

ABSTRACT OF PHD THESIS

„Study on the mechanism of the nitriding processes of nanocrystalline iron and the decomposition of nanocrystalline iron nitrides”

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The aim of the doctoral thesis was to understand the mechanism of the nitriding processes of an iron catalyst, the main component of which is nanocrystalline iron, and the reduction of nanocrystalline iron nitrides γ' -Fe₄N in an ammonia-hydrogen-nitrogen atmosphere.

The research was conducted in a prototype installation built at the Institute of Inorganic Chemical Technology and Environmental Engineering, enabling the measurement of the reaction rate of nanocrystalline materials with gases of different chemical composition in in situ conditions under normal pressure at temperatures up to 750°C. As part of the implementation of the doctoral thesis, during the research, the reactor was modernized, reducing its reaction capacity and building in a sensor for measuring magnetic permeability. Pressure control and automatic regulation of gas flows at the reactor inlet were also introduced, and the sensitivity of mass and composition measurements of the gas phase was increased. The modernizations introduced allowed obtaining more accurate results of measurements of the conducted chemical reactions.

The kinetics of the processes of nitriding nanocrystalline α -iron to nanocrystalline iron nitride ϵ -Fe₃-2N were studied in the temperature range of 325°C -375°C in an ammonia atmosphere and reducing nanocrystalline ϵ nitride to iron in hydrogen-nitrogen mixtures with different hydrogen concentrations at a temperature of 400°C by measuring the mass, composition of the gas phase and temperature.

It was found that in the nitriding and reduction processes the reaction rate ($\frac{dx}{dt}$) of both processes depends on the degree of nitriding and this relationship is cyclical. The occurrence of cyclic changes in the chemical reaction rate in the solid phase was observed. Such an oscillatory process has not been described before. Therefore, for the first time it was shown that in nanocrystalline solid-gas systems, the processes are cyclical. 6 cycles of changes in the

reaction rate of nitriding nanocrystalline iron and reduction of γ' -Fe₄N nitride were observed. The oscillations are the result of successive nitrogen sorption reactions in the volume of iron nanocrystallites and the transformation of the iron nanocrystalline network from α -Fe to γ' -Fe₄N. The mechanism of the observed phenomenon was explained, taking into account the processes occurring in the volume of the solid phase. Changes in the oscillation rate of the described processes prove the non-monotonic degree of surface coverage with nitrogen, which is caused by a step change in the free enthalpy of nitrogen segregation. Based on model calculations, changes in the free enthalpy of segregation were determined in the process of both nitriding and reduction of nitrides, and a modification of the Fowler-Guggenheim equation was proposed.

The nitriding process of nanocrystalline iron was studied at a temperature of 350°C in an ammonia atmosphere, additionally measuring the magnetic permeability of the catalyst sample during the reaction. By measuring the rate of the nitriding process and the relative magnetic permeability, three reaction areas with variable magnetic permeability were observed, depending on the degree of nitriding. The size distribution of iron nanocrystallites was determined depending on the specific active surface of the nanocrystal and it was found that the catalyst is bimodal as a sum of two Gaussian distributions, which also differ in the value of relative magnetic permeability. The relative magnetic permeability of small α -Fe crystals is higher by 0.02 compared to large crystals. In the $\alpha \rightarrow \gamma'$ transformation region, the dependencies of magnetic permeability change, which proves the existence of two mechanisms of the α -Fe structure change in the α -Fe $\rightarrow \gamma'$ Fe₄N transformation. In the first region, an α -Fe(N) solution is formed with a continuous and slight change in the parameters of the iron crystal lattice. In the second region, a stepwise, oscillatory change in the parameters of the iron crystal lattice in Fe_xN occurs. In the third region of the γ' -Fe₄N $\rightarrow \epsilon$ -Fe₃₋₂N transformation region, a solution is formed with a nitrogen concentration varying in the range of 0.25-0.45 [mol/mol]. In the final phase of the nitriding process, at a constant value of relative magnetic permeability, only the nitrogen concentration in the ϵ -Fe₃₋₂N solution increases. The rate of the process is limited by the nitrogen diffusion through the phase boundary – between the solid and the gas phase. The value of the nitrogen diffusion coefficient was estimated, changing exponentially with the degree of nitriding.

26. 08. 2024

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