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Research Article

Influence Parameters on Nitriding Process of Ferromanganese Alloy

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A 2^4 factorial design technique was used to investigate the magnitude effect of temperature, time, carbon percent, and pressure of the nitriding process of gas solid reaction of ferromanganese. The design was based on experiments results obtained from nitriding of two grades of ferromanganese alloys containing 0.23% C and 7.1% C at temperatures 700°C and 950°C, during time of 2 hours and 6 hours and with nitrogen pressure of 1 and 8 bar. The required calculations were carried out by Matlab. It was found that the highest positive effect was temperature while the carbon content has the highest negative effect. Nitrogen pressure has more positive effect than time. The interaction combination between two parameters or more of temperature, nitrogen pressure, and time has positive influence with different extent. The interaction combination between carbon and one or more of parameters of time, temperature, or nitrogen pressure has negative effect on nitriding process. The driven models were found to be in good agreement with the experiments and published work of nitriding process of ferromanganese containing different carbon contents (0.23–7.1%) in temperature range 700°C–950°C, with nitrogen pressure up to 8 bar, and during time of 2–6 hours.

1. Introduction

The reaction process of nitrogen gas with ferroalloys in solid state is called "nitrogen pickup." This process includes four stages; the first stage is diffusion of nitrogen gas into the bulk of ferroalloys, the second stage is the adsorption process of nitrogen gas on the surface of ferroalloys. Third stage includes dissociation of nitrogen gas molecules into atoms. In the fourth stage, nitrogen atoms react with ferroalloys to form ferroalloys bearing nitrogen [1].

Nitriding of ferroalloys was investigated in previous literature [2–9]. Ammonia gas is one of the most common sources of nitrogen which can be used in nitriding of ferromanganese in liquid state [4] or in the solid finely divided form [5]. Also, nitrogen gas was used as a source of nitrogen in nitriding of fine ferroalloys [6, 7]. There are different parameters that control nitriding of ferromanganese alloy. Fabo [5] and Hunsbedt and Olsen [8] showed that the nitrogen pickup increased with increasing exposed surface area. On the other hand, the reaction temperature has positive significant effect on the rate of nitriding process as Hunsbedt and Olsen [8] found. The physical meaning of nitrogen pickup quantity is described in detail by previous published work [10].

Nitrogen was considered for long period to be as certain undesirable residual elements in steel. Nitrogen has harmful effects on steel properties. This was believed as high nitrogen contained steel is subject to ageing with deterioration of its plasticity with time. Recently, it was noticed that nitrogen has positive significant effect on mechanical properties, phase stability, corrosion behavior, and oxidation resistance [10–24]. Moreover, nitrogen as opposed to carbon did not reduce the corrosion resistance of steel [25]. The most essential advantage of nitrogen as an alloying element is its availability and its being almost unlimited as a natural resource. As nitrogen only occurs in nature in the form of gas, in order to introduce it into steel it is necessary to turn nitrogen into a solid matter, and such a nitrogen-bearing material must be compatible with molten steel [26]. Despite the fact that there are new technologies of the direct introduction of gaseous nitrogen into liquid ferroalloys which are successfully developing now, alloying with the use of solid nitrogen sources still remains the principal method of nitrogen-bearing steel

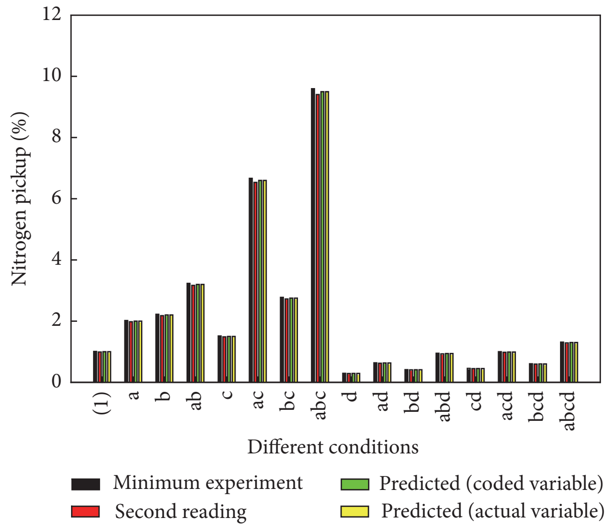

Figure 1: The variation between the predicted (coded and actual variables) and measured nitrogen pickup of low and high carbon ferromanganese.

melting due to the possibility of applying this process to different steel grades [27].

At this point, it is crucial that the base of the nitrogen source is compatible with the steel composition, and the nitrogen percent in it is just enough for the frugal introduction of its required quantity into steel. Historically, the first sources of nitrogen were chrome based alloys, because first produced nitrogen-bearing steels were stainless chrome alloys. Then, manganese-based nitrogen-bearing rich alloys appeared as a response to the development of nitrogen-bearing Cr-Mn-steels [25]. The kinetic and activation energy of nitriding process was investigated through previous work [10, 28]. And other efforts were attempted to predict the nitrogen pickup in nitriding process of low carbon ferromanganese at steady state [29].

The previous survey summarized some work carried out experimentally on the effect of various conditions of nitriding process especially of ferromanganese alloy. However, the effective magnitude of these parameters individually or collectively on the nitriding process is still required. This can be carried out by the application of factorial design approach which has several advantages in the prediction of process yield, process performance, and the estimation of key parameters that control the overall process [30–33].

In the current work, a 2^4 factorial design is used to estimate the individual and mutual combination influence of temperature, time nitrogen pressure, and carbon content on nitriding process of ferromanganese alloy. This model is built on experimental work at temperatures 700°C and 950°C, nitrogen pressure of 1 bar and 8 bar, and the nitriding time of 2 hours and 6 hours for each ferromanganese containing 0.23% C and 7.1% C. The predicted data is fit very well with experimental data. In addition, the model is tested with the experimental data of previous work [10, 27–29]. Matlab was used to carry out the required calculations.

2. Experiments, Controlling Parameters, and Mathematical Formulations

A 2^4 factorial design is built based on the experimental data of nitriding process of fine ferromanganese alloys containing 0.23% C and 7.1% C at temperatures 700°C and 950°C for time of 2 hours and 6 hours under nitrogen gas pressure of 1 bar and 8 bar. The derived model is applied on experimental data. Also, the model was applied on previous published work [10, 27–29, 34].

The chemical analysis of low carbon ferromanganese alloy used in the experimental work was 0.23% C, 87.60% Mn, and 0.01% Si and chemical analysis of high carbon ferromanganese was 7.1% C, 76.7% Mn, and 0.14% Si. Experiments were carried out on laboratory scale using 50 gm of fine low and high carbon ferromanganese alloy. Nitrogen gas was used as source of nitrogen. Figure 1 shows a schematic diagram of laboratory nitriding system. The system is described in previous work [10]. Experimental method was described in previous work [29]. Each trail was repeated two times under the same conditions in order to confirm the results reproducibility.

Total nitrogen content in the produced ferromanganese bearing nitrogen was determined by Kjeldahl method [35]. This determination was carried out three times using represented samples. The final result was the mean value of these three determinations.

The experimental variables (nitriding temperature 700–950°C, time 2–6 h, nitrogen pressure 1–8 bar, and carbon content 0.23–7.1% in ferromanganese alloy) and their levels were given in Table 1. 2^4 factorial design is derived square matrix (16×16). Matlab was used to solve this matrix.

2.1. Definition of the Controlling Parameters. The effect of temperature, time, nitrogen pressure, and carbon content are the controlling parameters of nitriding process. The effect of

Table 1: Nitrogen pickup of low (0.23%) and high (7.1%) carbon ferromanganese at different experimental conditions.

Number	Temp., °C	Time, H	Nitrogen pressure, bar	Carbon content, wt.%	Nitrogen pickup, wt.%	
					1st exp.	2nd exp.
1	700	2	1	0.23	1.010	0.990
2	950	2	1	0.23	2.020	1.980
3	700	6	1	0.23	2.222	2.178
4	950	6	1	0.23	3.232	3.168
5	700	2	8	0.23	1.515	1.485
6	950	2	8	0.23	6.666	6.534
7	700	6	8	0.23	2.778	2.723
8	950	6	8	0.23	9.595	9.405
9	700	2	1	7.1	0.293	0.287
10	950	2	1	7.1	0.636	0.624
11	700	6	1	7.1	0.414	0.406
12	950	6	1	7.1	0.949	0.931
13	700	2	8	7.1	0.455	0.446
14	950	2	8	7.1	1.000	0.980
15	700	6	8	7.1	0.606	0.594
16	950	6	8	7.1	1.313	1.287

each factor was denoted by a letter. Thus "A" refers to the effect of applied temperature; "B" refers to the effect of time; "C" refers to the effect of nitrogen pressure; "D" refers to effect of carbon content. The interaction combinations of two, three, and four parameters were also taken into account.

The low and high levels of different parameters (A, B, C, and D) are denoted by "−" and "+", respectively. The sixteen treatment combinations in the design are usually represented by lowercase letters. The high level of any factor in the treatment combination is denoted by the corresponding lowercase letter (a, b, c, and d) and the low level of each factor in the treatment combination is denoted by the absence of the corresponding letter.

For illustration, "c" represents the treatment combination of nitrogen pressure (C) at high level with low levels of temperature (A), time (B), and carbon content (D). "ad" refers to working conditions of high temperature level (A), high carbon content level (D), low levels of time (B), and nitrogen pressure (C). "abc" refers to working conditions at high levels of temperature (A), time (B), and nitrogen pressure (C) with low level of carbon content (D). "abcd" refers to working conditions at high levels of temperature (A), time (B), nitrogen pressure (C), and carbon content (D). Finally (1) is used to denote all parameters at low levels.

2.2. Mathematical Formulations. The effect of different parameters on the nitrogen pickup is estimated by using mathematical formulations. The effect of A (temperature) at low levels of B (time), C (nitrogen pressure), and D (carbon content) is $[a - (1)]/n$, the effect of A (temperature) at high levels of B (time), C (nitrogen pressure), and D (carbon content) is $[abcd - bcd]/n$, the effect of A (temperature) at low level of B (time) and high levels of C (nitrogen pressure) and D (carbon content) is $[acd - cd]/n$, the effect of A (temperature) at low level of C (nitrogen pressure) and high levels of B (time) and D (carbon content) is $[abd - bd]/n$, the effect of A (temperature) at high level of C (nitrogen pressure) and low levels of B (time) and D (carbon content) is $[ac - c]/n$, the effect of A (temperature) at low level of D (carbon content) and high levels of B (time) and C (nitrogen pressure) is $[abc - bc]/n$, the effect of A (temperature) at high level of B (time) and low levels of C (nitrogen pressure) and D (carbon content) is $[ab - b]/n$, and the effect of A (temperature) at high level of D (carbon content) and low levels of B (time) and C (nitrogen pressure) is $[ad - d]/n$. The main effect of A (temperature) is the average quantities of its effect at low and high levels of B (time) and C (nitrogen pressure). In a similar way, the average main effect of one, two, three, or four factors and their interactions can be calculated (dividing its contrast by 16, i.e., number of experiments) according to factorial design of 2^4. The effect of all affecting parameters on the reduction yield and its interaction are given in (A.1) (see the Appendix).

3. Results and Discussion

Table 1 shows the results of nitriding process of low and high carbon ferromanganese alloys according to the experimented conditions.

Application and Validation of Regression Model. The plus and minus signs which can be developed from the contrasts of the effective factors are given in Table 2. The high level is referred to by (+) sign and low level is referred to by (−) sign.

Sum of squares for the effects in the 2^4 design with n replicates is $SS = (\text{Contrast})^2/16\,n$. The total sum of squares (SS_T) has ($abcdn - 1$) degrees of freedom and the error sum of squares (SS_E) has $abcd\,(n-1)$ degrees of freedom. Based on the experimental results, which are mentioned in Table 1, the

Table 2: Algebraic signs representing the contrast constants for the 2^4 factorial design.

Treatment combination	Factorial effect															
	I	A	B	AB	C	AC	BC	ABC	D	AD	BD	ABD	CD	ACD	BCD	ABCD
(1)	+	−	−	+	−	+	+	−	−	+	+	−	+	−	−	+
a	+	+	−	−	−	−	+	+	−	−	+	+	+	+	−	−
b	+	−	+	−	−	+	−	+	−	+	−	+	+	−	+	−
ab	+	+	+	+	−	−	−	−	−	−	−	−	+	+	+	+
c	+	−	−	+	+	−	−	+	−	+	+	−	−	+	+	+
ac	+	+	−	−	+	+	−	−	−	−	+	+	−	−	+	−
bc	+	−	+	−	+	−	+	−	−	+	−	+	−	+	−	−
abc	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	+
d	+	−	−	+	−	+	+	+	+	−	−	+	−	+	+	+
ad	+	+	−	−	−	−	+	+	+	+	−	−	−	−	+	−
bd	+	−	+	−	−	+	−	−	+	−	+	−	−	+	−	−
abd	+	+	+	+	−	−	−	−	+	+	+	+	−	−	−	+
cd	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−	+
acd	+	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−
bcd	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−
abcd	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Table 3: Analysis of variances (average effect, sum of square, degree of freedom, mean square, and magnitude effect).

Source of variance	Average effect	Sum of square (SS)	Degree of freedom	Mean square (MS)	F_o (magnitude effect)
A (temperature)	1.995	31.8402	1	31.8402	15119.9
B (time)	0.93	6.9192	1	6.9192	3285.708
AB	0.25	0.5	1	0.5	237.4341
C (nitrogen pressure)	1.6275	21.19005	1	21.19005	10062.48
AC	1.2775	13.05605	1	13.05605	6199.903
BC	0.2225	0.39605	1	0.39605	188.0715
ABC	0.2025	0.32805	1	0.32805	155.7805
D (carbon content)	−2.8925	66.93245	1	66.93245	31784.09
AD	−1.4675	17.22845	1	17.22845	8181.243
BD	−0.7075	4.00445	1	4.00445	1901.586
ABD	−0.1625	0.21125	1	0.21125	100.3159
CD	−1.36	14.7968	1	14.7968	7026.53
ACD	−1.185	11.2338	1	11.2338	5334.574
BCD	−0.215	0.3698	1	0.3698	175.6063
ABCD	−0.21	0.3528	1	0.3528	167.5335
Error		0.033694	16	0.002106	
Total		189.3931	31		

main effects of variables such as sum of squares, magnitude effect, and the mean square are given in Table 3.

Based on the obtained data, the magnitude and direction of the different affecting parameters can be estimated to determine which variable is relatively more effective compared to the others. The nitriding temperature (A) exhibited the highest positive significant effect on the nitriding process followed by the applied nitrogen pressure (C) followed by the interaction effect of temperature with nitrogen pressure (AC) and then the effect of time (B). The interaction combination of time with temperature or/and nitrogen pressure (AB, BC, and ABC) has little positive effect on nitrogen pickup. On the other hand, the highest significant negative effect on the nitrogen pickup of ferromanganese was revealed by carbon content (D) followed by the interaction effect of temperature-carbon content (AC), nitrogen pressure-carbon content (CD), and time-carbon content (BD). The interaction combination of temperature-nitrogen pressure-carbon content (BCD) and temperature-time-nitrogen pressure-carbon content (ABCD) has little negative effect on nitrogen pickup. Based on the previous estimated values, the parameters with relatively high and negative magnitude will retard the

Table 4: Contrast coefficients of effects.

Effects	(1)	a	B	Ab	c	ac	bc	abc	d	ad	bd	abd	cd	Acd	bcd	abcd
A	−1	+1	−1	+1	−1	+1	−1	+1	−1	+1	−1	+1	−1	+1	−1	+1
B	−1	−1	+1	+1	−1	−1	+1	+1	−1	−1	+1	+1	−1	−1	+1	+1
AB	−1	−1	−1	+1	+1	−1	−1	+1	−1	+1	+1	+1	−1	+1	+1	+1
C	−1	−1	−1	−1	+1	+1	+1	+1	−1	−1	−1	−1	+1	+1	+1	+1
AC	−1	−1	+1	−1	−1	+1	−1	+1	−1	+1	−1	+1	+1	+1	+1	+1
BC	−1	+1	−1	−1	−1	−1	+1	+1	−1	−1	+1	+1	+1	+1	+1	+1
ABC	−1	+1	+1	−1	+1	−1	−1	+1	−1	+1	+1	+1	+1	+1	+1	+1
D	−1	−1	−1	−1	−1	−1	−1	−1	+1	+1	+1	+1	+1	+1	+1	+1
AD	−1	+1	−1	+1	−1	+1	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1
BD	−1	−1	+1	+1	−1	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
ABD	−1	+1	+1	+1	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
CD	−1	−1	−1	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
ACD	−1	+1	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
BCD	−1	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
ABCD	−1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1

nitrogen pickup process while the parameters with high and positive magnitude will enhance the nitriding process.

The contrast coefficients which are used in the calculations are summarized in Table 4. The contrast coefficient is always either (+1) or (−1) referring to the maximum and minimum level for the affecting factor.

Equation (1) illustrates the regression model to predict nitrogen pickup of ferromanganese.

$$\begin{aligned}\text{Nitrogen pickup, \%} = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 \\ & + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 \\ & + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 \\ & + \beta_{34} x_3 x_4 + \beta_{123} x_1 x_2 x_3 \\ & + \beta_{124} x_1 x_2 x_4 + \beta_{134} x_1 x_3 x_4 \\ & + \beta_{234} x_2 x_3 x_4 + \beta_{1234} x_1 x_2 x_3 x_4 \\ & + \epsilon,\end{aligned} \tag{1}$$

where x_1, x_2, x_3, and x_4 are coded variables that represent the temperature, time, nitrogen pressure, and carbon content, respectively and β's are regression coefficients. β_0 is the intercept which is the grand average of all 32 observations (i.e., $\beta_0 = 2.1475$), the regression coefficients β_1, β_2, β_3, and β_4 are one-half the corresponding factors A, B, C, and D, respectively ($\beta_1 = 0.9975$, $\beta_2 = 0.465$, $\beta_3 = 0.81375$, and $\beta_4 = -1.44625$), the regression coefficients β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, and β_{34} are one-half the corresponding factors AB, AC, AD, BC, BD, and CD ($\beta_{12} = 0.125$, $\beta_{13} = 0.63875$, $\beta_{14} = -0.73375$, $\beta_{23} = 0.11125$, $\beta_{24} = -0.35375$, and $\beta_{34} = -0.68$), and β_{123}, β_{124}, β_{134}, and β_{234} and β_{1234} are one-half the corresponding factors ABC, ABD, ACD, BCD, and ABCD, respectively, which are $\beta_{123} = 0.10125$, $\beta_{124} = -0.08125$, $\beta_{134} = -0.5925$, and $\beta_{234} = -0.1075$ and $\beta_{1234} = -0.105$, and ϵ is the residual (the difference between observed and fitted point of the design).

The sign of coded variables taken from Table 2 has been used to estimate the residual (ϵ) and to calculate the nitrogen pickup at (1), a, b, c, ab, ac, bc, abc, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd. The experimental and estimated values of the nitrogen pickup are given in Table 5. The average residence is ±0.021 which can be neglected. Based on this, (1) will be modified to (2).

$$\begin{aligned}\text{Nitrogen pickup, \%} = {} & 2.1475 + 0.9975 x_1 + 0.465 x_2 \\ & + 0.81375 x_3 - 1.44625 x_4 \\ & + 0.125 x_1 x_2 + 0.63875 x_1 x_3 \\ & - 0.73375 x_1 x_4 + 0.11125 x_2 x_3 \\ & - 0.35375 x_2 x_4 - 0.68 x_3 x_4 \\ & + 0.10125 x_1 x_2 x_3 \\ & - 0.08125 x_1 x_2 x_4 \\ & - 0.5925 x_1 x_3 x_4 \\ & - 0.1075 x_2 x_3 x_4 \\ & - 0.105 x_1 x_2 x_3 x_4.\end{aligned} \tag{2}$$

The relation between the natural variables and the coded variable is demonstrated in previous work [30, 33]. Consequently, the nitrogen pickup in ferromanganese alloys can be predicted as a function of nitriding temperature, time of nitriding process, nitrogen pressure, and carbon content of ferromanganese as given in (3).

$$\begin{aligned}\text{Nitrogen pickup, \%} = {} & -1.18354 + 0.002171 * T \\ & + 0.482307 * t - 1.28154 \\ & * P_{N_2} + 0.111666 * C \\ & - 0.00025 * T * t + 0.00193\end{aligned}$$

Table 5: Experimental and calculated nitrogen pickup (wt. percent, %) under the influence of different parameters.

Trail number	Variable	Calculated nitrogen pickup, mass content in %	Experimental nitrogen pickup, mass content in %		Residence (ϵ)		The residence variation
			1st	2nd	1st	2nd	
1	(1)	1	1.010	0.990	0.010	−0.010	±0.010
2	A	2	2.020	1.980	0.020	−0.020	±0.020
3	B	2.2	2.222	2.178	0.022	−0.022	±0.022
4	Ab	3.2	3.232	3.168	0.032	−0.032	±0.032
5	C	1.5	1.515	1.485	0.015	−0.015	±0.015
6	Ac	6.6	6.666	6.534	0.066	−0.066	±0.066
7	Bc	2.75	2.778	2.723	0.027	−0.028	±0.0275
8	Abc	9.5	9.595	9.405	0.095	−0.095	±0.095
9	D	0.29	0.293	0.287	0.003	−0.003	±0.003
10	Ad	0.63	0.636	0.624	0.006	−0.006	±0.006
11	Bd	0.41	0.414	0.406	0.004	−0.004	±0.004
12	Abd	0.94	0.949	0.931	0.009	−0.009	±0.009
13	Cd	0.45	0.455	0.446	0.005	−0.004	±0.004
14	Acd	0.99	1.000	0.980	0.010	−0.010	±0.010
15	Bcd	0.6	0.606	0.594	0.006	−0.006	±0.006
16	Abcd	1.3	1.313	1.287	0.013	−0.013	±0.013

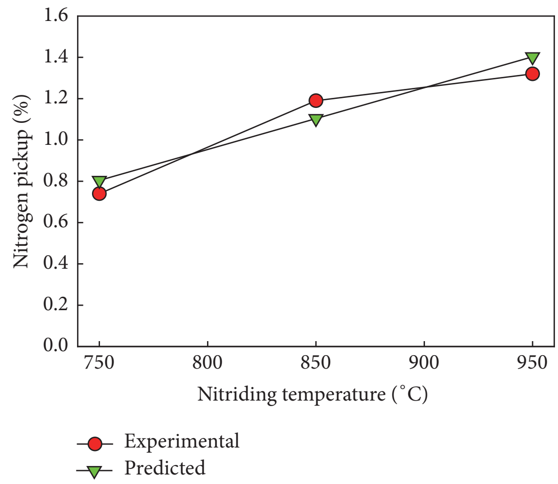

FIGURE 2: Variation between the predicted and published nitrogen pickup of high carbon (7.1%) ferromanganese at different nitriding temperatures [34].

$$
\begin{aligned}
&* T * P_{N_2} - 0.00019 * T * \mathrm{C} \\
&- 0.16881 * t * P_{N_2} - 0.08301 \\
&* t * \mathrm{C} + 0.171304 * P_{N_2} * \mathrm{C} \\
&+ 0.000244 * T * t * P_{N_2} \\
&+ 6.26 * 10^{-5} * T * t * \mathrm{C} \\
&- 0.00025 * T * P_{N_2} * \mathrm{C} \\
&+ 0.02435 * t * P_{N_2} * \mathrm{C} - 3.5 \\
&* 10^{-5} * T * t * P_{N_2} * \mathrm{C},
\end{aligned}
\tag{3}
$$

where T is temperature in Celsius, t is time in hour, P_{N_2} is nitrogen pressure in bar, and C is carbon content of ferromanganese in %.

The derived mathematical models represented in (2) and (3) were applied to calculate the nitrogen pickup of ferromanganese alloys. The calculated values from coded and actual variables ((2) and (3), resp.) are compared to the experimental work as can be seen in Figure 1. It can be seen that the estimated values of nitrogen pickup are close to and in good agreement with the average values of the experimental results. Based on the previous results, it can be concluded that the factorial design is good to precisely predict the nitrogen pickup in nitriding process of ferromanganese alloy. Also, it was noticed that the predicted values of nitrogen pickup by using (2) or (3) (coded or actual variables) are the same.

The derived mathematical model is given in (3) and was applied to previous published work [23, 24, 29] to calculate the nitrogen pickup of ferromanganese alloys under the influence of different parameters: percentages of carbon (mass content of 0.23, 2.2, and 7.1%), nitrogen pressure (2, 4, 6, and 8 bar), applied temperatures (700, 750, 800, 850, 900, and 950°C), and time of nitriding process (2, 4, and 6 hours).

The calculated values are compared to the published work [34] of high carbon ferromanganese after nitriding time of 6 hours at different nitriding temperature as illustrated in Figure 2. It can be seen that the estimated values of nitrogen pickup of high carbon ferromanganese based on the application of regression model are close to and in good agreement with the values of the previous published work [34].

For medium carbon (1.2% C), the predicted and previous published [10, 34] work of nitrogen pickup after nitriding time of 6 hours at working temperature 950°C at different nitrogen pressure are close to each other as given in Figure 3.

Figure 4 shows the variation between the predicted and published work [10, 27] of nitrogen pickup of medium carbon (1.2% C) ferromanganese under nitrogen pressure of 8 bar, at temperatures 750°C, 850°C, and 950°C after 2, 4, and 6 hours. It is clear that the difference between the predicted and published nitrogen pickup increases as the temperature of nitriding process increases.

Figures 5 and 6 show the variation between the predicted and published [28, 29] values of nitrogen pickup for low carbon (0.23% C) ferromanganese at temperatures 800, 850, 900, and 950°C (after 6 hours and at nitrogen pressures of 4, 6, and 8 bar) and (after 2, 4, and 6 hours under nitrogen pressure), respectively. It was noticed that the difference between the predicted and published values decrease as the working temperature increases from 800°C to 950°C as illustrated in Figure 5. Also, the predicted values are greater than the published values. This may be attributed that after 6 nitriding hours with increasing temperature the leveling nitrogen content was reached.

Figure 6 shows the predicted values are greater than the published [28, 29] values when nitriding takes place at 800°C for low carbon (0.23% C) ferromanganese. The difference between the predicted and actual values finishes at 850°C; then by increasing temperature up to 900°C then to 950°C, the published values become greater than the predicted values and the difference increases by increasing the nitriding temperature from 850°C up to 950°C.

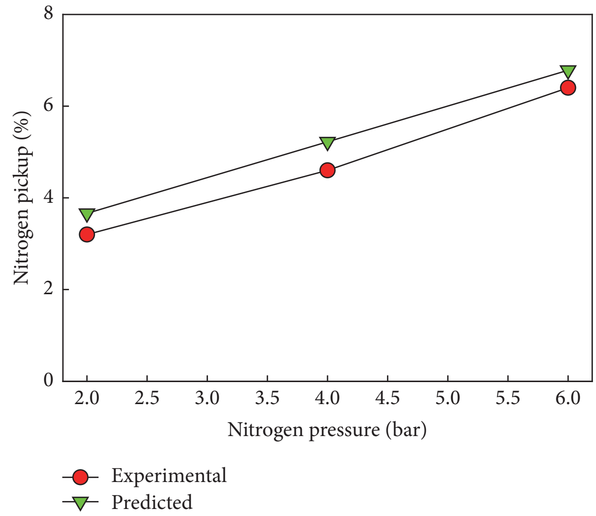

FIGURE 3: Variation between the predicted and published nitrogen pickup of medium carbon (1.2% C) ferromanganese at different nitrogen pressure at 950°C and after 6 hours [10, 27].

For medium carbon (2.2% C), the predicted and previous published [34] work of nitrogen pickup after nitriding time of 4, 6, and 8 hours at working temperature 950°C and at different nitrogen pressure are close to each other as given in Figure 7. It is noticed that the variation between the previous experimental published works [34] is close to the predicted nitrogen pickup at high pressure and at long time. This can be attributed to the difference in size distribution, where the size distribution contributes in the factors affecting the nitrogen pickup process (diffusion, adsorption, dissociation, and nitrogen combination with ferroalloys).

Based on the previous work, it can be said that the factorial design is a good approach to precisely predict the nitrogen pickup in nitriding process of ferromanganese alloy as a function of carbon content, nitrogen pressure, nitriding temperature, and time of nitriding process.

4. Conclusions

The experimental results of nitrogen pickup of ferromanganese alloy (carbon content 0.23–7.1%, under nitrogen pressure 1–8 bar, nitriding temperature 700–950°C, and time range 2–6 hours) are fit very well with the predictions from derived model of experimental design. Based on the factorial design of the process, it can be found that nitriding temperature has the highest significant positive effect on the nitriding process. Applied nitrogen pressure has positive effect followed by the interaction effect of temperature with nitrogen pressure and then the effect of time. The interaction combination of time with temperature or/and nitrogen pressure has little positive effect on nitrogen pickup. It was found that carbon content has highest negative effect on the nitrogen pickup in ferromanganese followed by the interaction effect of temperature-carbon content, nitrogen pressure-carbon content, and time-carbon content. The interaction combination of temperature-nitrogen pressure-carbon content and temperature-time-nitrogen pressure-carbon content has little negative effect on nitrogen pickup.

The previous published results of nitrogen pickup of ferromanganese alloy at different working temperatures, time duration, carbon content, and nitrogen pressure are in good agreement to large extent with the predicted results from the derived model. Based on the results of this study, factorial design can be used to precisely predict the nitrogen pickup in nitriding process of ferromanganese alloy.

Appendix

$$A = \frac{1}{8n}\left[(abcd + abc + abd + acd + ab + ac + ad + a) - (bcd + bc + bd + cd + b + c + d + (1))\right]$$

$$B = \frac{1}{8n}\left[(abcd + abc + abd + bcd + ab + bc + bd + b) - (acd + ac + ad + cd + a + c + d + (1))\right]$$

$$C = \frac{1}{8n}\left[(abcd + abc + cbd + acd + cb + ac + cd + c) - (abd + ab + bd + ad + b + a + d + (1))\right]$$

$$D = \frac{1}{8n}\left[(abcd + bcd + abd + acd + bd + cd + ad + d) - (abc + bc + ab + ac + b + c + a + (1))\right]$$

$$AB = \frac{1}{8n}\left[(abcd + acd + bcd + cd + ab + a + b + (1)) - (abc + ac + bc + c + abd + ad + bd + d)\right]$$

$$AC = \frac{1}{8n}\left[(abcd + abd + bcd + bd + ac + a + c + (1)) - (abc + ab + bc + b + acd + ad + cd + d)\right]$$

$$AD = \frac{1}{8n}\left[(abcd + abc + bcd + bc + ad + a + d\right.$$

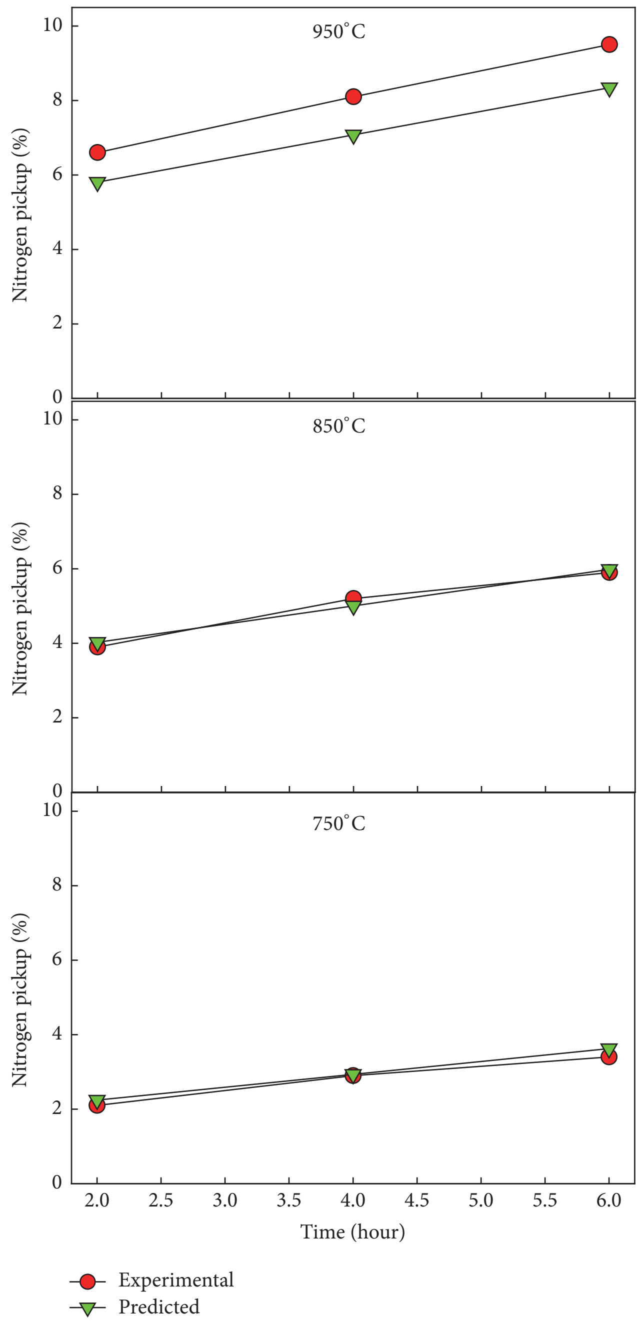

FIGURE 4: Variation between the predicted and published nitrogen pickup of medium carbon (1.2% C) ferromanganese at 8 bar and at different time and temperature [10, 27].

$$+ (1)) - (acd + ac + cd + c + abd + ab + bd + b)]$$

$$BC = \frac{1}{8n}[(abcd + abd + acd + ad + bc + b + c + (1)) - (abc + ab + ac + a + bcd + bd + cd + d)]$$

$$BD = \frac{1}{8n}[(abcd + abc + acd + ac + bd + b + d + (1)) - (bcd + bc + cd + c + abd + ab + ad + a)]$$

$$CD = \frac{1}{8n}[(abcd + abc + abd + ab + cd + c + d + (1)) - (acd + ac + ad + a + bcd + bc + bd + b)]$$

$$ABC = \frac{1}{8n}[(abcd + abc + ad + cd + bd + a + b + c) - (abd + acd + bcd + ab + ac + bc + d + (1))]$$

$$ABD = \frac{1}{8n}[(abcd + abd + ac + cd + bc + a + b + d)$$

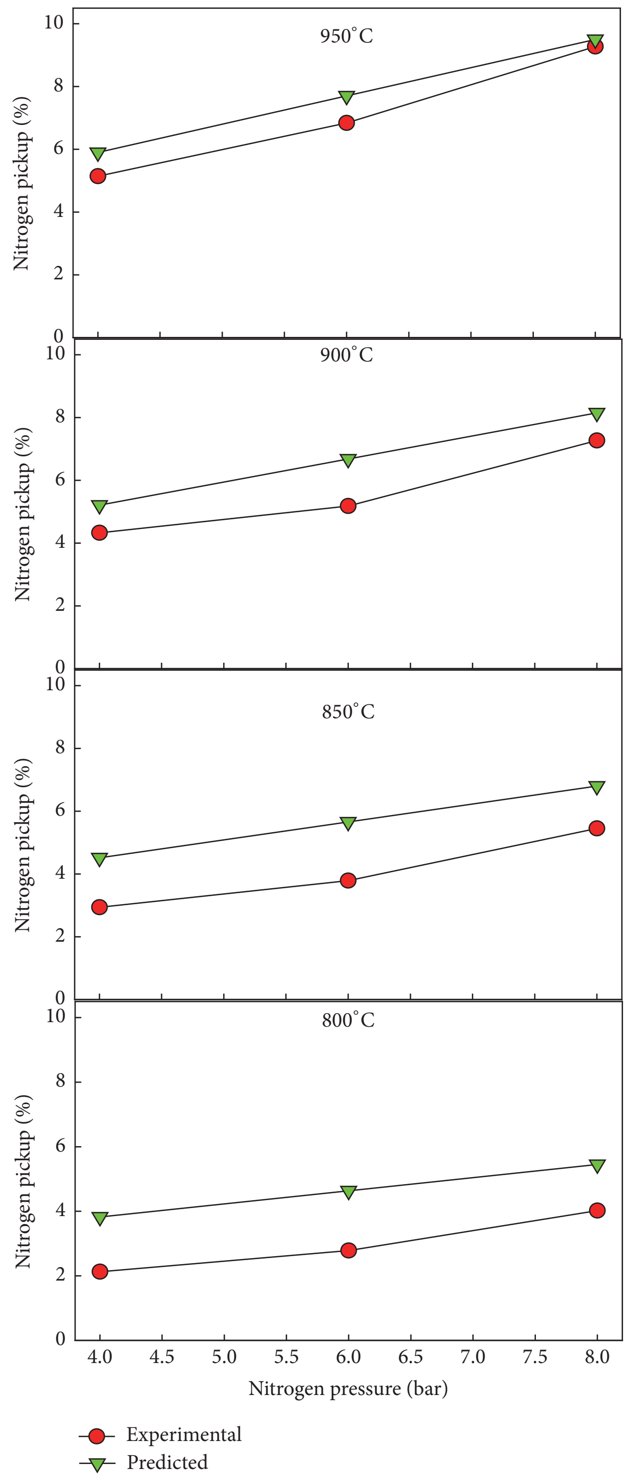

Figure 5: Variation between the predicted and published nitrogen pickup of low carbon (0.23% C) ferromanganese at 6 hours and at different nitrogen pressure and temperature [28, 29].

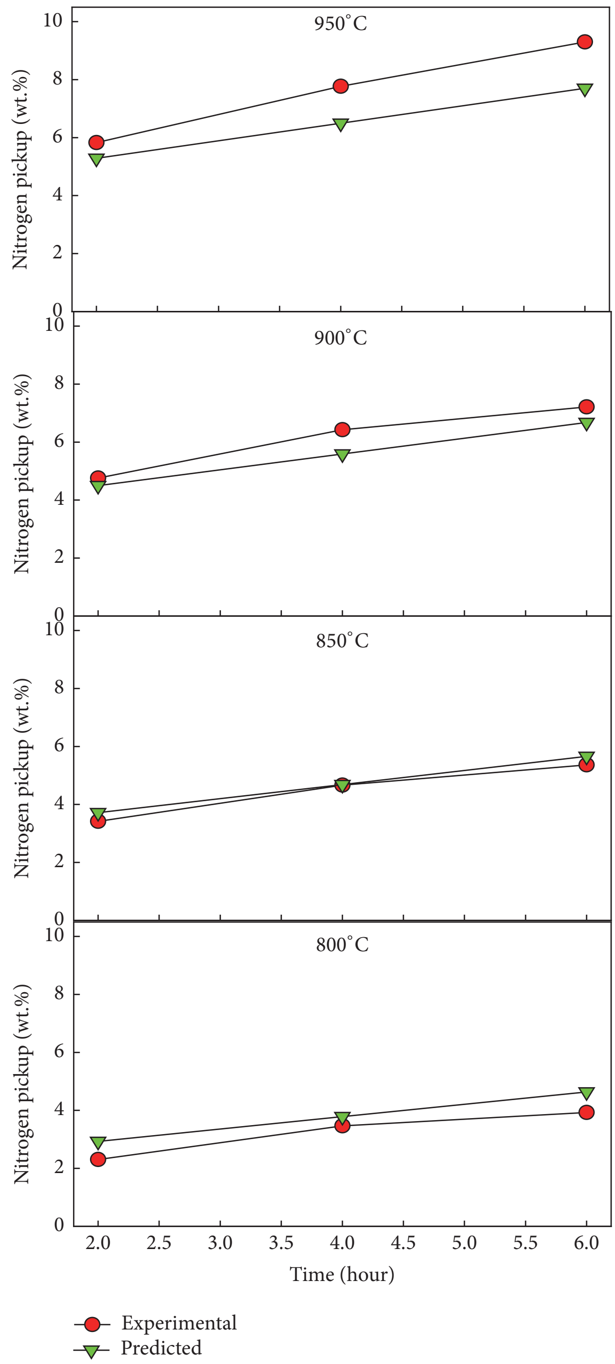

FIGURE 6: Variation between the predicted and published nitrogen pickup of low carbon (0.23% C) ferromanganese at 6-bar nitrogen pressure at different temperature and time [28, 29].

$$- (abc + acd + bcd + ab + ad + bd + c + (1))]$$

$$ACD = \frac{1}{8n}[(abcd + acd + ab + bd + bc + a + c + d) - (abc + abd + bcd + ac + ad + cd + b + (1))]$$

$$BCD = \frac{1}{8n}[(abcd + bcd + ab + ad + ac + b + c + d) - (abc + abd + acd + bc + bd + cd + a + (1))]$$

$$ABCD = \frac{1}{8n}[(abc + ab + ac + ad + bc + bd + cd + 1) - (abc + abd + bcd + acd + a + b + c + d + (1))]. \quad (A.1)$$

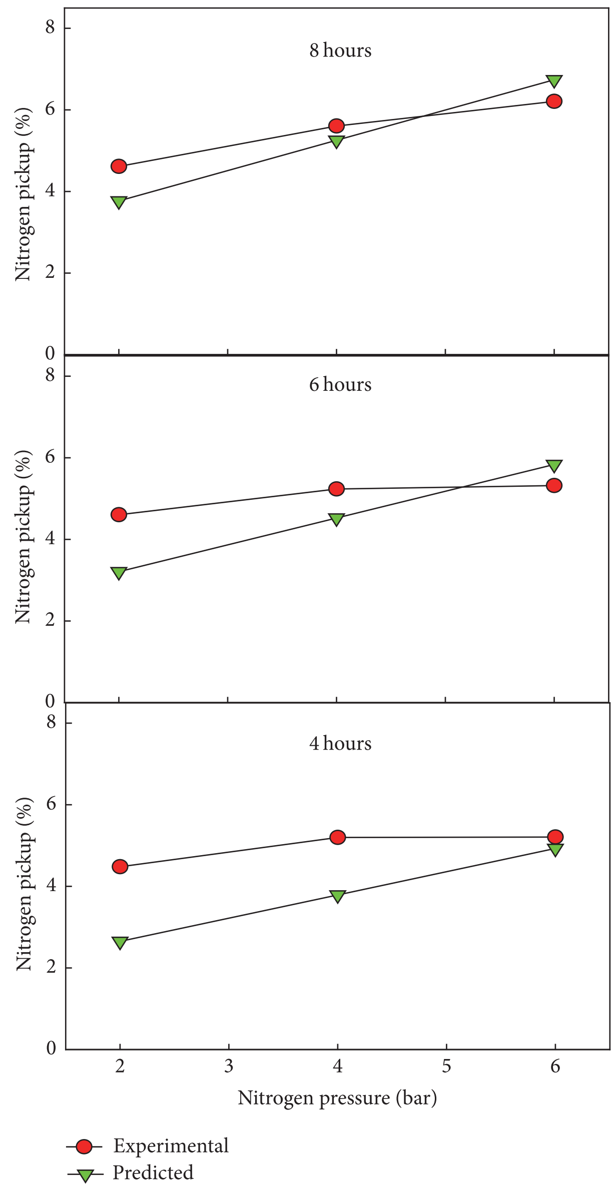

Figure 7: Variation between the predicted and published nitrogen pickup of medium carbon (2.2% C) ferromanganese at 4, 6, and 8 hours with nitrogen pressure at 950°C [34].

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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