

# Control of iron nitride formation by a high magnetic field

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The influence of high magnetic field on nitriding behavior was investigated in a mixture of  $\text{NH}_3$  and  $\text{H}_2$ . It was found that high magnetic field could shift the equilibrium of nitriding reaction; this proved that the critical nitrogen potential to form  $\gamma'$ - $\text{Fe}_4\text{N}$  and  $\varepsilon$ - $\text{Fe}_3\text{N}$  phase was evidently enhanced compared with conventional nitriding. This research provides a new approach for a selective nitriding process.

It is well known that nitrides are of great industrial importance.<sup>1,2</sup> For more than a century, nitriding has been used as a versatile method to improve surface properties of iron and steel. The case nitride can be subdivided into a compound layer consisting mostly of  $\gamma'$ - $\text{Fe}_4\text{N}$  and/or  $\varepsilon$ - $\text{Fe}_3\text{N}$  phases and a diffusion zone where N is dissolved interstitially in ferritic matrix.<sup>3,4</sup> To be certain of obtaining the specified properties, it is necessary to control accurately the nitriding process. On the basis of the well-established Lehrer diagram, the exact composition of nitrides formed during nitriding depends on the temperature and the nitrogen potential.<sup>5-7</sup> In the past decades, a controlled nitriding has been developed using computer technology.<sup>8,9</sup> This nitriding layer only contains a diffusion zone and exhibits a good combination property (fatigue strength, hardness, wear resistance, etc.). However, this is not enough for practical application. It is possible that different nitrides are demanded at different places in a workpiece. Selective nitriding is still a major challenge in modern industry, because it is very difficult to adjust local temperature and nitrogen potential in a nitriding furnace.

Recently, with the development of superconducting magnet technology, a new branch of electromagnetic processing of materials has been dramatically highlighted.<sup>10-12</sup> The magnetic field, especially high magnetic field, has a considerable influence on solid phase transformation in materials because the Gibbs free energy of a phase can be changed by the amount corresponding to its magnetization. Previous investigations showed that the critical nitrogen potential to form  $\gamma'$ - $\text{Fe}_4\text{N}$  or  $\varepsilon$ - $\text{Fe}_3\text{N}$  phase is decided by the standard

Gibbs free energy of nitriding reaction.<sup>1,13</sup> Hence, it is reasonable to expect that the formation of nitride may be controlled by a high magnetic field.

This article investigates the formation of nitride under a high magnetic field during gas nitriding, using pure iron as an example. Experimental observations indicate that a magnetic field can obviously affect the nitriding behaviors of iron, and different nitrides can be obtained at the same nitriding condition when a high magnetic field is applied.

Nitriding is performed in a tube furnace with a continuous flow of a mixture of  $\text{NH}_3$  and  $\text{H}_2$ . Figure 1(a) shows the schematic view of the experimental setup. The setup consists of the static superconductor magnets, the heater, the water cooled jacket, and the temperature controller. Flux density of the static magnetic field is up to 12 T, which was imposed by the superconductor magnet located in the middle part of the tube furnace. The nitrogen potential  $r_{\text{N}}$ , which is directly proportional to the nitrogen activity in the nitriding reaction, is defined by partial pressures of gas components:  $r_{\text{N}} = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$ . To adjust a certain nitrogen potential, a constant flow of a  $\text{NH}_3/\text{H}_2$  gas mixture has been used by means of commercially available flow controllers. The nitriding temperature and the nitrogen potential were thoroughly calibrated before the nitriding experiments.

An iron foil (8 mm  $\times$  8 mm  $\times$  0.5 mm in size) with a purity of 99.95 wt% was used. It was placed in the central region where magnetic force is zero [sample position as shown in Fig. 1(a)]. Nitriding of iron foil both with and without a magnetic field of 12 T was carried out at the same nitriding condition. The treatment temperatures were divided into two groups, 400 and 450 °C for  $\gamma'$ - $\text{Fe}_4\text{N}$  formation and 450 and 500 °C for  $\varepsilon$ - $\text{Fe}_3\text{N}$  formation, respectively. The duration was 9 h under various nitrogen potentials. Phase identification in the

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surface layer of the samples was performed using a Rigaku D/max 2400 x-ray diffractometer (12 kW, Tokyo, Japan) using Cu K $\alpha$  radiation.

Figure 2 shows x-ray diffraction (XRD) spectra of the sample nitrided at 450 °C for 9 h with and without a high magnetic field. It can be seen that at various nitrogen potentials, the diffraction peaks of nitrides of the magnetic sample (under 12 T) are weaker than those of nonmagnetic sample (under 0 T), which indicates a substantial reduction of the volume fraction of nitride phases in magnetic sample. Under a nitrogen potential of 0.00146 Pa $^{-1/2}$ , which is slightly higher than the critical value to form the  $\gamma'$ -Fe $_4$ N phase according to the Lehrer diagram,<sup>5</sup> the XRD patterns can be indexed certainly by  $\gamma'$ -Fe $_4$ N and  $\alpha$ -Fe phases in a nonmagnetic sample (under 0 T). However, for the magnetic sample (under 12 T), no  $\gamma'$ -Fe $_4$ N phase can be detected on the same nitriding condition. The faint peaks of  $\gamma'$ -Fe $_4$ N phase can be identified only when the nitrogen potential reaches 0.00173 Pa $^{-1/2}$  [see Fig. 2(a)]. This indicates that the critical value to form  $\gamma'$ -Fe $_4$ N phase at 450 °C moves to a high nitrogen potential region (close to 0.00173 Pa $^{-1/2}$ ) in the magnetic field of 12 T. Similarly, from the XRD results of the magnetic samples (under

12 T) nitrided at nitrogen potential of 0.01304 Pa $^{-1/2}$ , there is no trace of the  $\epsilon$ -Fe $_3$ N phase, although this nitrogen potential is beyond a critical one and the  $\epsilon$ -Fe $_3$ N phase can be formed in the nonmagnetic sample (under 0 T) on the same condition, as shown in Fig. 2(b). Thus, the critical nitrogen potential to form  $\epsilon$ -Fe $_3$ N phase for magnetic sample is also higher than that in the Lehrer diagram.<sup>5</sup> According to XRD measurements, it can be confirmed that the critical value to form the  $\epsilon$ -Fe $_3$ N phase should be between 0.01304 Pa $^{-1/2}$  and 0.01515 Pa $^{-1/2}$  in a magnetic field of 12 T.

Other nitriding experiments at 400 and 500 °C for different nitrogen potentials with and without a high magnetic field were also performed, and the XRD patterns of nitride from nitrided samples were indexed. All experimental results are summarized in Figs. 3(a) and 3(b). It is found that the critical nitrogen potential line to form  $\gamma'$ -Fe $_4$ N and  $\epsilon$ -Fe $_3$ N phases in the magnetic samples is obviously higher than that in the nonmagnetic samples. In other words, the observations show that the relevant nitride phase under the high magnetic field cannot be formed when the nitrogen potential is beyond its critical value determined by the Lehrer diagram to some extent. These nitriding experiments were repeated several times and consistent results were obtained, which indicated that the formation of nitrides can be hindered by a high magnetic field.

Magnetic field hindering the formation of nitrides may be attributed to a changed thermodynamic state in a nitriding reaction under a high magnetic field relative to that in a nonmagnetic field environment.

Generally, the equilibrium between nitrogen in  $\alpha$  iron and  $\gamma'$ -Fe $_4$ N phase or  $\epsilon$ -Fe $_3$ N phase is given by the following chemical reaction:



and the equilibrium conditions is

$$\Delta G = \Delta G^\circ + RT \ln \frac{p_{\text{H}_2}^{3/2} \alpha_{\text{Fe}_x\text{N}}}{p_{\text{NH}_3} \alpha_{\text{Fe}}^x} = 0 \quad (2)$$

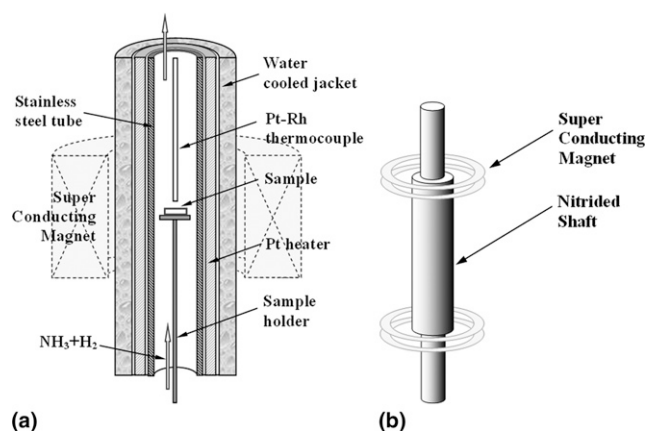


FIG. 1. Experimental setup for (a) magnetic field nitriding and (b) selective nitriding.

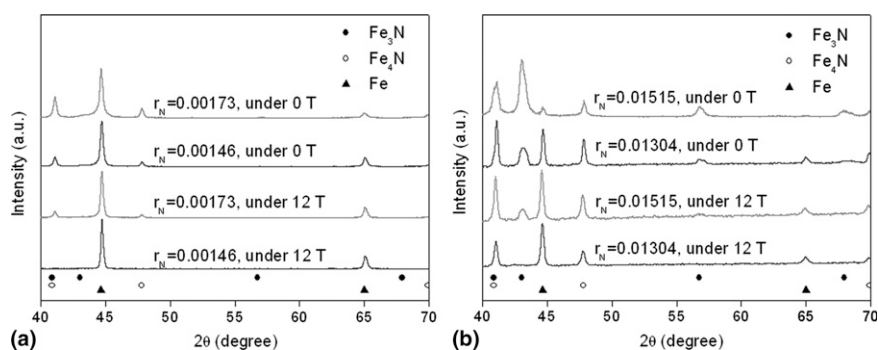


FIG. 2. XRD patterns of the samples nitrided at 450 °C for 9 h under different nitrogen potentials with or without a high magnetic field of 12 T as indicated; (a) for  $\gamma'$ -Fe $_4$ N phase formation and (b) for  $\epsilon$ -Fe $_3$ N phase formation.

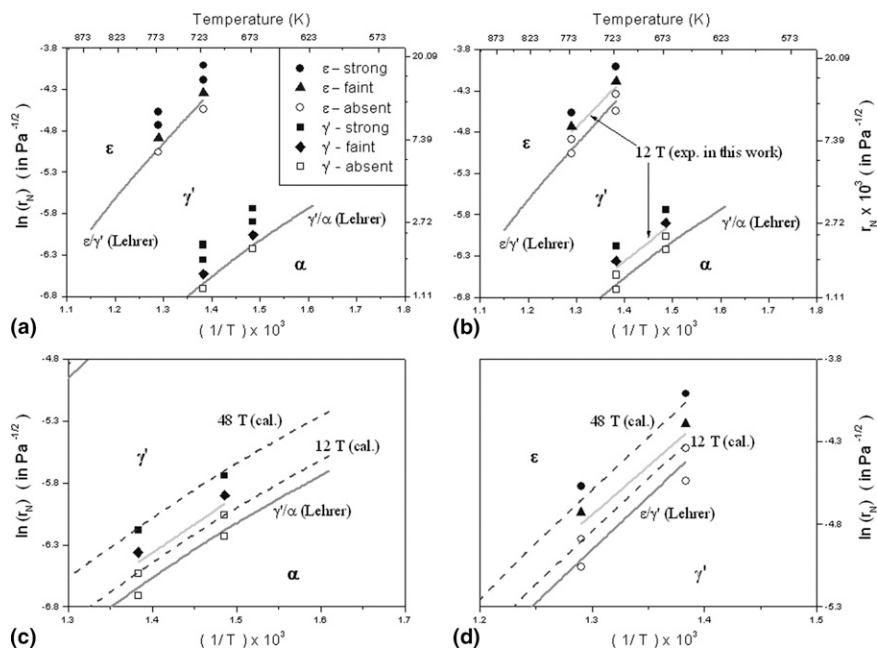


FIG. 3. Experimental data showing the XRD analysis of samples nitrided (a) under a nonmagnetic field and (b) under a magnetic field of 12 T, the critical nitrogen potential to form  $\gamma'$ -Fe<sub>4</sub>N and  $\epsilon$ -Fe<sub>3</sub>N phases for magnetic samples in comparison with that for Lehrer diagram reported in references.<sup>5</sup> Calculation results using magnetic density 12 T and 48 T in terms of Eq. (9) are included (dashed lines) in (c) and (d).

where  $\Delta G^\circ = (\mu_{\text{Fe}_x\text{N}}^\circ + 3/2\mu_{\text{H}_2}^\circ) - (\mu_{\text{NH}_3}^\circ + x\mu_{\text{Fe}}^\circ)$  denotes the standard Gibbs free energy of the reaction;  $\mu_I^\circ$  is the chemical potential of  $I$  in the reference state;  $\alpha_I$  is the activity of  $I$  in the dissolved state with respect to the reference state (in the reference state  $\alpha_I = 1$ );  $p_I$  is the partial pressure of  $I$ . The reference state for a pure solid Fe<sub>x</sub>N phase is assumed to be itself ( $\alpha_{\text{Fe}_x\text{N}} = 1$ ). By considering  $r_N = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$  and  $\alpha_{\text{Fe}} = 1$  (pure Fe is taken as the reference state), the critical nitrogen potential to form Fe<sub>x</sub>N phase is

$$\ln r_{\text{Fe}_x\text{N}} = \frac{\Delta G^\circ}{RT} \quad (3)$$

When a magnetic field  $H_0$  is applied, all thermodynamic functions will depend on the value of the magnetic field.<sup>14</sup> The equilibrium condition of the reaction described in Eq. (1) under a magnetic field should be

$$\Delta G + \Delta G^M = 0 \quad (4)$$

where  $\Delta G$  is described by Eq. (2), and  $\Delta G^M$  is the Gibbs free energy change owing to magnetic field for reaction (1). Thus, by combining Eqs. (2), (3), and (4), the critical nitrogen potential to form Fe<sub>x</sub>N phase under a high magnetic field is

$$\ln r_{\text{Fe}_x\text{N}}^M = \frac{\Delta G^\circ + \Delta G^M}{RT} = \ln r_{\text{Fe}_x\text{N}} + \frac{\Delta G^M}{RT} \quad (5)$$

For a paramagnetic or a ferromagnetic material  $I$ , the application of an external magnetic field  $H_0$  can lower its Gibbs free energy.<sup>15</sup> The magnetic contribution to the free energy  $\Delta G_I^M$  is simply expressed as

$$\begin{aligned} \Delta G_I^M &= - \int_0^{H_0} M_I dH \\ &\approx - \frac{\chi_I H_0^2}{2} \quad (\text{paramagnetic}) \\ &\approx -M_I H_0 \quad (\text{ferromagnetic}) \end{aligned} \quad (6)$$

where  $M_I$  is the molar magnetization and  $\chi_I$  is the molar magnetic susceptibility in the material  $I$ , respectively. The Gibbs free energy change owing to magnetic field for reaction (1) can be written as

$$\Delta G^M = (\Delta G_{\text{Fe}_x\text{N}}^m + 3/2\Delta G_{\text{H}_2}^m) - (\Delta G_{\text{NH}_3}^m + x\Delta G_{\text{Fe}}^m) \quad (7)$$

The magnetic property data for iron, Fe<sub>4</sub>N, and Fe<sub>3</sub>N are currently well documented and their Curie points are 770, 490, and 508 °C, respectively.<sup>16–18</sup> The temperature variations of magnetization of iron, Fe<sub>4</sub>N, and Fe<sub>3</sub>N can be calculated by the Weiss molecular field model.<sup>19–21</sup> The result shows that the magnetization of iron ( $M_{\text{Fe}}$ ) is about 11.49 JT<sup>-1</sup>mol<sup>-1</sup> in the nitriding temperature, but that of Fe<sub>4</sub>N and Fe<sub>3</sub>N phase is below 0.1 JT<sup>-1</sup>mol<sup>-1</sup> when the temperature exceeds 400 °C (close to their Curie points). Considering the susceptibilities for diamagnetic gas H<sub>2</sub> and NH<sub>3</sub> are less than 10<sup>-7</sup>, Eq. (7) can be calculated approximately as

$$\Delta G^M \approx (11.49x - 0.1)H_0 \quad (8)$$

Equation (5) can be changed as

$$r_{\text{Fe}_x\text{N}}^M = r_{\text{Fe}_x\text{N}} \exp\left(\frac{11.49x - 0.1}{RT} H_0\right), \quad (x = 3, 4) \quad (9)$$

From Eq. (9), one may find that the critical nitrogen potential to form the  $\text{Fe}_x\text{N}$  phase under a high magnetic field is higher than that in conventional nitriding and its value enhances with an increase in magnetic field intensity ( $H_0$ ). Figures 3(c) and 3(d) show the calculated lines of critical nitrogen potential to form  $\text{Fe}_x\text{N}$  from Eq. (9) under a magnetic field of 12 T, which is in good agreement with the x-ray measurements. When magnetic field intensity reaches 48 T during nitriding, the calculated result indicates that the critical nitrogen potential to form the  $\text{Fe}_x\text{N}$  phase became higher than that in 12 T, as shown in Figs. 3(c) and 3(d).

The magnetic field can be considered to be a candidate for a selective nitriding approach. For example, nitriding is usually used to enhance surface properties of various metallic shafts. It is well known that the compound layer is decisive in determining wear and corrosion characteristics, but it can increase fatigue crack initiation at the stress concentration site in service<sup>1,8</sup> [such as the step of shaft as shown in Fig. 1(b)]. If a high magnetic field is locally used at the site of shaft during nitriding, brittle nitride formation can be hindered effectively at the site. After nitriding, the compound layer will possess a selective nitride distribution according to special requirements. Its properties will be better than those of the conventional nitriding layer and of controlled nitriding layer (without a compound layer).<sup>8</sup>

In conclusion, magnetization can be introduced as a new thermodynamic function during nitriding processes. The external high magnetic field can shift the equilibrium of nitriding reaction, showing that the critical nitrogen potential to form  $\gamma\text{-Fe}_4\text{N}$  and  $\epsilon\text{-Fe}_3\text{N}$  phase is evidently enhanced compared with conventional nitriding. Using a local high magnetic field, the formation of nitride can be controlled at the desired site in the surface layer of a workpiece.

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