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The influence of iron nanocrystallite size on a nitriding process rate

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In the course of nitriding process of nanocrystalline iron promoted with aluminum and calcium oxides, nitrides such as Fe_4N and $Fe_{3-2}N$ were fabricated. The process rate was studied making use of a flow differential tubular reactor with thermogravimetric measurement of mass changes. Nanocrystalline iron was reduced under hydrogen atmosphere at 500 ºC and 800 ºC. Average crystallite sizes determined by the XRD method after reduction performed at 500 ºC as well as at 800 ºC and after passivation were 18 and 42 nm, respectively. The nitriding process rate as well as catalytic ammonia decomposition rate were limited by the ammonia dissociative adsorption rate on the surface of iron and were dependent on the ratio of the crystallite surface area to crystallite volume. Obtained results were explained based on the adsorption range model.

Key words: *nanocrystalline iron; nitriding process; ammonia decomposition; thermogravimetry; XRD*

1. Introduction

Ammonia and nanocrystalline iron react in two parallel reactions. Apart from nanocrystalline iron nitriding, catalytic ammonia decomposition occurs. Grabke [1, 2] assumed that the rate limiting step during the initial stage of iron nitriding is chemical reaction on the interface between solid and gaseous phases. Chemical reaction resulting in obtaining atomic nitrogen, interstitially dissolved in iron lattice is considered a sequence of the following reactions:

$$NH_{3\,(gas)} \rightarrow NH_{3\,(ads)} \tag{1}$$

$$NH_{3\,(ads)} \rightarrow NH_{2\,(ads)} + H_{(ads)} \tag{2}$$

$$NH_{2\,(ads)} \rightarrow NH_{(ads)} + H_{(ads)} \tag{3}$$

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$$NH_{(ads)} \to N_{(ads)} + H_{(ads)} \tag{4}$$

$$N_{(ads)} \to N_{(\alpha\text{-Fe})} \tag{5}$$

In the case of nanomaterials, diffusion in solid state can be regarded as negligible on the account of relatively short distances of mass transport. Thus, the diffusion through the product layer can be neglected [1]. When the equilibrium state between solid and gaseous phases is reached, only catalytic ammonia decomposition reaction occurs:

$$NH_3 \to NH_{3\,(ads)} \to NH_{n\,(ads)} \begin{array}{l} \nearrow \; N_{(ads)} \to N_{2\,(ads)} \to N_2 \\ \searrow \; H_{(ads)} \to H_{2\,(ads)} \to H_2 \end{array} \tag{6}$$

Thus the content of nitrogen in the nitrides is dependent on temperature and ammonia concentration in the reacting gas mixture [3, 4]. At temperatures higher than 400 °C, the catalytic reaction of ammonia decomposition on the nanocrystalline iron and created nitrides was observed [3, 4].

When the process is limited by the surface reaction of ammonia decomposition to atomic nitrogen, the phase transition of iron to γ'-Fe_4N phase occurs according to the adsorption range model [6]. It was assumed that mass transport between nanocrystallites was negligible. Thus the nanocrystallites react forming the product in a sequence of their sizes, viz. from the smallest to the largest crystallites.

2. Experimental

The kinetics of nitriding of nanocrystalline iron with ammonia was investigated making use of a set-up equipped with a flow tubular differential reactor enabling one to conduct thermogravimetric measurements (Fig. 1). Changes of the gas phase composition in the reaction volume of the reactor were analysed. Samples of the gas phase were collected from two sampling points placed over and under a platinum basket carrying solid sample. Hydrogen concentration in the reacting gas mixture was determined directly. Applied gases, i.e. hydrogen, ammonia and nitrogen were let to the reactor from a gas cylinder through reduction valves. Flow rates of gas reactants were determined by means of mass flow controllers. Mass and temperature of analysed solid samples as well as data concerning gas concentrations in the gas mixture were recorded digitally. In a platinum basket hanging on a balance arm, ca. 1 g of an analysed substance was placed in the form of a single layer of grains. The resolution of the measurements of mass changes was 0.1 mg.

In order to enhance the specific surface area of iron, aluminum and calcium oxides were used. Analysed nanocrystalline iron was obtained by fusion of magnetite with structured promoters of nanocrystalline iron. The obtained alloy was crushed and fraction of grains of the size in the range of 1.0–1.2 mm was separated. Prereduction process of the material so obtained was performed at 500 ºC and at pure hydrogen load (99.999 %) under atmospheric pressure. When the prereduction process was done, nanocrystalline iron was passivated at low temperature (< 100 ºC) and at low oxygen pressure.

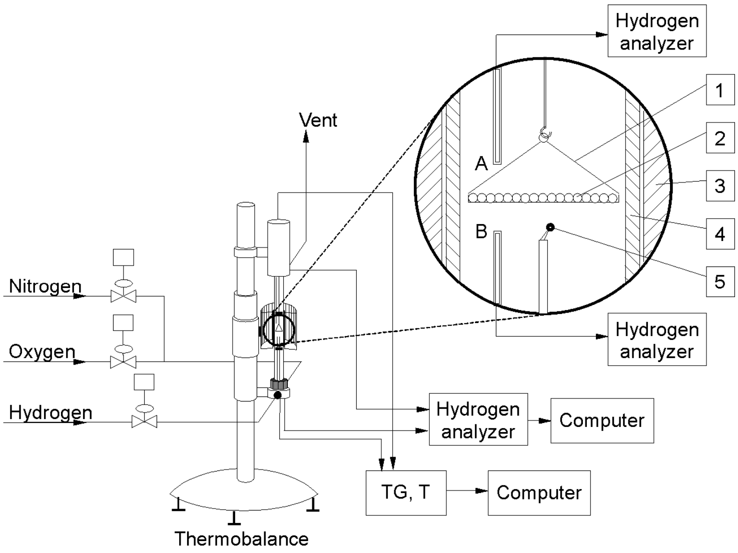

Fig. 1. Experimental setup: 1 – sample holder, 2 – single layer of grains, 3 – reactor furnace, 4 – reactor wall, 5 – thermocouple

The content of aluminum and calcium oxides stabilising the structure of enhanced surface of nanocrystalline iron was 3.3 wt. % and 2.8 wt. %, respectively, in relation to the prereduced form of the analysed material. The analysed material was divided into two parts. One part of material was reduced in a tubular furnace for 3 h under hydrogen atmosphere at 800 ºC in order to perform recrystallisation of nanocrystalline iron. Mean sizes of iron nanocrystallites before and after recrystallisation process were determined by means of the XRD method.

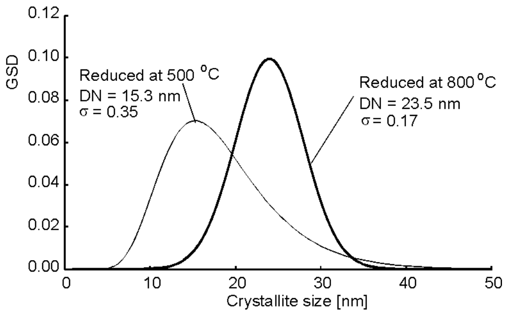

Fig. 2. Crystallite size distributions for nanocrystalline iron reduced at 500 ºC and 800 ºC

The recrystallisation resulted not only in increasing the mean size of iron crystallites, but also in changing their size distribution (Fig. 2). Analysed samples of nanocrystalline iron had the same chemical composition but different crystallite sizes resulting from the recrystallisation process performed at different temperatures. The specific surface area was determined by means of temperature-programmed desorption of nitrogen.

Reduction process of the obtained alloy, followed by nanocrystalline iron nitriding, was performed at 500 °C and at pure hydrogen (99.999 %) load of 500 $cm^3 \cdot min^{-1} \cdot g^{-1}$ under atmospheric pressure. The nitriding process was conducted under ammonia atmosphere (1 bar) at isothermal conditions, at temperatures ranging from 300 °C to 450 °C and ammonia load of 200–500 $cm^3 \cdot min^{-1} \cdot g^{-1}$ until analysed sample mass was stable, what could be seen on TG curves as a horizontal line.

3. Results and discussion

Steady values of the conversion degree of ammonia during its catalytic decomposition with applied grain diameters (Fig. 3) show that the process was conducted in the kinetic reaction region, and internal diffusion effects could be neglected. Thus the reaction rate does not depend on the gas flow rate as well, i.e., the reactor used in our experiments could be regarded as a differential one. In such a case, diffusion effects do not influence neither the catalytic ammonia decomposition nor the nitriding reaction.

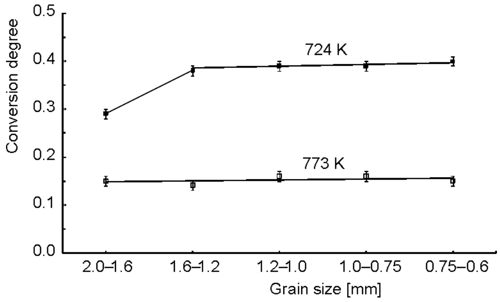

Fig. 3. Dependence of the ammonia conversion degree on the grain size

Results of gas phase composition measurements performed over and under the solid bed during nitriding prove that in the reactor, and hence also in the nanocrystalline iron bed, the mixing of components of reacting gas mixture occurs because of intensive convection. Platinum, of which the sample holder is made, did not affect the analysed process under process conditions. The mean size of crystallites of samples prereduced and then passivated was 18 nm, whilst the mean size of crystallites recrystallised and then passivated was 42 nm. The specific surface area of nanocrystalline iron reduced at 800 °C was 3.5 m^2/g, whereas that of nanocrystalline iron reduced at 500 °C was 11 m^2/g.

In the course of nanocrystalline iron nitriding, the mass of analysed samples increased. Exemplary TG curves obtained for nanocrystalline iron reduced at 500 °C and then nitrided under the ammonia load of 200 $cm^3 \cdot min^{-1} \cdot g^{-1}$ are presented in Fig. 4.

Stoichiometric compositions of γ'-Fe_4N and ε-$Fe_{3-2}N$ nitrides are marked in the figure. The composition of ε-$Fe_{3-2}N$ is unstable.

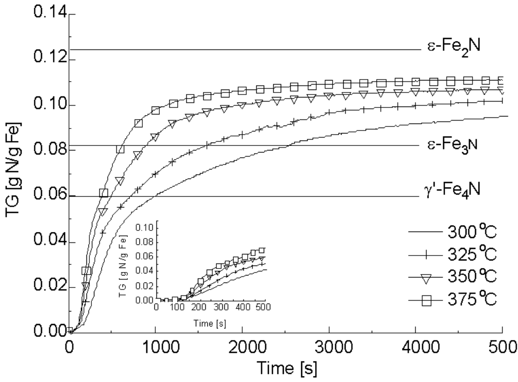

Fig. 4. TG curves for nitriding process of nanocrystalline iron reduced at 500 °C (ammonia load: 200 $cm^3 \cdot min^{-1} \cdot g^{-1}$)

Initially, a small increase of the sample mass (0.002–0.004 g N/g Fe during the first 100 s of the process) is observed. This is an effect of adsorption of ammonia upon nanocrystalline iron. Mass gain relevant to nitriding reaction did not occur, because concentration of ammonia mixed with hydrogen that left inside the reactor after reduction was too low. Then significant increase of the nitriding process rate is observed, because of formation of the γ'-Fe_4N phase.

In Figure 5, TG curves for nitriding process of nanocrystalline iron reduced at 800 °C (a) and 500 °C (b) under the ammonia load of 500 $cm^3 \cdot min^{-1} \cdot g^{-1}$ are presented.

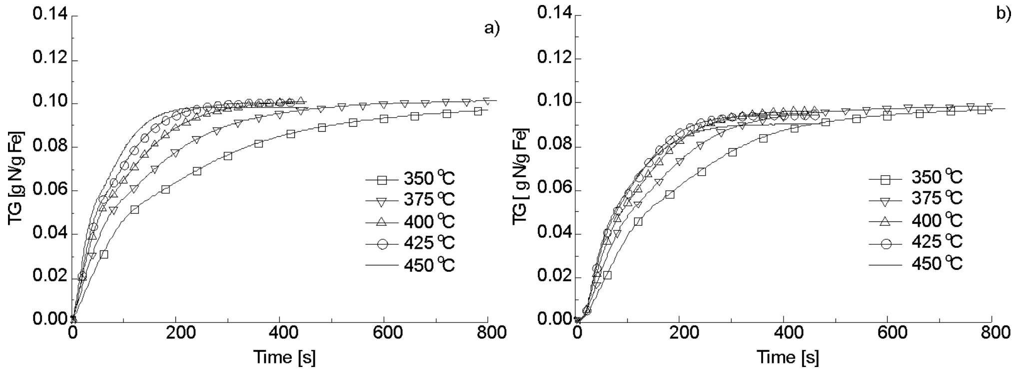

Fig. 5. TG curves for nitriding process of nanocrystalline iron reduced at: a) 800 °C, b) 500 °C (ammonia load 500 $cm^3 \cdot min^{-1} \cdot g^{-1}$)

The nitriding reaction rate increases with temperature. The conversion degree of the reaction reached the highest value and remained unchanged at each temperature through twice longer time than it is shown in Figs. 4 and 5, despite a prolonged exposure to the nitriding atmosphere. The process has many stages. Some inflection points on the TG curves in the vicinity of phase transitions can be seen. The sections of the curves observed between inflection points can be considered approximately linear.

Nanocrystalline iron nitriding process caused the changes of gas phase composition, recorded against a background of physical mixing process and gas exchange process taking place in the reactor. From the experimental data concerning hydrogen contents in the gas phase, hydrogen concentration in the reaction volume resulting from ammonia load feeding the reactor as well as from nitriding and catalytic ammonia decomposition has been determined. Taking into account the mass balance of a stirred tubular reactor, it was possible to determine the ammonia and nitrogen concentrations in the gas mixture. Changes of ammonia concentration for selected experiments concerning nitriding process of nanocrystalline iron reduced at 800 °C and 500 °C are presented in Figs 6a, b, respectively. In a stationary state, only catalytic ammonia decomposition occurred and ammonia concentrations were the lower the higher process temperature was maintained.

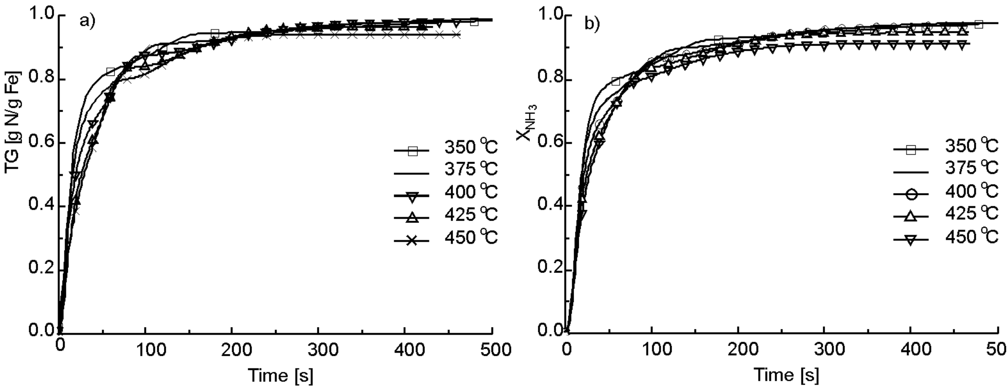

Fig. 6. Time dependence of ammonia concentration in the nitriding process (ammonia load 500 $cm^3 \cdot min^{-1} \cdot g^{-1}$) of nanocrystalline iron reduced at a) 800 °C, b) 500 °C

In Figure 7a, the TG curves for nitriding process (ammonia load 500 $cm^3 \cdot min^{-1} \cdot g^{-1}$) of nanocrystalline iron reduced at 800 °C and at 500 °C are shown. In Figure 7b, the comparison of obtained results concerning the gas phase composition is presented. Results for temperatures of 350 °C and 450 °C were selected. Based on TG curves from Fig. 7a, one can conclude that in the case of nitriding performed at relatively low temperature (350 °C), the same equilibrium composition of the solid is reached. In the stage of creation of γ'-Fe_4N nitride, the TG curves are parallel to each other, thus the crystallite size does not considerably influence the nitriding process. The rate of creation of ε-$Fe_{3-2}N$ phase at 350 °C is higher upon nanocrystalline iron reduced at 500 °C than that upon iron reduced at 800 °C.

The nitriding process performed at higher temperature (450 °C) proceeds faster, thus γ'-Fe_4N and ε-$Fe_{3-2}N$ phases occur below 350 °C. In the entire process of nitrides creation at higher temperatures, differences between nitriding reaction rates are observed for nanocrystalline iron reduced at 500 ºC and at 800 ºC because participation of decomposition of catalytic ammonia reaction in the entire nitriding process increases with temperature (Fig. 7b).

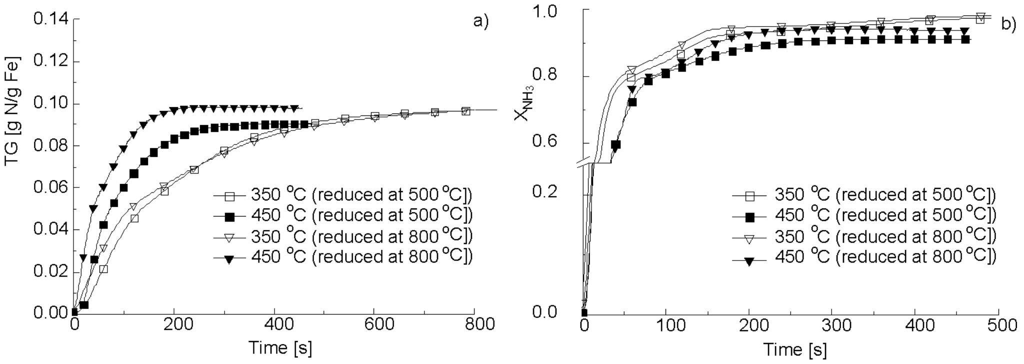

Fig. 7. TG curves (a) and time dependences of ammonia concentration (b) in the nitriding of nanocrystalline iron reduced at 800 ºC and 500 ºC under ammonia load 500 $cm^3 \cdot min^{-1} \cdot g^{-1}$

The activation energy of decomposition of catalytic ammonia is higher than the activation energy of reaction of nitriding [6], thus increasing the temperature results in increasing rate of the catalytic ammonia decomposition resulting in a decrease of ammonia concentration in the gas mixture and diminishing the nitriding reaction rate Catalytic decomposition of ammonia can proceed slower upon nanocrystalline iron reduced at 800 ºC than upon nanocrystalline iron reduced at 500 ºC (Fig. 7b) due to smaller specific surface area of the first material. Then, a higher nitriding potential occurs in the analysed system and nitriding reaction rate is higher.

4. Conclusions

The nitriding reaction rate depends mostly on the compositions of the solid and gas phases. Mean size of crystallites, and thus the specific surface area, influence the rate of reaction of catalytic ammonia decomposition being lower over nanocrystalline iron of the mean crystallite diameter of 42 nm than over nanocrystalline iron of the mean crystallite diameter of 18 nm. The higher temperature, the more important catalytic ammonia decomposition reaction is. This means that the value of mean crystallite size does not affect significantly the rate of nitriding process performed at lower temperatures. The obtained results were discussed on based on the adsorption range model.

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