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Research Article

Mathematical Model of Prediction of Nitrogen Pickup in Nitriding Process of Low Carbon Ferromanganese

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Low carbon ferromanganese was nitrided through gas-solid reaction. The nitriding process has been carried out on lab scale at temperature range 800°C–950°C at different nitrogen pressures. Temperature, time, and partial nitrogen pressure of nitriding process of fine low carbon ferromanganese were investigated. Nitrogen content, in weight percent, was more than 9%. MATLAB software was used to derive mathematical model to predict nitrogen content as a function of temperature and nitrogen pressure. According to derived model, nitrogen content can be calculated by the following equation: N content, wt.% $= (-30.8882 + 0.0326 * T)/(1+e^{-((P+0.0038*T-8.4155)/(3.6374-0.0018*T))})$, where, T is nitriding temperature in K and P is nitrogen pressure in bar. The experimental results are in good agreement with the predicted results. The results showed that nitrogen content, at steady state, is mainly depending on temperature and pressure of nitriding process. MATLAB is a good tool to make precision mathematical model.

1. Introduction

Ferromanganese nitrogen alloy has no use as it is but it is used as a source of nitrogen—in addition to manganese—in manufacturing high nitrogen steel, especially stainless steel, particularly austenitic stainless steel. Nitrogen is considered as a very strong austenitic stabilizer [1–3]. This is due to the fact that nitrogen atom occupies octahedral interstitial sites in the crystal lattice of austenite [4]. So, nickel can be replaced by nitrogen in manufacturing austenitic stainless steel. Many authors reported [5–9] that one unit of nitrogen is equivalent to not less than 18 units of nickel, so nitrogen is used as an alloying element in manufacturing different steel grades [10–12]. Nitriding of ferromanganese with carbon content 1–7%, was published by authors [13, 14]. It was found that medium and high carbon ferromanganese nitrogen are not suitable in manufacturing low carbon austenitic stainless steel containing high nitrogen. So, this work aims to investigate the nitriding process of low carbon ferromanganese.

Nitrogen is one of the strongest austenitic stabilizing elements. Since nitrogen is more effective at solid-solution strengthening and has greater solid solution solubility, compared to carbon with a decreased tendency for precipitation during processing, nitrogen has been the principal interstitial alloying element in austenitic stainless steel [1, 2]. High nitrogen stainless steels exhibit excellent mechanical properties as well as corrosion resistance properties, so considerable efforts have been made to develop high nitrogen stainless steels over the past decades. Nitrogen in solid solution confers many desirable properties to austenitic stainless steels. It enhances the stability of face centered cubic lattice and increases the yield strength of austenitic stainless steels. The hardening effect due to nitrogen has extended the usefulness and applicability of austenitic stainless steels [10–12].

All the previous work of nitriding of ferromanganese, ferrovanadium, ferrochromium, ferrosilicon, ferroniobium, and other ferroalloys [13–20] was concerned with investigation of the affecting parameters on nitriding process such as time, temperature, states of nitriding, nitriding gas composition, and chemical composition of ferroalloys. A few authors [19] studied the activation energy of nitriding process. But, there is no published work concerned with the prediction of nitrogen pickup. The novelty of this work is in simulation of nitriding process of ferromanganese by using MATLAB program, where mathematical model was built up to predict nitrogen pickup during nitriding process as a function of temperature and pressure. Also, this model can predict nitrogen pickup at temperature up to 950°C and pressure up to 12 bars, and it predicts the critical nitriding temperature of low carbon ferromanganese alloy.

This work is the extension of the previously published work [14, 19] which was concerned with the nitriding of medium carbon ferromanganese where carbon content is 1.2% C, while this work is concerned with nitriding of low carbon ferromanganese in which carbon content is 0.23%.

2. Experimental

Gas-solid reaction was used in nitriding of low carbon ferromanganese. Low carbon ferromanganese has carbon content 0.23%, silicon content 0.61%, manganese content 83.8%, and about 15% Fe. Nitriding process of low carbon ferromanganese was carried out on laboratory scale using 50 gm. The sieve analysis of fine low carbon ferromanganese was carried out. Gas mixture of nitrogen and hydrogen was used in nitriding process, where nitrogen gas was used as source of nitrogen and hydrogen gas was used as a deoxidizer. The system of the nitriding process has purification unit and nitriding unit. The purification unit purifies gases from oxygen, using tube furnace containing copper turning heated to 570°C, and moisture, using 4 drying towers filled with anhydrous calcium chloride and magnesium perchlorate, before entering the nitriding unit. The nitriding unit consists of an electric resistance tube furnace, with maximum temperature 1200°C.

The fine low carbon ferromanganese was placed into an alumina boat which was introduced into the hot zone of the nitriding furnace. The furnace at first was tested for gas leakage then the nitriding unit was flushed gently with hydrogen. The outlet valve was then closed and the gases (H_2 and N_2) were injected into the nitriding unit until the required pressure of gases was reached. The temperature was raised gradually to the required temperature. The nitriding process continued for the selected time. The furnace was, then, switched off and the outlet valve was opened gradually to reach the normal pressure and it was closed again and hydrogen gas was introduced in the unit and the nitrided sample was left in the furnace to cool to room temperature. Then the outlet valve was opened gradually to remove hydrogen.

Nitriding process was carried out at temperatures 800°C, 850°C, 900°C, and 950°C and at time intervals 2 hours, 4 hours, 6 hours, and 8 hours with different nitrogen pressures. Also, the partial nitrogen pressure was investigated. Kjeldahl apparatus was used in determination of nitrogen content in nitrided low carbon ferromanganese [21]. Each sample was analyzed three times and the average value of nitrogen content was considered.

3. Results and Discussion

The sieve analysis of low carbon ferromanganese is given in Table 1. Low carbon ferromanganese has carbon content of 0.23%, silicon content of 0.61%, manganese content of 83.8%, and about 15% Fe. The results of nitriding process of low carbon ferromanganese at different nitrogen partial pressures and temperatures after six hours were shown in Figure 1.

Table 1: Sieve analysis of fine low carbon ferromanganese alloy.

Size, mm	%
1.07–0.83	23.47
0.83–0.67	2.52
Less than 0.67	74.01

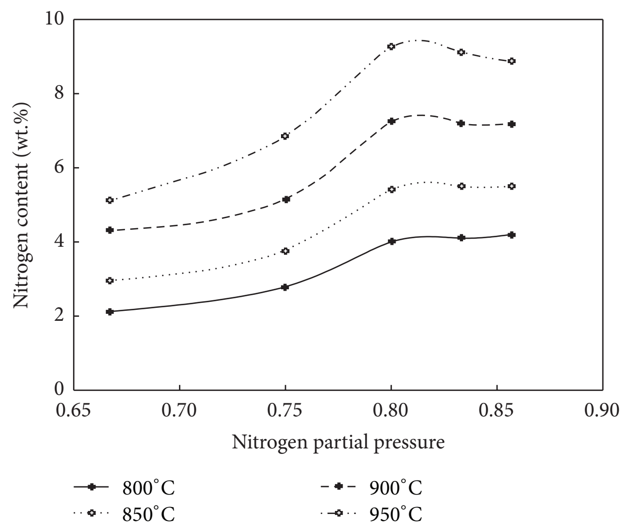


Figure 1: Effect of partial nitrogen pressure on nitrogen pickup at temperature range 800°C–950°C.

Figure 1 shows the relation between nitrogen pickup and partial nitrogen pressure within temperature range 800°C–950°C. It is clear that the nitrogen pickup increases by increasing partial nitrogen pressure from 0.667 to 0.800, after that leveling of nitrogen pickup occurs.

The overall gas-solid metal reaction (nitrogen-low carbon ferromanganese) which involves adsorption-desorption mechanism can be described as follows [22]:

$$N_{2\text{gas}} \longleftrightarrow N_{2i}, \quad \text{mass transfer in the gaseous phase} \tag{1}$$

$$N_{2i} \longleftrightarrow N_{2\text{ad}}, \quad \text{adsorption of } N_2 \text{ gas on ferromanganese surface} \tag{2}$$

$$N_{2\text{ad}} \longleftrightarrow 2N_{\text{ad.}} \quad \text{dissociation of } N_2 \text{ gas molecules} \tag{3}$$

$$N_{\text{ad}} \longleftrightarrow N_{i.}, \quad \text{change from physical adsorption into chemical adsorption} \tag{4}$$

$$N_{i.} \longleftrightarrow N_{\text{bulk}}, \quad \text{mass transfer in solid low carbon ferromanganese,} \tag{5}$$

where N_2 is free nitrogen gas molecules, N_{2i} is nitrogen gas molecules closest to low carbon ferromanganese surface, $N_{2\text{ad}}$ is adsorbed nitrogen gas molecule on the surface of low carbon ferromanganese, N_{ad} is adsorbed nitrogen atom on the surface of low carbon ferromanganese, N_i is nitrogen combined with manganese at the surface of low carbon ferromanganese, and N_{bulk} is nitrogen combined with manganese at the bulk of low carbon ferromanganese.

Therefore, the absorption of nitrogen gas by the solid ferromanganese passes through the following stages: N_2 gas transfer to the surface of ferromanganese, adsorption of N_2 gas molecules on the FeMn surface, dissociation of the nitrogen gas molecules into atoms, and diffusion of the adsorbed atoms from the surface of the metal into the bulk of solid ferromanganese particles.

Firstly, increasing partial nitrogen pressure from 0.667 to 0.800 increases the nitrogen pickup as a result of increasing nitrogen gas transfer to the surface of fine low carbon ferromanganese and hence rate of adsorption on the surface of particles will increase and the combination between nitrogen and manganese will increase.

By further increasing partial nitrogen pressure from 0.800 to 0.857, nitrogen pickup was not increment. This may be attributed to two opposite factors. The first one is that increasing nitrogen partial pressure increases nitrogen diffusion and physical adsorption on the surface of low carbon ferromanganese particles. The second one is that increasing partial nitrogen pressure hinders dissociation of adsorbed nitrogen molecule on surface of fine low carbon ferromanganese particles.

The variations of nitrogen pickup with time at different temperatures were illustrated in Figure 2. It is clear that nitrogen pickup of fine low carbon ferromanganese increases by increasing temperature and time. The rate of nitrogen pickup is affected by temperature more than time. At the first time of nitriding process, it was noticed that the rate of nitrogen pickup at different temperatures increases rapidly. Then, the rate of nitriding process decreases by time up to reaching leveling after about 6 hours. This behavior can be described by one or more of the following.

Firstly, leveling can be controlled by the nitrogen diffusion flow, which can be expressed by the following first-order equation:

$$\frac{dN}{dt} = \alpha \left(N_{eq.} - N_v \right), \quad (6)$$

where dN/dt is the diffusion flow, α is the nitrogen transfer coefficient into the ferromanganese alloy, $N_{eq.}$ is the nitrogen concentration in equilibrium with the gaseous phase, and N_v is the nitrogen concentration within the volume of the ferromanganese alloy. This equation indicates that the gas nitriding process of ferromanganese is controlled by the solid state diffusion of nitrogen in the ferroalloy, and it also shows that nitrogen adsorption becomes retarded as the nitrogen content in the ferromanganese alloy increases until it reaches $N_{eq.}$ [23, 24].

Secondly, the leveling can be attributed to the decomposition of nitrides especially manganese nitrides which dissociate in this range of temperature to form a solid solution with low nitrogen content [25, 26]. This is in agreement with the results which were obtained by Hundsbedt and Olsen who reported that the decomposition of formed nitrides (Mn and Fe) N from high nitrogen content (Mn_3N_2 and Mn_2N) into lower nitrogen content (Mn_4N) at high temperature more than 900°C [20].

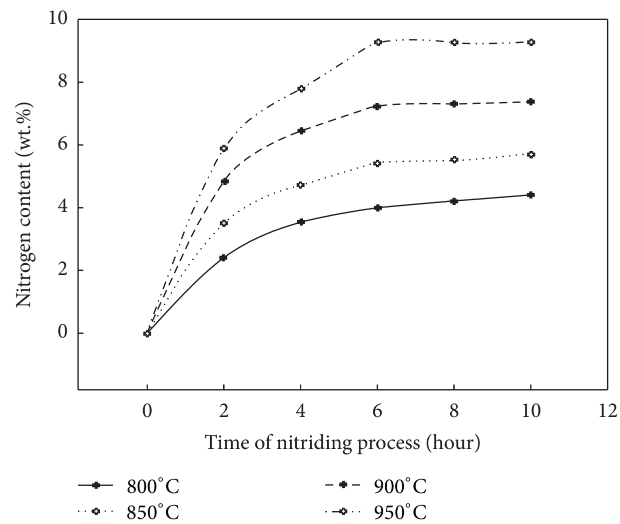


Figure 2: The variation of nitrogen pickup with time at temperatures 800°C, 850°C, 900°C, and 950°C.

MATLAB program was used to derive an equation to predict nitrogen content as a function of temperature and pressure of nitriding process as given in (7). The gained equation is used to predict the maximum nitrogen pickup, that is, at equilibrium state and the carbon content was not taken into consideration. Figure 3 describes the variation between actual nitrogen content (given by symbols) and predicted nitrogen content (given by solid and dashed lines) at different nitrogen pressures and temperatures. It is clear that nitrogen pickup in fine low carbon ferromanganese increases by increasing nitrogen pressure from 4 bar to 8 bar, while the rate of nitrogen pickup decreases sharply in nitrogen pressure range of 8 bar–12 bar until it reaches leveling. Figure 3 illustrates that the temperature has positive significant effect on the rate of nitrogen pickup.

$$\text{N content, wt.\%} = \frac{-30.8882 + 0.0326 * T}{1 + e^{-((P+0.0038*T-8.4155)/(3.6374-0.0018*T))}}, \quad (7)$$

where T is temperature of nitriding process in K and P is nitrogen pressure in bar.

It is clear that the experimental results of nitrogen contents are in good agreement with predicted results at different temperatures. The deviations between calculated and actual nitrogen content disappeared at high nitrogen pressures. This may be related to the fact that at high nitrogen pressures, nitrogen pickup reached its maximum, that is, equilibrium state. Also, this mathematical model can be used to predict nitrogen pickup for low carbon ferromanganese at lower temperatures. Adjust calculated nitrogen content to zero; the critical nitriding temperature at which nitriding pickup starts can be deduced. According to the model, the critical nitriding temperature was found to be 947.49 K (674.49°C).

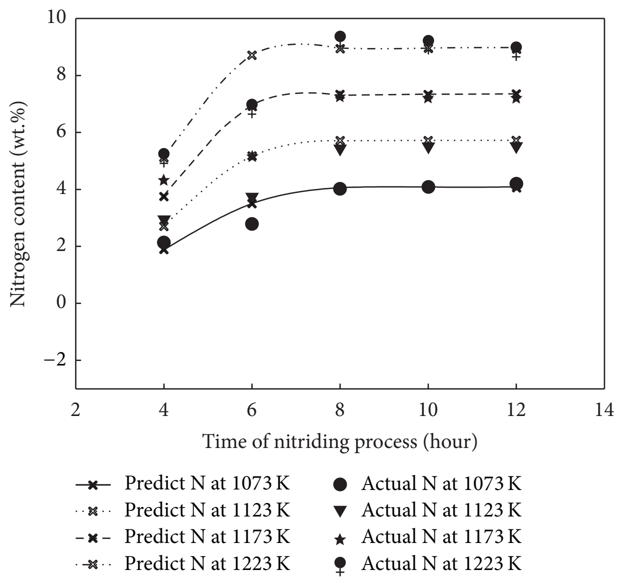


Figure 3: The variations between actual and predicted nitrogen contents at different nitrogen pressures and temperatures.

The literature [13, 14, 19, 20, 24] showed that the critical nitriding temperature of ferromanganese alloys in gas solid reaction by using nitrogen gas as a source of nitrogen took place at not less than 700°C.

4. Conclusions

From the experimental results, it can be concluded that the nitrogen content in low carbon ferromanganese increases by increasing temperature within range 800°C–950°C. Partial nitrogen pressure has positive significant effect on nitriding process of low carbon ferromanganese in range of 0.667–0.800. Nitrogen pickup reached leveling after 6 hours at temperatures 900°C and 950°C.

The increase in temperature in the range of 800°C–950°C has a positive significant effect on nitrogen pickup. The nitrogen pickup increases with increasing nitrogen pressure up to 8 bar while at more nitrogen pressure (8 bar–12 bar), the nitrogen pickup reached leveling.

Nitrogen pickup can be predicted by using the derived mathematical model by using MATLAB program as given in the following equation:

$$\text{N content, wt.\%} = \frac{-30.8882 + 0.0326 * T}{1 + e^{-((P+0.0038*T-8.4155)/(3.6374-0.0018*T))}}. \quad (8)$$

The mathematical model is function of temperature and nitrogen pressure of nitriding process and it restricted to low carbon ferromanganese. The model has enabled predicting the critical nitriding temperature of ferromanganese in gas-solid reaction, which is in good agreement with experiments of several authors.

The predicted nitrogen content from mathematical model is in good agreement with the actual nitrogen content especially at equilibrium state.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

References

[1] A. Ahmed, S. N. Ghali, M. Eissa, and S. A. El Badry, "Influence of partial replacement of nickel by nitrogen on microstructure and mechanical properties of austenitic stainless steel," *Journal of Metallurgy*, vol. 2011, Article ID 639283, 6 pages, 2011.

[2] S. N. Ghali, "Low carbon high nitrogen low nickel stainless steel," *Steel Research International*, vol. 84, no. 5, pp. 450–456, 2013.

[3] S. N. Ghali, M. M. Eissa, and K. M. El-Fawakhry, "Nitrogen solubility in stainless steels," in *Proceedings of the Advances in Theory of Ironmaking and Steelmaking Conference*, Department of Materials Engineering, Indian Institute of Science, Bangalore, India, December 2009.

[4] H.-B. Li, Z.-H. Jiang, M.-H. Shen, and X.-M. You, "High nitrogen austenitic stainless steels manufactured by nitrogen gas alloying and adding nitrided ferroalloys," *Journal of Iron and Steel Research International*, vol. 14, no. 3, pp. 64–69, 2007.

[5] M. O. Speidel, P. J. Uggowitzer, and R. A. Lula, Eds., *Materials Week '92 Chicago, Ill, USA, November 1992*, ASM International, 1993.

[6] K. H. Lo, C. H. Shek, and J. K. L. Lai, "Recent developments in stainless steels," *Materials Science and Engineering R: Reports*, vol. 65, no. 4–6, pp. 39–104, 2009.

[7] V. G. Gavriljuk and H. Berns, *High Nitrogen Steels: Structure, Properties, Manufacture, Applications*, Springer, Berlin, Germany, 1999.

[8] R. P. Reed and N. J. Simon, "Nitrogen, strengthening of austenitic stainless steels at low temperatures," in *High Nitrogen Steels, HNS88*, J. Foct and A. Hendry, Eds., pp. 180–188, Institute of Metals, London, UK, 1989.

[9] Y. Ikegami and R. Nemoto, "Effect of thermo-mechanical treatment on mechanical properties of high-nitrogen containing Cr-Mn-Ni austenitic stainless steels," *ISIJ International*, vol. 36, no. 7, pp. 855–861, 1996.

[10] S. Nabil Ghali, A. Ahmed, M. Eissa, H. El-Faramawy, M. Mishreky, and T. Matta, "Production and application of advanced high nitrogen steel," in *Proceedings of the International Conference on Science and Technology of Ironmaking and Steelmaking*, Jamshedpur, India, December 2013.

[11] S. Ghali, M. Eissa, H. El-Faramawy, M. Mishreky, and T. Mattar, "New grades of stainless steel," in *Proceedings of the International Conference on Advances in Refractories and Clean Steel Makin (ARCS '13)*, Ranchi, India, June 2013.

[12] S. Ghali, F. Baiomy, and M. Eissa, "Investigation the effect of nitrogen on oxidation behavior of stainless steel," in *Proceedings of the 7th European Stainless Steel Conference Science and Market*, Como, Italy, September 2011.

[13] A. Ahmed, T. Mattar, A. Fathy, H. El-Faramawy, and M. Eissa, "Solid state nitriding of high and medium carbon ferromanganese," *Canadian Metallurgical Quarterly*, vol. 45, no. 4, pp. 493–498, 2006.

[14] S. N. Ghali, "Nitriding of medium carbon ferromanganese alloy in gas solid reaction," *Journal of Minerals & Materials Characterization & Engineering*, vol. 10, no. 4, pp. 315–322, 2011.

[15] A. K. Suri, K. Singh, and C. K. Gupta, "A nitriding process for the recovery of niobium from ferroniobium," *Metallurgical Transactions B*, vol. 23, no. 4, pp. 437–442, 1992.

[16] P. S. Kislyi and V. M. Filipenko, "*Compacting silicon nitride under the effect of the effect of high—pressure gas media*," 1991, http://www.science.gov/topicpages/t/temperature+gas+nitriding.html.

[17] R. Durrer and G. Volkert, *Metallurgy of Ferroalloys*, Springer, Berlin, Germany, 1972.

[18] Z. Pirowski, J. Olszyńsk, and A. Gwiżdż, "Ferrous alloys cast under high pressure gas atmosphere," *Archives of Foundry Engineering*, vol. 7, no. 1, pp. 107–112, 2007.

[19] S. N. Ghali, M. M. Eissa, and M. L. Mishreky, "Activation energy of nitriding medium carbon ferromanganese alloy," *Journal of Iron and Steel Research International*, vol. 20, no. 1, pp. 58–61, 2013.

[20] L. Hunsbedt and S. E. Olsen, "Nitriding of ferromanganese," in *Proceedings of the 5th Electric Furnace Conference*, pp. 129–136, Warrendale, Pa, USA, November 1993.

[21] A. Vogel, *A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, Woolwich Polytechnic, London, UK, 1992.

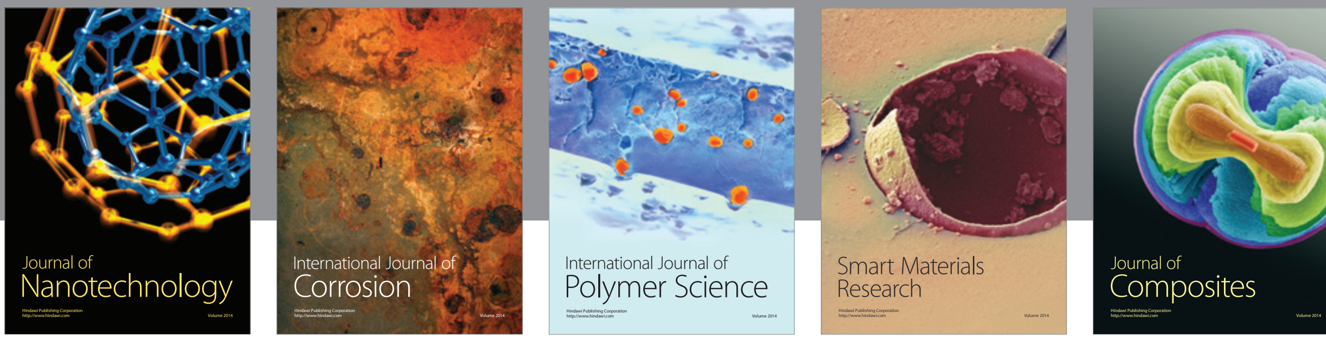
[22] V. Grigoryan, L. Belyanchikov, and A. Stomakhin, *Theoretical Principles of Electric Steelmaking*, Mir, Moscow, Russia, 1979.

[23] S. Filipov, *The Theory of Metallurgical Process*, Mir, Moscow, Russia, 1979.

[24] L. Torchane, P. Bilger, J. Dulcy, and M. Gantois, "Control of iron nitride layers growth kinetics in the binary Fe-N system," *Metallurgical and Materials Transactions*, vol. 27, no. 7, pp. 1823–1835, 1996.

[25] H. Okamoto, Ed., *Phase Diagrams of Binary Iron Alloys*, ASM International, The Material Information Society, Material Park, Ohio, USA, 1993.

[26] T. B. Mossalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak, Eds., *Binary Alloy Phase Diagrams*, vol. 3, ASM International, The Material Information Society, Cleveland, Ohio, USA, 2nd edition, 1996.



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