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Electronic Supporting Information B

Hysteresis phenomenon in the reaction system of nanocrystalline iron with mixture of ammonia and hydrogen

Walerian Arabczyk, Ewa A. Ekiert, Rafał Pelka*

West Pomeranian University of Technology, Szczecin, Institute of Chemical and Environment Engineering, 10 Pułaskiego Str., 70-322 Szczecin, Poland

* *Corresponding author: tel. +48 91 449 47 30, fax +48 91 449 46 86, e-mail: rpelka@zut.edu.pl*

Thermodynamics of the process of gaseous ammonia nitriding of nanocrystalline iron

In the process of nitriding with gas mixtures containing ammonia there on the surface of α-Fe nanocrystallite the disassociative adsorption of NH_3 molecules takes place:

$$NH_3^g \leftrightarrow N^a + {}^3/_2 H_2^g \tag{S1}$$

The equilibrium constant of dissociation reaction, K, of an ammonia molecule for the above reaction can be expressed as:

$$K = \frac{p_N \cdot p_{H_2}^{3/2}}{p_{NH_3}} \tag{S2}$$

Substituting the expression for the nitriding potential, we obtain:

$$p_N = K \cdot P \tag{S3}$$

where: p_N – hypothetical nitrogen partial pressure.

Atomic nitrogen species adsorbed at the nanocrystallite surface diffuse into its bulk and creates solid state solution with iron, α-Fe(N). At steady state for the Fe-NH_3-H_2 system, between nitrogen atoms in the gas phase and adsorbed on the surface of iron nanocrystallite and dissolved in its volume the chemical equilibrium is established. Chemical potentials of nitrogen (μ_N) present in the system in different states are equal to each other. Apart from that, chemical potential of nitrogen in a gas phase equals p_N:

$$\mu_{N_g} = p_N \tag{S4}$$

Assuming that the activity coefficient in dilute solutions is close to unity, $\gamma = 1$:

$$\mu_{N_b} = \gamma \cdot x_{N_b}^{\alpha} = x_{N_b}^{\alpha} \tag{S5}$$

$$x_{N_b}^{\alpha} = p_N = K \cdot P \tag{S6}$$

If the equivalent concentrations of nitrogen: in the gas-phase and adsorbed on the surface meet the assumptions for the Langmuir's equation then nanocrystallite is in the chemical equilibrium:

$$\frac{\theta_N^\alpha}{1-\theta_N^\alpha} = p_N \cdot exp^{\frac{-\Delta G_{ads}}{RT}} \quad \text{(S7)}$$

where: ΔG_{ads} – Gibbs energy of nitrogen molecule adsorption process; R – gas constant; θ_N^α – surface coverage degree defined as ratio of the concentration of surface iron atoms covered with nitrogen, x_{Fe-N}^{α}, to the sum of the concentrations of surface iron atoms covered with nitrogen and free adsorption sites $x_{Fe-N}^{\alpha} + x_{Fe-}^{\alpha}$:

$$\theta_N^\alpha = \frac{x_{Fe-N}^{\alpha}}{x_{Fe-N}^{\alpha} + x_{Fe-}^{\alpha}} \quad \text{(S8)}$$

Concentration of nitrogen dissolved in a volume of iron crystallite, $x_{N_b}^{\alpha}$, and adsorbed on nanocrystallite surface, $x_{N_s}^{\alpha}$, are connected with each other in accordance with the McLean-Langmuir equation:

$$\frac{\theta_N^\alpha}{1-\theta_N^\alpha} = \frac{x_{N_b}^{\alpha}}{1-x_{N_b}^{\alpha}} \cdot exp^{\frac{-\Delta G_{seg}^{\alpha}}{RT}} \quad \text{(S9)}$$

where ΔG_{seg}^{α}, it is Gibbs energy of the nitrogen segregation process in α phase.

With an increase in chemical potential of nitrogen in the gas phase the iron nanocrystallite surface coverage degree, θ_N^α, increases as well as nitrogen concentration in nanocrystallite volume, $x_{N_b}^{\alpha}$, in accordance with the McLean-Langmuir equation, up to the maximum critical levels, $\theta_{N_{max}}^{\alpha}$ and $x_{N_{bmax}}^{\alpha}$, respectively.

For dilute solutions, i.e. solution of nitrogen in α-iron, where $n_N << n_{Fe}$ and nFe = 1 (number of moles of iron), number of moles of nitrogen is equal to nitrogen molar fraction according to the equation:

$$x_N^\alpha = \frac{n_N}{n_{Fe} + n_N} \approx n_N \quad \text{(S10)}$$