Abstract - Dissertation entitled *"Study on the nitriding processes of nanocrystalline iron under atmospheres with a variable nitriding potential"* by Izabela Moszyńska, M. Sc.

The dissertation copes with the nitriding of nanocrystalline iron and the reduction of iron nitrides in the system: nanocrystalline iron – ammonia – hydrogen. The iron catalyst for ammonia synthesis was used as a substrate due to its nanocrystalline structure. A series of samples containing iron nitrides with different nitriding level was prepared by thermogravimetric method. Various factors influencing the studied processes, especially temperature and nitriding potential was studied. The experiments were carried out in four different temperatures: 400, 450, 500 and 550 °C. Nitriding potential was varied between $1{,}23 \cdot 10^{-4}$ and 0,97 $Pa^{-1/2}$. The nitriding processes were performed in the direction of increasing ammonia concentration as well as in the reversed direction. Basing on the experimental results some deviation of examined system from the behaviour observed for classic iron - nitrogen system were observed. The stationary states of nitriding reaction were observed both in the direction of iron nitriding and in the direction of iron nitride reduction. The threshold nitriding potential which corresponds to the formation of given phase is dependent on the process direction. This observation is demonstrated by the characteristic hysteresis phenomenon. The structure of iron nitrides was evaluated by XRD analysis. Some XRD measurements were performed under in situ conditions in reaction camera of x-ray diffrectometer. Two or three crystallographic phases coexisted in a limited set of conditions. During nitriding process two-component mixtures were observed: α-Fe(N) + γ'–Fe_4N and γ'–Fe_4N + ε-Fe_xN. During reduction process three-component mixtures were observed: α-Fe(N) + γ'–Fe_4N + ε-Fe_xN. Lattice parameter *a* of α-Fe(N) phase varies in the range between 0,2881 and 0,2885 nm during nitriding process, while during the reduction of iron nitrides it varies between 0,2883 and 0,2882 nm. Lattice parameter *a* of γ'–Fe_4N phase varies in the range between 0,3805 and 0,3811 nm during nitriding process, and lattice parameter *a* varies in the range between 0,3810 and 0,3808 nm during reduction of nitrides. The variation of lattice constants for ε-Fe_xN phase is substantial. Lattice parameter *a* of ε-Fe_xN phase varies in the range between 0,4688 and 0,4821 nm during nitriding process and between 0,4826 do 0,4650 nm during reduction of iron nitrides, and lattice parameter *c* of ε-Fe_xN phase varies in the range between 0,4444 and 0,4691 nm during nitriding and 0,4660 and 0,4444 nm during reduction of iron nitrides. Mean size of crystallite size for all observed crystallographic phases was observed in Fe – NH_3 – H_2 system during studied processes. The mean size of iron crystallites as well as

the mean size of product crystallites decreases during nitriding process. The biggest crystallites of the substrate are converted first, while the smallest reacts as last. The phase transitions occurs in the sequence of decreasing crystallites. The statistical model of phase transition and its influence on the mean crystallite size was proposed for nanocrystallite iron nitriding process. Lehrer diagram was modified for nanocrystalline samples basing on thermogravimetric and diffraction observations. A physical model of nitriding in the atmospheres with variable nitriding potential was proposed.

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