ACTIVATION ENERGY OF NITRIDING 0.23%C FERROMANGANESE

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ABSTRACT

This article aims at studying the kinetics of the reaction between nitrogen and 0.23%C ferromanganese through gas – solid reaction. The nitriding process of fine ferromanganese was carried out at temperature range of 1073 K – 1223 K, under nitrogen and hydrogen gas pressure of 16-18 bar and at time range up to 360 min. Sample weight was 150 gm nitrided in cylindrical chamber with inner diameter of 56 mm and length of 2000 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 energies of nitriding process of fine ferromanganese at time range from 0 sec. to 2700 Sec. and from 5400 sec. to 21600 sec. were around 60.8 KJ/mol and 41.8 KJ/mol respectively.

KEY WORDS: *kinetics, nitriding, ferromanganese, gas - solid reaction, activation energy*

1 INTRODUCTION

Nitrogen was considered for a long period to be in the same category as certain undesirable residual elements in steel, which are generally harmful due to its properties. Recently, it was noticed that nitrogen has significant effect on mechanical properties, phase stability, corrosion behavior and oxidation resistance [1-11].

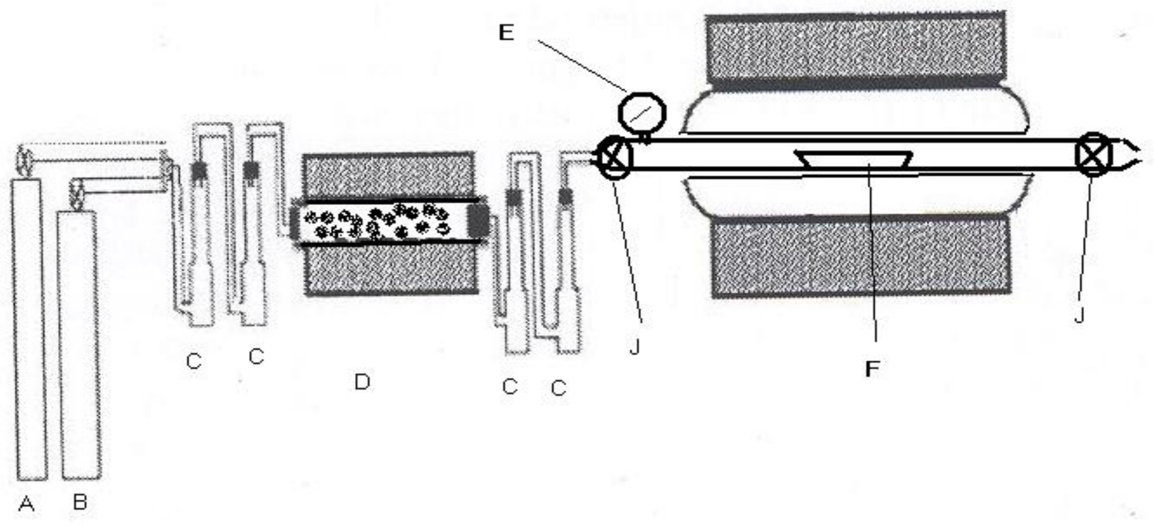
Nitrogen became promising alloying element in steel where nitrogen alloyed different steel grades have applications in different fields such as transportations, environment technologies, industrial plants civil engineering and equipment, etc. [6].

Ferroalloys bearing nitrogen are considered the main source in manufacturing different steel grades containing nitrogen. Ferromanganese nitrogen is considered one of the most important one as a source of nitrogen in manufacturing stainless steels especially [12]. Many techniques for nitriding ferroalloys were described in the literature [13 - 15]. One of these techniques is gas solid reaction between nitrogen gas and ferromanganese. The rate of reaction between nitrogen gas and manganese in fine ferromanganese was found to be dependent on the surface area, reaction temperature and carbon content in the ferromanganese [13, 14, 16]. At the same time, several studies [15-17] showed that the maximum nitrogen content contained in nitrided ferromanganese depends mainly on the temperature, nitrogen pressure of the nitriding process, grain size of ferromanganese and its carbon content.

This work aims at evaluation the activation energy of nitriding process of 0.23%C ferromanganese through nitriding fine ferromanganese with the size of 0.1 – 0.25 mm by nitrogen gas in gas solid reaction.

2 EXPERIMENTAL

Nitriding process was carried out using fine 0.23%C ferromanganese with size 0.1 – 0.25 mm. The nitriding process was carried out at four different temperatures; 1073 K, 1123 K, 1173 K, and 1223 K using 0.150 kg sample of this ferromanganese contained in alumina boat. The apparatus used in nitriding is given in **Figure 1**. It consists mainly 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 second part is the nitriding system which consists of an electric resistant tube furnace with maximum temperature of 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 of 56 mm, and length of 2000 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 of 8 and 2 bars respectively, at room temperature was injected into the reaction tube at 673 K after flushing it by hydrogen, to prevent oxidation of the alloy. The temperature is then gradually raised to the selected reaction temperature. About 1800 seconds is needed to reach the required temperature. The readings of the pressure gauge were taken after 300, 600, 1800, 2700, 5400, 10800 and 21600 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 and carbon content was determined.



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	

Figure 1: Schematic diagram of nitriding apparatus

3 RESULTS AND DISCUSSIONS

Nitriding of ferromanganese in gas solid reaction pass through three stages. The first stage is transportation of nitrogen gas molecules and adsorbed physically at the solid surface of fine ferromanganese. The second stage is the change of physical adsorption into chemical adsorption and therefore chemical reaction takes place at the surface of fine ferromanganese particles, and the concentration of nitrogen atoms set up on the surface. The third stage is the 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 [18]

The determination of chemical composition of the fine ferromanganese used was found to contain 0.23%C, 83.8% Mn and 0.61%Si. Its size is in between 0.1 – 0.25 mm. The surface area of 0.150 kg ferromanganese fines was found to be about 0.69498 m^2.

Based on the dimensions of the reaction tube its volume was calculated to be $4.926*10^{-3}$ m^3. The weight equivalent of each one bar of nitrogen gas at each reaction temperature is given in **Table (1)**. **Table (2)** shows the results of measured pressure change of gas with reaction time in the range of 300 – 21600 seconds for each working temperature.

Based on the results given in **Tables (1-2)**, the total weight gain (kg) and weight gain (kg) per m^2 were calculated at different temperatures. **Figure 2** represents the relation between the nitrogen weight gained by 0.150 kg fine ferromanganese and time at different temperatures of nitriding process. The weight gained, at different temperatures, relative to the surface area with time is shown in **Figure 3**. These figures clarify that the rate of reaction increases with the reaction temperature. The reaction rate between nitrogen and the ferromanganese fines is high at the first, then slow down gradually at all working temperatures (1073 K -1223 K). The rate of reaction is extremely slow after 10800 sec.

However the amount of nitrogen gas gained at the end of experiment i.e. at 21600 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 of 1073 K, 1123 K, 1173 K and 1223 K after 21600 seconds and represented in **Figure 4**.

The mechanism of the nitriding process of fines low carbon ferromanganese is controlled by diffusion mechanism according to Torchane et al. [18]. In this case the kinetic is said to be parabolic behaviour. 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 as given in equation (1).

$$\frac{\partial x}{\partial t} = k\frac{1}{x} \qquad (1)$$

Where, x is the nitrogen content in ferromanganese, k is the parabolic rate constant which may be related to the diffusion coefficient as illustrated in equation (2).

$$x^2 = 2kt + \text{constant, or } (\Delta m)^2 = 2kt + \text{constant} \qquad (2)$$

Figure 5 shows the variation between $(\Delta m)^2$ and time. It is clear that this figure has high regression values at temperatures 1073 K, 1123 K, 1173 K and 1223 K at two time regions. This means that the nitriding process of ferromanganese is controlled by diffusion mechanism with different activation energies at two time regions. The slopes of these lines represent the reaction rate constants of the nitriding process at different temperatures. It is clear that the slopes of time region II (5400 – 21600 Sec.) is lower than that of time region I(0 – 2700 Sec.). This is due to the nitrogen pickup taken by fine ferromanganese and hence the rate of nitriding process decreases gradually as a result of concentration gradient of nitrogen in ferromanganese.

Figure 6 shows the Arrhenius' plots of the nitriding process of fine ferromanganese based on the Arrhenius' equation as given in equation (3)[19]:

$$k = Ae^{-E_a / RT} \tag{3}$$

Where: k is expressed as reaction rate constant, E_α is activation energy of diffusion (kJ /mol), A is the frequency factor, R is universal gas constant (8.314 $JK^{-1}mol^{-1}$) and T is absolute temperature in Kelvin (K)

The slope of the plot between lnk and $\frac{1}{T}$ is equal - E_α/R. The values of E_α were found to be about 60.79 KJ mol^{-1} and 41.78 KJ mol^{-1} for time region I (0 – 2700 Sec.) and time region II (5400 – 21600 Sec.), respectively. It was found that the activation energy of time region II is smaller than the activation energy of time region I. This may be attributed to the lower carbon content. During nitriding process at high temperature occur dusting for carbon i.e. diffusion of carbon outward ferromanganese. It was found that carbon content after nitriding process decreases as temperature increases. The carbon contents after nitriding process were 0.13%, 0.12%, 0.11% and 0.10% at nitriding temperatures 1073 K, 1123 K, 1173 K and 1223 K, respectively. This description is confirmed by the previous work [16] where it was found that the activation energy of 1 % C is 140 KJ/mol.

Table 1: The equivalent gas pressure of 10 bar at different temperatures.

Temp., ^oC	Calculate pressure, bar	Actual pressure, bar	Temp., K	Number of mole (n)	Wt., gm	Wt. of gas in every 1bar
400	10	10	673	0.8921	24.9788	2.4978
800	15.94	15.5	1073	0.8921	24.9788	1.5667
850	16.68	16.1	1123	0.8921	24.9788	1.4969
900	17.42	16.8	1173	0.8921	24.9788	1.4331
950	18.17	17.4	1223	0.8921	24.9788	1.3745

Table 2: Measured pressure at different time at different temperatures

Time, sec.	Pressure at different temp., bar			
	1073 K	1123 K	1173 K	1223 K
0	15.9	16.7	17.4	18.1
300	14.8	14.9	14.5	14.2
600	13.5	12.9	12.6	11.5
1800	12.3	11.7	11.4	10.5
2700	11.2	10.3	10.1	9.3
5400	10	9.3	8.7	7.9
10800	9	8.3	7.5	6.4
21600	8.9	8.1	7.4	6.3

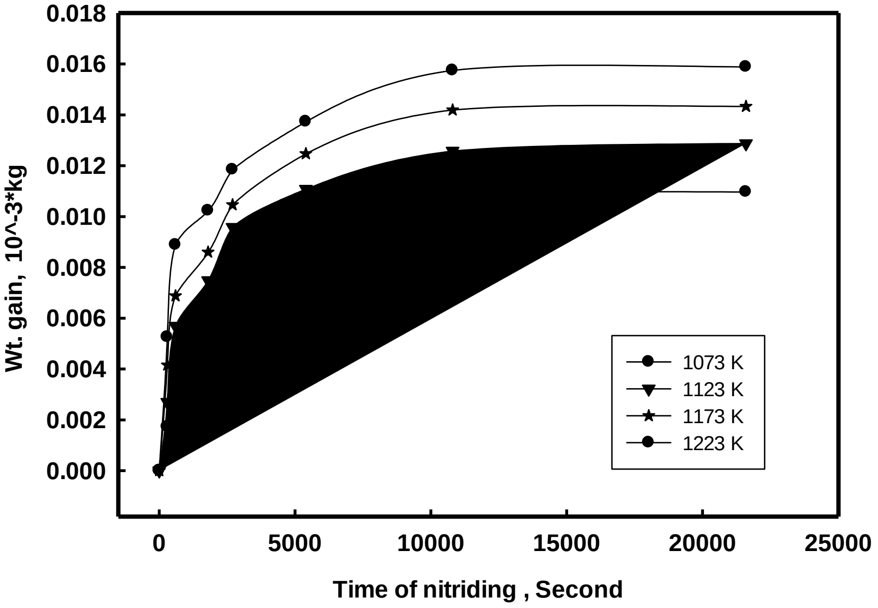


Figure 2: The variation of nitrogen weight gain – by 0.150 kg 0.23%C ferromanganese – over time at temperatures 1073 K, 1123 K, 1173 K and 1223 K

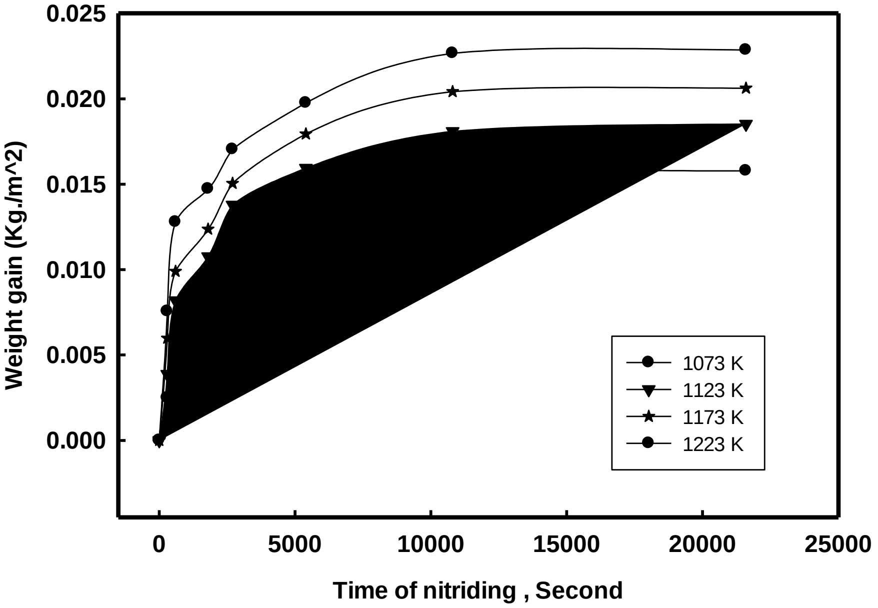


Figure 3: The variation of weight gain (kg) per m^2 over time at temperatures 1073 K, 1123 K, 1173 K and 1223 K

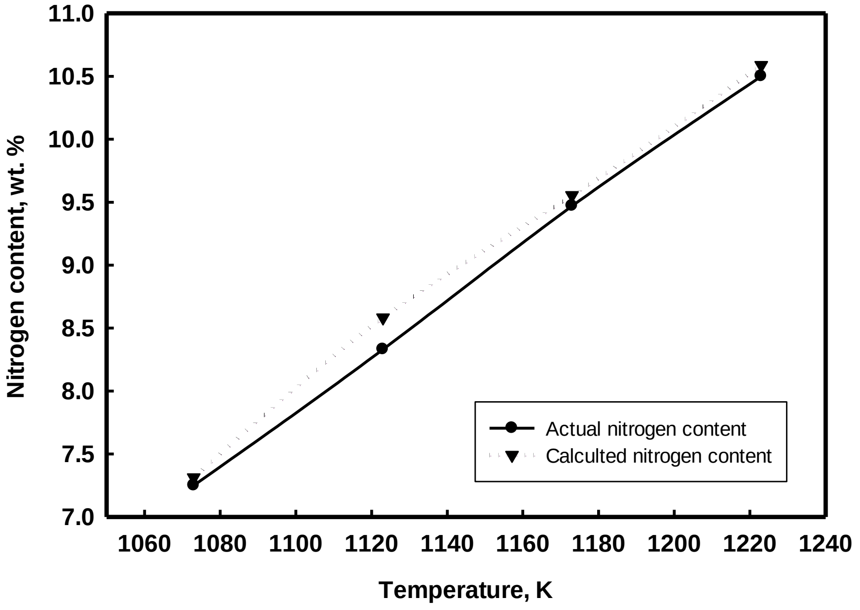


Figure 4: The variation between calculated and actual nitrogen content over nitriding time 21600 sec. at different temperatures.

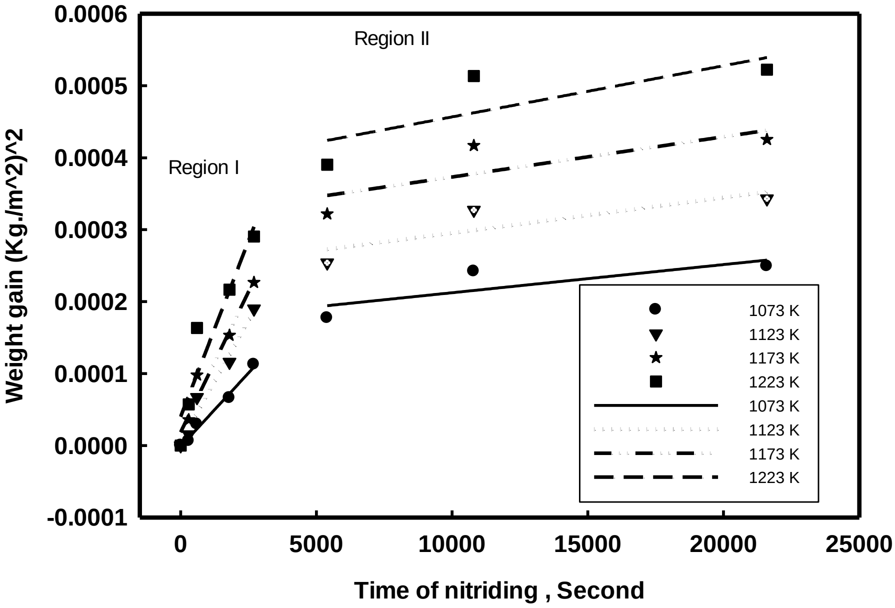


Figure 5: Variation of mass gain square with time of the nitriding of 0.23%C ferromanganese at temperature range of 1073 K- 1223 K up to 21600 Sec.

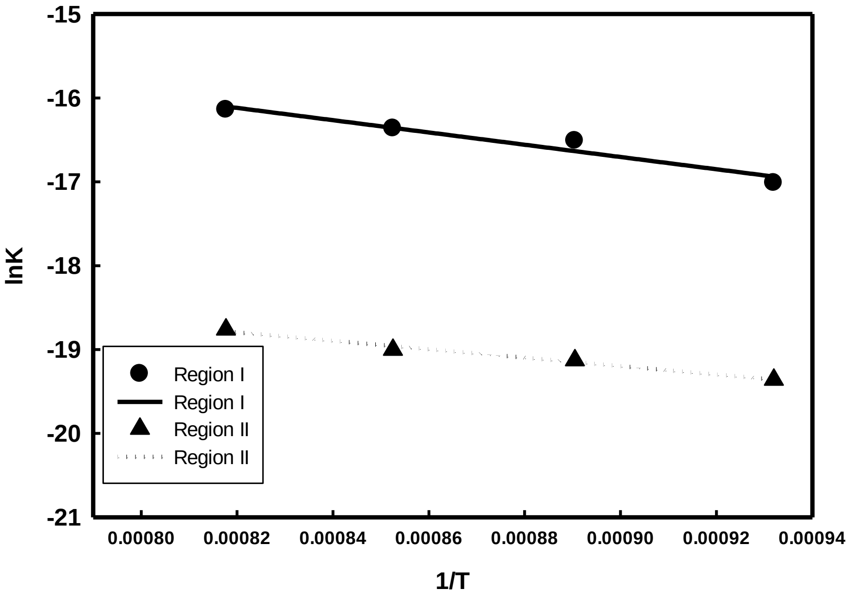


Figure 6: Arehenius plot, lnK against (1/T) of nitriding process of 0.23%C ferromanganese in time region I(0 – 2700 Sec.) and time region II(5400 – 21600 Sec.)

4 CONCLUSIONS

The nitriding of 0.23%C ferromanganese by nitrogen gas is controlled by diffusion mechanism. The rate of reaction is dependent on temperature and region time of nitriding process. The activation energy of nitriding process of 0.23 %C ferromanganese by nitrogen gas in time region (0 – 2700 Sec.) is 60.79 K Jmol^{-1}, while in time region (5400 – 21600 Sec.) it is 41.78 K Jmol^{-1}. Carbon retard nitriding process of ferromanganese and increase the activation energy of nitriding process.

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