

Many aspects of life in the late 20th and early 21st century was dominated by issues related to nanomaterials. Nanomaterials are materials whose size in at least one direction is less than 100 nm. The properties of nanomaterials are significantly different from the properties of bulk substances which are chemically identical. There were also observed differences in the kinetics and thermodynamics of processes involving nanomaterials. Nanomaterials are already being used for hundreds of years, e.g. as pigments, and in recent decades, e.g. as metal catalysts, but only thanks to modern measuring techniques it was possible to study such small structures. It was found that physicochemical properties of nanomaterials depend on the size of crystallites, but nanomaterials are the most polycrystalline substances with a wide crystallite size distribution. The interest in nanomaterials and their properties continues to grow. Thus, it is observed, especially in recent years, a more intensive development of nanotechnology. Research teams in highly developed countries deal with production of nanomaterials and study of their electrical, magnetic, mechanical or otherwise properties.

According to current knowledge, the correlations between the properties of nanomaterials and parameters regarding the process for obtaining them (temperature, pressure etc.) are determined in an experimental way. This means that currently the nanomaterials synthesis is carried out in an empirical way, by trial and error, which consumes considerable amounts of money. The lack of knowledge about the thermodynamics of nanomaterials prevent conducting the synthesis of these materials in a controlled manner. Studying the basics of thermodynamics of processes involving nanomaterials will enable one to design a technology of obtaining (inspection and control of the synthesis) of nanocrystalline materials with desired, predesigned properties.

Iron ammonia synthesis catalyst was used in the production of approx. 100 years ago. Much later it was found that its activity in the synthesis of ammonia is a result of the nanocrystalline structure. The iron catalyst, viz. nanocrystalline iron, whose surface is coated with oxide promoters (mainly  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ) is used as a model structure to study the surface effects in the reactions between solid and gas phase. There are still conducted analyses and discussions on its functioning.

Works on obtaining and properties of nanocrystalline iron are conducted at the Institute of Chemical and Environment Engineering, ZUT in Szczecin for several years. It was developed a method for the preparation of nanocrystalline iron promoted with aluminum, calcium and potassium oxides. Research on the phenomena occurring on the surface of nanocrystalline iron concerning: synthesis and decomposition of ammonia, as well as nitriding, carburizing and oxidation were performed. In addition, it was developed a method that allows separation from polycrystalline nano-material, a material with a specific and desired sizes of nanocrystallites.

In the chemical process involving the nanocrystalline iron and the gas mixtures of  $\text{NH}_3/\text{H}_2$  the following states are established: (1) stationary states in which the composition of a gas phase and solid state do not change in time and degree of conversion ( $\alpha$ ) of the nanocrystalline substance is a function of the temperature and the chemical potential ( $P$ ) vapour phase; and (2) chemical equilibrium states between gas and solid. In the stationary states in a two-phase system there was observed a hysteresis phenomenon (for the dependence  $\alpha = f(P)$ ) for chemical processes of nitriding of nanocrystalline iron and reduction of reaction products (hysteresis phenomenon has been associated with physical phenomena so far).

The research work undertaken in this project will help to determine the thermodynamic relations between physicochemical properties of nanomaterials (nanocrystalline Fe, Ni, Co promoted with  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ) and the carburizing potential of the gas phase, with which they react in equilibrium states or close to equilibrium by using the Chemical Potential Programmed Reaction method.