its volume was calculated to be $1.0899*10^{-3}$ m^3 . The weight equivalent of each one bar of nitrogen gas after correction to the selected reaction temperatures is given in table 2. Table (3) shows the results of measured pressure change of gas with reaction time in the range 300 – 28800 seconds for the selected temperatures.

Table1: Sieve analysis of low carbon ferromanganese fines

Size,mm	Wt. %
-3+2	1.18
-2+1.6	40.01
-1.6+0.5	11.76
-0.5+0.25	23.16
-0.25+0.1	15.26
-0.1	8.57

Based on the results given in tables 2 & 3, the total weight gain and weight gain (kg) per m^2 were calculated at different temperatures. Fig.2 represents the relation between the weight gained of 0.035 kg alloy and time at different temperatures of nitriding process. The weight gained, at different temperatures, relative to the surface area with time is shown in Fig. 3. These figures clarify that the rate of reaction increases with the reaction temperature. The reaction rate between nitrogen and the ferromanganese fines is relatively high for the first 1800 seconds and then slow down gradually in all temperatures selected (973 K -1223 K). The rate of reaction is extremely slow after 21600 sec.

However the amount of nitrogen gas gained at the end of experiment i.e. at 28800 seconds is greater the higher the nitriding temperature. These calculated nitrogen contents were confirmed by the results obtained from chemical analysis of nitride samples at temperatures 973 K, 1023 K, 1123 K and 1223 K after 28800 seconds and represented in Fig. (4).

The mechanism of the nitriding process of fines low carbon ferromanganese is controlled by diffusion mechanism according to Torchane et al [12]. In this case the kinetic is said to be parabolic behavior. The rate determining step is expected to be the diffusion of nitrogen inward the ferromanganese. The rate of nitriding with time is inversely proportional with the nitrogen content in ferromanganese.

$$\frac{\partial x}{\partial t} = k\frac{1}{x} \tag{1}$$

Where:
x : is the nitrogen content in ferromanganese
k: is the parabolic rate constant which may be related to the diffusion coefficient.
x^2 = 2kt + constant
Or $(\Delta m)^2$ = 2kt + constant

Plotting $(\Delta m)^2$ versus time should give straight line as given in Fig. 5. It is clear that, this figure has high regression values at temperatures 973 K, 1023 K, 1123 K and 1223 K. This means that the nitriding process of fine low carbon ferromanganese is actually controlled by diffusion mechanism. The slopes of these lines represent the reaction rate constants of the nitriding process at different temperatures.

Fig. 6 shows the Arrhenius' plots of the nitriding process of fine low carbon ferromanganese, based on the Arrhenius' equation [13]:

$$k = Ae^{-E_a/RT} \tag{2}$$

Where: k : is expressed as reaction rate constant, E_α: is activation energy of diffusion (kJ /mol), A : is the frequency factor, R: universal gas constant & T :is absolute temperature in Kelvin (K)

The slope of the plot between lnk and $\frac{1}{T}$ equals - E_α/R. The value of E_α was found to be about 140 KJ mol^{-1}

Table 2: The equivalent gas pressure of 12 bar at 573 K

Temp. °C	Calculate pressure, bar	Measured pressure, bar	Temp. K	Number of mole (n)	Wt., gm	Wt. of gas in every 1bar
300	12	12	573	0.278196	7.789483	0.649124
700	20.37698	20.2	973	0.278196	7.789488	0.382269
750	21.4241	21.1	1023	0.278196	7.789488	0.363585
850	23.51834	23	1123	0.278196	7.789488	0.331209
950	25.61258	24.8	1223	0.278196	7.789488	0.304127

Table 3: Measured pressure at different time at different temperatures

	Pressure at different temp., bar			
Time, sec.	973 K	1023 K	1123 K	1223 K
0	20.20	21.10	23.00	24.80
300	20.00	20.60	21.75	23.00
900	19.75	20.10	21.00	21.30
1800	19.60	19.85	20.25	20.00
3600	19.50	19.60	19.75	18.80
7200	19.40	19.10	18.90	17.30
14400	19.10	18.30	17.50	15.60
21600	18.95	17.85	16.75	13.90
28800	18.90	17.70	16.60	13.60

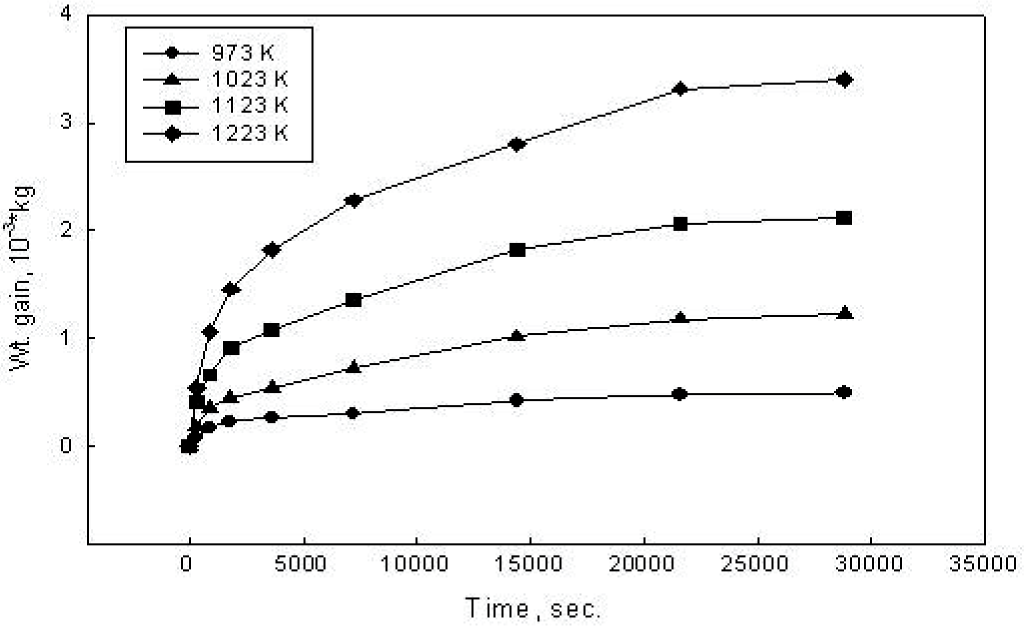

Figure 2: Total weight gain of 35 gm fine FeMn - at different time for each temperature (973 K, 1023 K, 1123 K, & 1223 K)

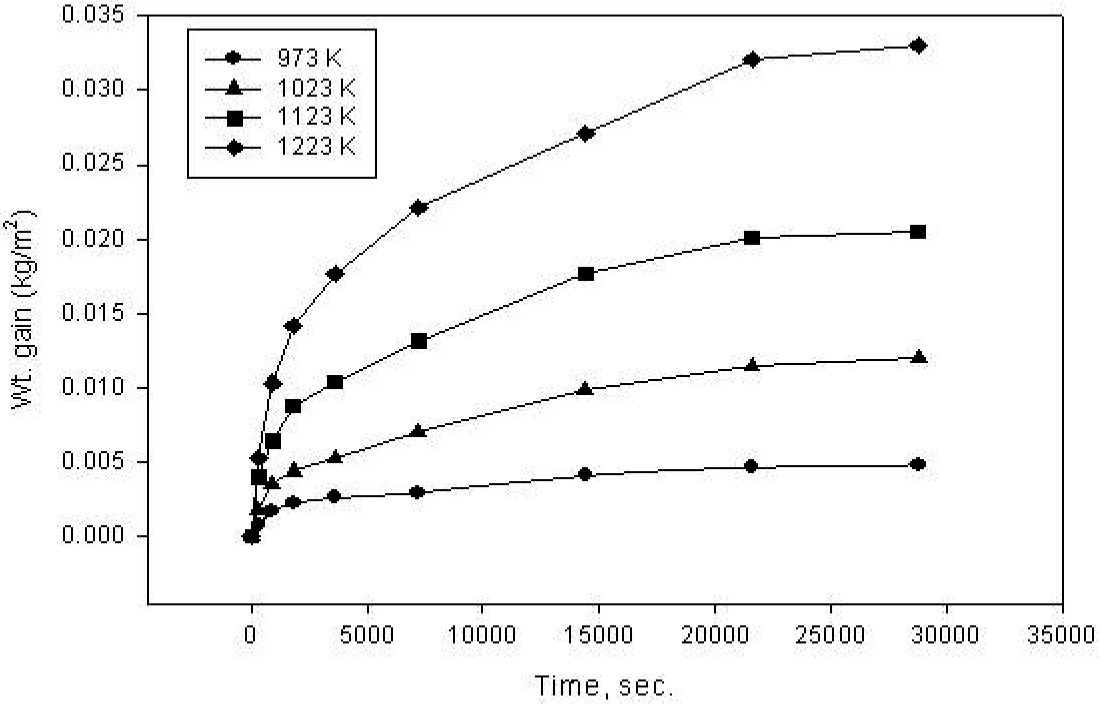

Figure 3: eight gain (kg) per m^2 at different time for each temperatures (973 K, 1023 K, 1123 K, & 1223 K)

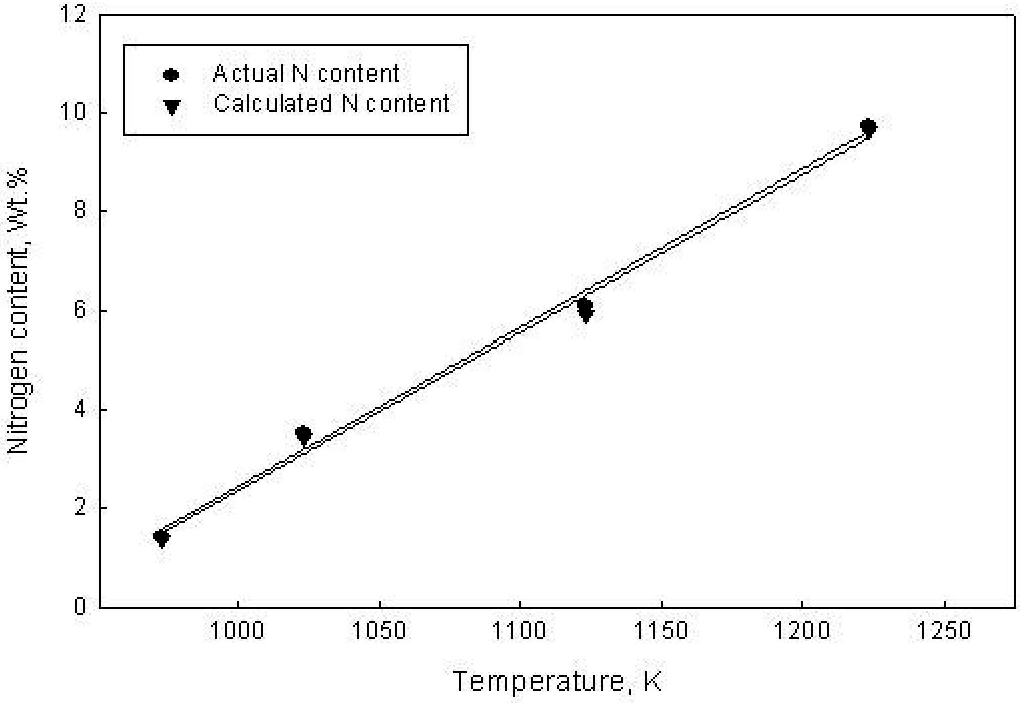

Figure 4: Te variation of calculated nitrogen content from the experimental values

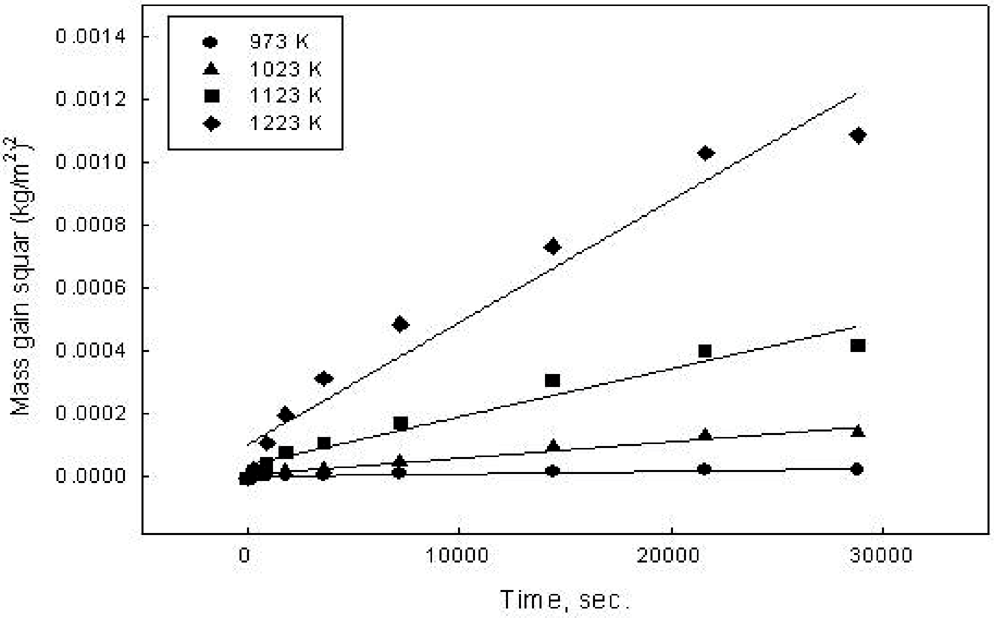

Figure 5: Variation of mass gain square with time of the nitriding of low carbon ferromanganese at temperature range 973 K- 1223 K up to 28800 sec.

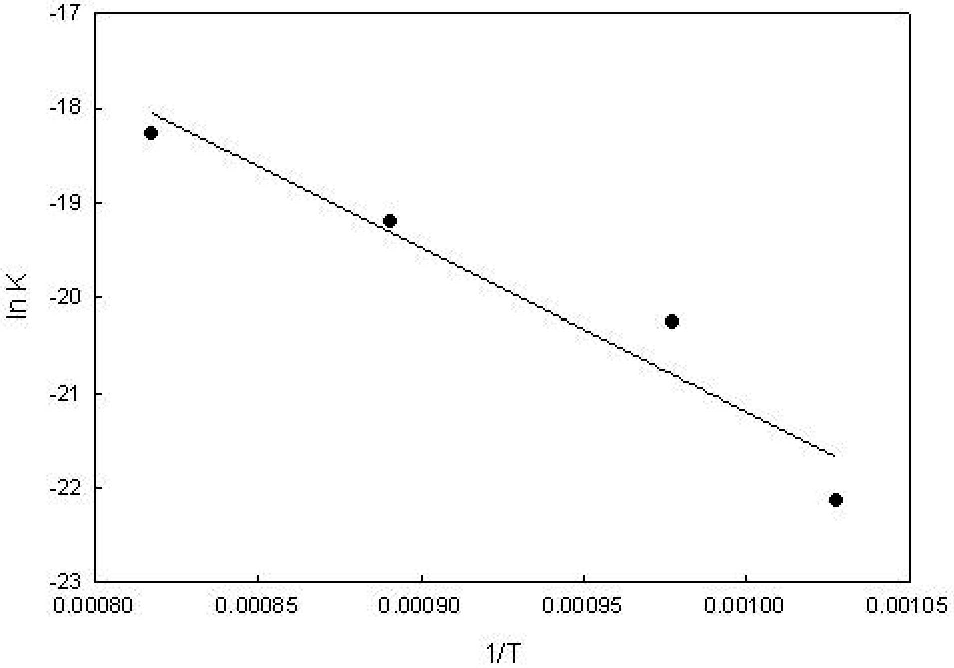

Figure 6: Arehenius plot, ln K & (1/T) for the nitriding process of fine low carbon ferromanganese in time range up to 480 min

4 CONCLUSIONS

- The gas-solid reaction of nitrogen with fine low carbon ferromanganese is controlled by diffusion mechanism
- The rate of reaction is dependent on temperature
- The activation energies of nitriding process of fine low carbon ferromanganese by nitrogen and hydrogen gas in time ranges (0 – 28800 sec.) is 140 K $Jmol^{-1}$
- The weight gain technique used in nitrogen determination is confirmed with the Kjheldal method for nitrogen determination.

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