Nitriding is a thermochemical surface treatment in which nitrogen is transferred from an ammonia atmosphere into steel below the eutectoid temperature [1, 2]. Due to the low solubility of nitrogen in ferrite [3], ε and/or γ nitrides (Fe$_{2-3}$(C, N) and Fe$_4$N, respectively) precipitate during the nitriding process. A compound layer and underlying diffusion zone (case) are formed near the steel surface after nitriding. The compound layer (also known as white layer) consists of nitrides, and can greatly improve wear and corrosion resistance [4]. The hardened diffusion zone significantly enhances fatigue endurance. Because nitriding is a low temperature process, it minimizes distortion and deformation of the heat treated parts [2].

The properties of nitrided steels depend on nitriding process parameters. Conventionally, trial and error methods were used to define parameters to meet specifications; an expensive, time consuming, and hard to control method. Therefore, an effective simulation tool is needed to pre-define process parameters and predict nitriding performance of a variety of steels.

Efforts to simulate the nitriding process have been ongoing for the past 20 years. Much work has been done to simulate nitriding of pure iron [5–7]. Good agreement has been achieved using various models. However, pure iron is never used for nitriding in industry, and simulations for steels are more complicated, because the well-defined ε and/or γ sublayers in nitrided iron are replaced by the mixture of the two phases in nitrided steels [8].

In this work, the compound layer growth model derived from the nitride layer growth model [5] is developed to simulate the compound layer growth kinetics for nitriding AISI 4140 based on the customized Lehrer diagram [9]. The model can be used to calculate concentration profiles of nitrogen as a function of time and position during the nitriding process and to predict the thickness of the compound layer.

### Experimental work

AISI 4140 cylindrical bars used in this study (supplied by Peterson Steel Corp.) had the following chemical composition: 0.399% C, 0.91% Mn, 0.01% P, 0.029% S, 0.266% Si, 0.88% Cr, 0.166% Mo, bal Fe. Before nitriding, bars were heat treated at 843°C for 1.5 h in Endothermic gas at 0.4% C potential to harden the core, followed by quenching in agitated 54°C mineral oil, washed in hot water, and tempered in air at 579°C for 3 h (Bodycote Worcester, Mass.). Bars were mached into 3.175 cm diameter by 1 cm thick disks. A 2-mm diameter hole was drilled near the edge for holding the sample during the process. Disks were washes with alcohol prior to nitriding using a standard two-stage industrial nitriding process. During the first stage, nitriding was carried out using ammonia gas with a dissociation rate of 24–28% at 527°C for 10 h, followed by 50 h at 548°C with a dissociation rate of 79–82%. Dissociation rate represents the percentage of ammonia dissociated into hydrogen and nitrogen, and is measured using a burette in the furnace exhaust gas.
demonstrates the presence of very fine secondary phases.

**TEM analysis**

Figure 2 shows a detailed TEM analysis for a nitrided 4140 cross section with three distinct regions\(^9\). Regions A and B correspond to the two layers in the compound layer (compare with Figure 1), and Region C corresponds to the diffusion zone. Region A consists of three phases: \(\gamma', \varepsilon, \) and \(\text{Fe}_7\text{C}_3\); Region B consists of \(\gamma'\) and \(\text{Fe}_7\text{C}_3\); and Region C contains martensite and carbides.

**Microhardness and nitrogen concentration**

Microhardness of the nitrided cross section was measured to determine change in hardness from the surface layer to bulk material. Measurements started at a depth of 50 \(\mu\)m from the edge followed by 100 \(\mu\)m increments. Nitrogen concentration (measured using OES) was determined at four different locations on the surface of each layer; layers of metal were removed to measure concentration each layer. Plots of microhardness and weight percentage of nitrogen vs. depth from surface (Fig. 3) show excellent correlation.

**Customized Lehrer diagram for 4140**

The Lehrer diagram\(^10\) depicts the development of phase constituents in pure iron as functions of nitriding potential and temperature. Nitriding potential \((K_n)\) is defined as:

\[
K_n = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}}
\]

where \(P_{\text{NH}_3}\) and \(P_{\text{H}_2}\) are the partial pressures of the ammonia and hydrogen gases, respectively. The dissociation rate used in this work can be converted to nitriding potential based on thermodynamics.

The Lehrer diagram of pure iron (Fig. 4) and the customized Lehrer diagram of 4140 (Fig. 5) were developed using computational thermodynamics\(^11\). TCFE6 database was used to make calculations, which were carried out using the Thermo-Calc software\(^12\). The Gibbs energy of fcc phase in the TCFE6 database was modeled to describe the regular austenite of Fe alloys and the \(\text{M(C, N)}\) carbonitrides, because both share the same crystal structure. Two-sublattice model \((\text{M})_1(\text{C}, \text{N}, \text{Va})_1\) was adopted for fcc according to its crystal structure. Metallic elements (M), such as Fe, Mn, Mo, and Cr, occupy the first sublattice that corresponds to the 4a site of fcc structure; while C, N, and vacancy occupy the second sublattice that corresponds to the 4b site of fcc structure. If the 4b site is mainly occupied by a vacancy, it is the austenite of Fe alloys. In the current calculations, there are more than two fcc phases due to the immiscibility of the Gibbs energy description of the fcc phase in the TCFE6 database.

The customized Lehrer diagram of 4140 (Fig. 5a) is very different from that of pure iron (Fig. 4a). The latter shows two single-phase sublayers (\(\varepsilon\) layer and \(\gamma'\) layer) in the compound layer. However, a single nitride phase layer in the compound layer does not exist in nitrided 4140 at the typical nitriding temperature (<550°C).
In addition, the relationship between nitriding potential and nitrogen concentration at fixed temperature can be calculated. Figure 5b shows nitriding potential as a function of nitrogen concentration at 548°C, which is the nitriding temperature used in the second stage of this experiment. Two horizontal lines appear in the plot of nitriding potential vs. nitrogen concentration diagram represent constant nitrogen activity when local equilibrium between gaseous atmosphere and steel surface is assumed, which indicate the interface between γ' and ε single-phase regions. These lines correspond to the (a and γ') and (γ' and ε) two-phase regions, and the nitriding potentials are invariant along these two lines.

According to Eq 1, \( P_n \) is proportional to nitrogen activity \( (a_N) \) in the atmosphere. Therefore, the invariant lines on nitriding potential vs. nitrogen concentration diagram represent constant nitrogen activity when local equilibrium between gaseous atmosphere and steel surface is assumed, which indicate the interface between γ' and ε sublayers and the interface between γ' and diffusion zone on the microstructure.

Note there is a horizontal line on Fig. 5b for 4140 when nitrogen concentration varies from 2.3 to 6.5 wt% N, which indicates nitrogen activity is constant in nitrided 4140 when nitrogen concentration is in this range. There is no bcc phase in the region above, while there is in the region below. Therefore, the compound layer exists at nitrogen concentrations >6.5 wt%, and the diffusion zone exists for concentrations <2.3 wt%. The interface between compound layer and diffusion zone is well defined (Fig. 5b).

**Compound layer growth model**

The kinetics of diffusion-controlled compound layer growth can be modeled by the shift of the interface between compound layer and diffusion zone when local equilibrium is assumed at the interface. In nitrided pure iron, single-phase layers exist in the compound layer, and nitrogen concentrations on the interfaces between the layers can be defined from the binary Fe-N phase diagram based on local equilibrium assumption[7]. Somers et al. successfully adopted this model to derive the γ'-monolayer and ε and γ' bilayer growth into the substrate for the pure iron nitriding process[8]. However, it is challenging to apply this model for steels. In nitrided steels, well-defined single phase layers are replaced by the multiphase mixture, which makes it hard to define the nitrogen concentrations at the interface between compound layer and diffusion zone.

The compound layer growth model on nitriding steels was developed following Somers’ model (Fig. 6), where \( N^i \) is nitrogen concentration on the outside steel surface, and \( N^c \) and \( N^d \) are concentration at the interface and in the diffusion zone in the compound layer at the compound layer/diffusion zone interface, respectively. \( N^0 \) is the nitrogen concentration in steel before nitriding.

The initial position of the interface between compound layer and diffusion zone is \( \xi \). If the interface shifts a distance \( d\xi \) into the substrate within a time increment \( dt \), the mass conservation in the compound layer is expressed as:

\[
(N^c - N^d) \cdot d\xi + dW = (J^c \big|_{x=0} - J^d \big|_{x=\xi}) \cdot dt \tag{2}
\]

where \( J^c \) is nitrogen flux entering the compound layer at the steel surface and \( J^d \) is nitrogen flux leaving the compound layer at the interface, and \( dW \) is the amount of solute that accumulates in the compound layer to maintain a concentration-depth profile.

Nitrogen diffusion in steel follows Fick’s First Law,

\[
J^c \big|_{x=0} = (-D^c \frac{\partial c}{\partial x}) \big|_{x=0} \tag{3}
\]

\[
J^d \big|_{x=\xi} = (-D^d \frac{\partial c}{\partial x}) \big|_{x=\xi} \tag{4}
\]

where \( D^c \) and \( D^d \) are diffusion coefficients of nitrogen in compound layer and diffusion zone, respectively. Substituting Eq 3 and 4 into Eq 2 yields

\[
(N^c - N^d) \cdot d\xi + dW = \left[ (-D^c \frac{\partial c}{\partial x}) \big|_{x=0} - (-D^d \frac{\partial c}{\partial x}) \big|_{x=\xi}) \right] \cdot dt \tag{5}
\]

where \( N^c, N^d, N^i, D^c, \) and \( D^d \) are the main parameters that need to be defined to simulate the nitriding process of steels.

Continued
Results

Based on the compound layer growth model and above analysis, $N_s$, $N_c$, and $N_d$ are determined by the Lehrer diagram of 4140. $D'$ and $D''$ are still unknown. The effective diffusivity in the compound layer ($D'$) is fitted using the compound layer thickness, which is about 19 $\mu$m. An inverse method that compares results of simulated and experimental nitrogen concentration profiles from OES measurements was used to determine the diffusivity in the diffusion zone ($D''$). Values of $D' = 6.5 \times 10^{-14}$ cm$^2$/s and $D'' = 5 \times 10^{-17}$ cm$^2$/s are applied for 4140 in this work. The nitrogen diffusion coefficient in ferrite was reported as $7.3 \times 10^{-17}$ cm$^2$/s$^{[10]}$, which is similar to the diffusion zone diffusivity used in the current simulation. The difference may be due to the tempered martensite matrix in this work, which consists of ferrite and carbides.

The initial simulation of the nitrogen concentration profile from the compound layer growth model for 4140 is shown in Fig. 8. The red lines are nitrogen concentration profile calculated from the compound layer growth model. It shows very good agreement with the experimental data by OES.

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For more information: R. D. Sisson Jr., FASM, Center for Heat Treating Excellence; Worcester Polytechnic Institute; 100 Institute Rd; Worcester, MA 01609; sisson@wpi.edu; www.me.wpi.edu/mte.