



Modeling and Simulation of Surface Reactions and Reactive Flow of a Nitriding Process

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INTRODUCTION

Due to its metallurgical achievements like high surface hardness, improvement in fatigue life and increased wear resistance and antigalling properties, gas nitriding is recently becoming an attractive case-hardening process where nitrogen is diffused into the surface of a solid ferrous alloy in contact with ammonia in a furnace environment [1]. Because of relatively low temperatures employed in this process, nitriding produces less distortion and deformation of parts than conventional hardening techniques [2]. However, in most nitriding processes, dissociation rate of ammonia vary even though the controlling factors such as ammonia flow rate, surface area and nitriding temperature remain constant. This leads to variation of hardness and nitriding depth on internal and external surfaces of the parts. It is therefore essential and also challenging task to improve furnace control concepts. Key to develop a nitriding process with limited compound layer is to homogenize diffusion mechanism, which requires an increased understanding of reaction kinetics and of gas flow on the part surfaces in the furnace. However, ammonia dissociation in a gas nitriding atmosphere diluted with excess N₂ is a temperature dependent heterogeneous reaction where the dissociative adsorption process leads to atomic hydrogen and nascent nitrogen on the surface [3].

SURFACE CHEMISTRY

Surface interactions can be envisaged schematically as in Figure 1.

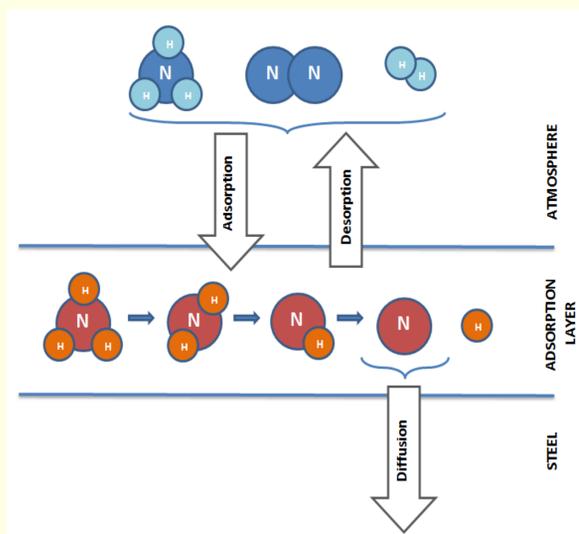


Figure 1. Surface reactions of ammonia.

The equations of the R_r (which is 12 in this case) elementary reactions on the surface can be put in a general form [4],

$$\sum_{s=1}^{S_g+S_a} v_{rs}^e A_s \rightarrow \sum_{s=1}^{S_g+S_a} v_{rs}^p A_s \quad (r = 1, \dots, R_r).$$

The mass rate of change of species is then given as,

$$\dot{m}_i = M_i \sum_{r=1}^{R_r} k_r (v_{ri}^p - v_{ri}^e) \prod_{s=1}^{S_g+S_a} c_s^{v_{rs}^e} \quad (i = 1, \dots, S_g + S_a)$$

where forward rate coefficient of reaction r is calculated by a modified Arrhenius expression [5],

$$k_r = A_r T^{\beta_r} \exp\left[\frac{-E_{ar}}{RT}\right] \prod_{s=1}^{S_a} \theta_s^{\mu_{sr}} \exp\left[\frac{\epsilon_{sr} \theta_s}{RT}\right].$$

For adsorption reactions, surface reaction rate constant is given,

$$k_r = \gamma_r \frac{1}{\Gamma_{Fe}^n} \sqrt{\frac{RT}{2\pi W_s}}$$

where

$$\gamma_r = \min\left\{1, A_r T^{\beta_r} \exp\left[\frac{-E_{ar}}{RT}\right]\right\}.$$

Surface coverage, θ_s , is expressed as,

$$\theta_s = \frac{Y_s \rho_g V_{cs}}{\left[\sum_{j=1}^{S_g} Y_j\right] A_{eff} \Gamma_s M_s}$$

and must satisfy

$$0 \leq \theta_s \leq 1 \text{ and } \sum_{s=1}^{S_a} \theta_s = 1.$$

CFD

For an unsteady flow of a multicomponent gas mixture, Eulerian equations expressing conservation of mixture mass, momentum, enthalpy and species concentrations can be given in a generic form as

$$\frac{\partial \rho \Phi}{\partial t} + \frac{\partial}{\partial x_i} (\rho U_i \Phi - \rho \Gamma_\Phi \frac{\partial \Phi}{\partial x_i}) = S_\Phi.$$

At the reacting surface, mass concentrations of species are not constant due to the surface reactions,

$$\dot{m}_s = (\vec{j}_s + \rho Y_s \vec{u}) \cdot \vec{n} \quad (s = 1, \dots, S_g).$$

Mass transfer between the gas and the surface results in a net flux and a velocity perpendicular to the surface, which is called Stefan velocity,

$$\vec{u} \cdot \vec{n} = \frac{1}{\rho} \sum_{s=1}^{S_g} \dot{m}_s = \frac{(\Delta Y_{NH_3} + \Delta Y_{N_2} + \Delta Y_{H_2}) M_{tot}}{\rho \Delta t A_{eff}}.$$

The equilibrium of energy can be expressed with the equation,

$$-\lambda \nabla T|_g \cdot \vec{n} = \sum_{s=1}^{S_g} \dot{m}_s h_s.$$

The computational setup for surface reactions and furnace flow modeling was designed to match the in-service furnace used in Bosch production plants, which is discretized in a mesh with 4600000 cells. Unsteady Reynolds Averaged Navier-Stokes (URANS) and 4 other scalar equations (enthalpy and mass fractions of NH₃, N₂ and H₂) were solved.

RESULTS

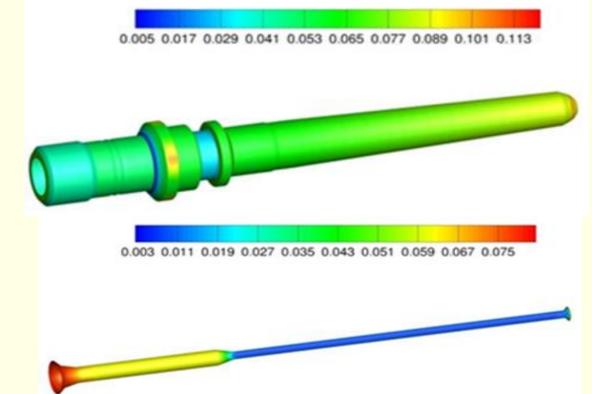


Figure 2. Adsorbed nitrogen concentration (coverage) on the outer and inner surfaces of the injector.

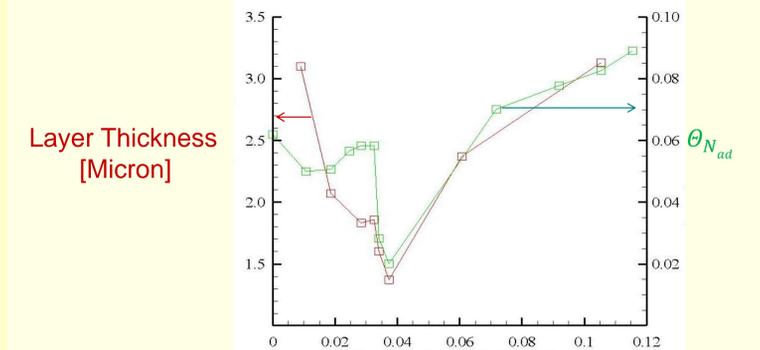


Figure 3. Comparison of model (□) and measurements (○).

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ABSTRACT

Due to wide use of ammonia in gas nitriding processes, a numerical study has been undertaken to determine the ammonia decomposition rates on an injector body which was used as a steel catalyst under conditions likely to be employed in such applications. With the extrapolation of the data available for noble surfaces, intrinsic rate data have been obtained for the process temperatures of around 520°C in furnace conditions with pressures varying between -100 and 900 Pa around the atmospheric pressure. The detailed chemical mechanism included 12 reactions and 9 species. The computational setup for surface reactions and furnace flow modeling was designed to match the in-service furnace used in Bosch production plants and contained 4.6 million mesh points and results obtained with URANS k-ε turbulence model.

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