Study of the kinetics of carburisation and nitriding of nanocrystalline iron

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Abstract. In the course of nitriding process of nanocrystalline iron that was promoted with aluminium and calcium oxides, nitrides such as Fe₄N and Feₓ₋₂N were created. In the process of carburisation, carbide Fe₃C was created. The nanocrystalline iron nitriding and carburisation process rate was studied making use of the flow differential tubular reactor with thermogravimetric measurement of mass changes. Nitriding and carburisation process rates were limited by dissociative adsorption rate on the surface of iron and were dependent on the crystallite surface to crystallite volume ratio. Assuming the adsorption is the rate limiting step, the numerical simulations were performed. Theoretical considerations were compared with the experimental results of the iron nitriding or carburisation reaction. Kinetics and thermodynamic parameters of nitriding and carburisation were determined.

1. Introduction

Chemical properties of nanomaterials differ from the properties of the relevant bulk substances [1-7]. The reaction rate of a solid state with a gas phase is limited by the rate of diffusion of substrates and/or products through a layer of the formed product. Considering nanocrystalline materials, the distances of diffusion in a solid state are considerably shorter in comparison with bulk materials and do not affect the rate of chemical reactions very much. The chemical reaction rate limiting step can be the rate of gas adsorption on a solid state.

Kinetics of chemical processes between a nanocrystalline solid state and a gas phase was studied making use of models which were elaborated for bulk materials [8, 9]. The shrinking core model [10] or the crackling core model [11] were used.

Classical kinetics calculations regarding carburisation were performed, but without taking into account specific features of nanomaterias [12-14]. Intensive studies of kinetics concerning formation of nanotubes and carbon deposit were conducted. Practically, one can separate the range where either carbide or carbon deposite is formed. It requires to use such process conditions so as carbon deposit was formed after Fe₃C phase has been obtained.

Nitriding process was studied over bulk iron [15], iron catalyst for the ammonia synthesis [16] and iron thin films [17]. Nitrogen content in the obtained nitrides depends on temperature and ammonia concentration in a gas phase [18-20]. The experimentally measured catalytic ammonia decomposition on nanocrystalline iron surface occurs at temperatures higher than 400 °C [18, 19].

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Modelling of the reaction of a single crystallite or a crystallite population with a gas phase, taking into account the assumption that the adsorption is the rate limiting step [21], was described earlier [19]. Crystallites are isolated and there is no mass transfer between them. The rate of adsorption for the \( i \)th single crystallite can be described by the following equation [22]:

\[
 r_i = p_i k_{ads} S_i (1 - \theta_i^n) - k_{des} S_i \theta_i^n \text{[mol/s]}
\]

where: \( r \) – the adsorption rate, \( p \) – the partial pressure of adsorbate, \( k_{ads} \) – the adsorption constant, \( k_{des} \) – the desorption constant, \( S \) – the surface area of the crystallite, \( n \) – the number of adsorption sites occupied by one adsorbed molecule, \( \theta \) – the surface coverage.

It can be assumed for typical metals, that one surface atom is one adsorption site, viz. \( n = 1 \). The value of the surface and the volume of crystallite can be calculated, if the shape and size of crystallite is assumed. Between the substance on the surface and the one dissolved in the bulk of crystallite the state of the thermodynamic equilibrium is held. This equilibrium is expressed by the McLean-Langmuir equation [23]:

\[
 \frac{\theta}{1 - \theta} = \frac{X_b}{1 - X_b} e^{-\frac{\Delta G(X_b)}{RT}}
\]

where: \( X_b \) – the bulk concentration, \( \Delta G \) – the Gibbs free energy of segregation of the reactant, \( R \) – the gas constant, \( T \) – temperature.

There is no concentration gradient of the reactant in the bulk, and when the critical bulk concentration, \( X_{bcri} \), is exceeded the phase transition of the whole crystallite occurs. The value of \( X_{bcri} \) depends on the surface area, \( S \), to volume, \( V \), ratio. Crystallites react in the order of decreasing \( S/V \) ratio, from higher to lower values. It implies that at the beginning the smallest crystallites react and then greater and greater.

Additionally it was assumed, that the Gibbs free energy of segregation is a linear function of the bulk concentration, \( X_b \), described by Fowler equation [24]:

\[
 \Delta G(X_b) = \Delta G_b + \alpha X_b
\]

where: \( \alpha \) – the factor considering change of the Gibbs free energy of segregation with a change in bulk concentration.

In the systems of chemical reactions without phase transitions the \( \Delta G(X_b) \) function is continuous in the whole range of concentrations, \( X_b \). In the case considering the phase transitions it is assumed, that the maximal bulk concentration before the phase transition is the critical concentration, \( X_{bcri} \). When the critical concentration, \( X_{bcri} \), is exceeded, the phase transition occurs, what causes the Gibbs free energy of segregation to change sharply. It means, that the \( \Delta G \) function is not continuous at points of \( X_{bcri} \).

The real materials usually do not consist of crystallites of the same size. Thus, for modeling, it was assumed, that the set of isolated crystallites has a certain grain size distribution (GSD) for example of Gaussian type:

\[
 \text{GSD}(d, \sigma) = \frac{1}{\sigma \sqrt{2 \pi}} \exp \left( -\frac{(d - d_0)^2}{2 \sigma^2} \right)
\]

In the present paper the analysis of carburisation and nitriding catalytic reaction rates in the range of \( \text{Fe}_3\text{C} \) and \( \text{Fe}_4\text{N} \) formation is presented. Experimental thermogravimetric results (TG) are compared with the theoretical ones, obtained by means of modelling.

2. Experimental

The kinetics of carburisation and nitriding processes of nanocrystalline iron with, respectively, methane and ammonia was investigated making use of analytical installation equipped with flow tubular differential reactor that enabled one to conduct thermogravimetric measurements (Fig. 1). In a platinum basket hanging on balance arm ca. 1 g of analysed substances was placed in a form of a single layer of grains. The resolution of mass changes measurement was 0.1 mg. Gas phase composition changes in reaction volume of reactor were analysed. The samples of gas phase were collected from two sampling points. One of them was placed over, and the other under platinum
basket. Hydrogen concentration in the reacting gas mixture was determined directly. Mass and temperature of the analysed solid sample as well as hydrogen concentrations in the gas mixture were recorded digitally. Applied gases, i.e. hydrogen, ammonia, methane and nitrogen were let to reactor from gas cylinder through reduction valves. The flow rate of gas reactants was determined by means of electronic mass flow controllers.

The subject of investigations was the nanocrystalline iron. In order to enhance the specific surface area of iron, aluminium and calcium oxides were used. Analysed samples were obtained by a fusion of magnetite with structured promoters of nanocrystalline iron. Obtained alloy was crushed and a fraction of grains of the size in the range 1.0-1.2 mm was separated. A prereduction process of such obtained material was performed at temperature 500 °C at pure hydrogen (99.999 %) under atmospheric pressure. After the prereduction process, nanocrystalline iron was passivated at low temperature (< 100 °C) and at low oxygen pressure. The content of aluminium 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 analysed material. The mean size of iron nanocrystallites was determined by means of the X-Ray Diffraction method (XRD) to be 18 nm.

![Figure 1. Experimental equipment: 1 – sample holder, 2 – single layer of grains, 3 – reactor furnace, 4 – reactor wall, 5 – thermocouple.](image)

Reduction process of obtained alloy, followed by nanocrystalline iron nitriding process, was performed at temperature 500 °C and at pure hydrogen (99.999 %) load 150 cm³ min.⁻¹ g⁻¹ mat, under atmospheric pressure. Reduction process, followed by carburisation process, was performed at temperature 580 °C at pure hydrogen (99.999 %) load 150 cm³ min.⁻¹ g⁻¹ mat, under atmospheric pressure.

Nitriding process was conducted under ammonia atmosphere (atmospheric pressure), isothermally at 400 °C, until the analysed sample mass was stable. Ammonia load was 200 cm³ min.⁻¹ g⁻¹ mat.

Carburisation process was performed isothermally at 580 °C under atmospheric pressure. Methane-hydrogen mixture of composition, respectively, 300 and 130 cm³/min was let to the reactor.

3. Results and discussion

Mass changes of samples were observed as thermogravimetric TG curves (Fig. 2). In Figure 2 also gas phase compositions corresponding with nitriding and carburisation are presented.

At the beginning of both processes, the adsorption of ammonia or methane and then dissolution of nitrogen or carbon in α-iron occurred. Kinetics of adsorption in the initial stage of reaction on the pure surface is difficult to interpret because of the high rate of this process and small mass gains (ca. 3 mg/g Fe). Nitrogen or carbon dissolution in α-iron is shown in Figure 4 (I. stage) as horizontal parts of theoretical lines TG curves. At the end of this stage there is an inflection resulting from a sharp increase of reaction rate after phase transition is done. Thus, saturation process of α-iron(N) with
nitrogen or \( \alpha \)-iron(C) with carbon after phase transition up to Fe\(_4\)N or Fe\(_3\)C phase was analysed and interpreted.

The analysed nanocrystalline iron nitriding process has many stages. There can be seen an inflection point on obtained TG curves in the vicinity of phase transition. Considering the nitriding process of nanocrystalline iron, the gas phase composition changes as a result of gas mixing and catalytic ammonia decomposition reaction resulting in formation of hydrogen and nitrogen (Fig. 2a). On the basis of TG data and hydrogen concentration in gas phase, taking into account mass balance of reactor with ideal mixing, ammonia and nitrogen concentrations in gas phase were determined. Practically the whole nitriding reaction runs at variable gas phase composition (the first 800 s of nitriding process). At the end stage of nitriding, the sample mass did not change, despite prolonged exposure to the nitriding atmosphere. In this stationary state only catalytic ammonia decomposition reaction took place.

Carburisation began after the stabilisation of chemical composition of gas phase was reached and thus the reaction of creating of carbide Fe\(_3\)C took place at the constant concentration of methane in the gas phase. After iron carbide Fe\(_3\)C was created, carbon deposition took place, what can be observed as the continuous sample mass gain. Stabilisation of sample mass did not occur.

Considering the stage of saturating \( \alpha \)-iron with nitrogen to obtain \( \alpha \)-iron(N), assuming that gas adsorption is irreversible and there is no catalytic decomposition of substrate on solid surface, one can transform equation (1) to the form valid for a set of crystallites [18]:

\[
r = k \cdot p_{NH_3} f(X_{s,cri} - X_b) \quad (5)
\]

where: \( r \) – nitriding reaction rate; \( k \) – nitriding reaction rate constant; \( p_{NH_3} \) – partial pressure of ammonia in gas phase.

After the critical concentration, \( X_{s,cri} \), is exceeded, the saturation of iron with nitrogen up to Fe\(_4\)N phase takes place and the rate of reaction can be described as follows:

\[
r = k \cdot (p_{NH_3} - p_{NH_3}^0) f(1 - \alpha) \quad (6)
\]

where: \( p_{NH_3}^0 \) – minimum partial pressure of ammonia in gas phase, required to begin the nitriding reaction after phase transition of \( \alpha \)-iron up to \( \gamma' \)-Fe\(_4\)N phase is formed; \( \alpha \) – conversion degree.

Analogical equation can be used to describe carburisation reaction.

Equations (5) and (6) describe the set of crystallites defined by means of the grain size distribution (GSD). Crystallites react according to their sizes, so the conversion degree depends on the grain size distribution, thus \( f(1 - \alpha) = f(GSD) \). On the basis of thermogravimetric data, the rates, \( r \), of nitriding and carburisation reactions were determined. Values of \( k \cdot f(\alpha) \) are presented as a function of, respectively, nitrogen and carbon mass gain (Fig. 3). Pressure \( p_{NH_3}^0 = 60000 \) Pa was determined on the basis of data from a plot in Figure 2a. Value of \( p_{CH_4}^0 = 50000 \) Pa was taken from [25].

The shape of curves, corresponding with the formation of Fe\(_4\)N or Fe\(_3\)C, is the same in both cases. The intensity of peaks is connected with the adsorption rate. Adsorption rate constant does not change at given temperature. If so, the shape of peaks results from the type of the crystallites size distribution. The shift of curves representing nitriding and carburisation is caused by different mean size of...
crystallite sets. Gaussian distribution with such parameters as mean size of crystallites = 25 nm (nitriding), 50 nm (carburisation) and standard deviation = 5 (nitriding), 4 (carburisation) was assumed. Theoretical function of type GSD/t = f(α) was compared with experimental relationships k f(α) = f(α) (Fig. 3). It allows to assess the values of reaction rates.

Fig. 3. Comparison of experimental relationship k f(α) vs. mass gain with modelling results of GSD/t for nitriding (400 °C) and carburisation (580 °C) reactions.

Modelling of nitriding and carburisation was performed making use of equations (1)-(3) by means of the model described earlier [19, 21]. It was assumed, that the crystallites size distribution was of the Gaussian type. Table 1 contains values of parameters, which were used during the modelling of the chemical reaction between the solid state and gas phase and values of some parameters taken from literature.

**Table 1. Values of parameters used during modelling and respective literature data.**

| Parameter                                                                 | Calculations | Literature |
|---------------------------------------------------------------------------|--------------|------------|
| Temperature [°C]                                                          | Nitriding    | Carburisation | Nitriding | Carburisation |
| ±80                                                                        | 400          | 580        | -         | -            |
| Critical bulk concentration of nitrogen or carbon dissolved in α-iron, [mole/mole] | 0.0012       | 0.0015     | 0.0012 [26] | 0.0005 [27] |
| ∆G₀ [kJ/mole] (α-iron phase)                                             | -85          | -107       | -110 [28] | -83 [28]     |
| α coefficient in Eq. (3) (α-iron phase)                                  | 0 [28]       | -          | -         | -            |
| ∆G₀ [kJ/mole] (Fe₄N or Fe₃C phase)                                        | -32          | -35        | -         | -            |
| α coefficient in Eq. (3) (Fe₄N or Fe₃C phase)                            | -40          | -30        | -         | -            |
| Adsorption rate constant [(mole g)/(m² s Pa)]                             | 2.1 · 10⁻⁹   | 1.5 · 10⁻⁹ | -         | -            |
| Mean size of crystallites, nm                                            | 25           | 50         | -         | -            |
| Standard deviation                                                        | 5            | 4          | -         | -            |

In Figure 4 the comparison of experimental TG results with modelling ones for analysed processes is presented.
Fig. 4. Comparison of experimental and modelling TG results for a) nitriding, b) carburisation of nanocrystalline iron.

Conclusions

For bulk materials, usually, the reaction rate decreases with decreasing concentration of substrates. In case of nanomaterials, initially the reaction rate increases, because crystallites of greater and greater sizes react. After the moment crystallites of the mean size react, the reaction rate decreases. Crystallites react according to their sizes, so the conversion degree depends on the grain size distribution. Carburisation and nitriding of nanocrystalline iron can be described by means of the model, which assumes the reaction rate is limited by the rate of adsorption. From comparison of theoretical data with experimental ones, kinetics and thermodynamic parameters of nitriding and carburisation reactions were determined. The numerically obtained TG curves were successfully fitted to the real ones. The best fitting of theoretical TG curves with experimental data was obtained considering nitriding for: $\Delta G_0$ (a-iron phase) = -85 kJ/mole, $\Delta G_0$ (Fe$_2$N phase) = -32 kJ/mole, critical bulk concentration of nitrogen dissolved in a-iron = 0.0012 mole/mole, adsorption rate constant 2.1 $\times$ 10$^{-9}$ (mole g)/(m$^2$ s Pa). In the case of carburisation: $\Delta G_0$ (a-iron phase) = -107 kJ/mole, $\Delta G_0$ (Fe$_3$C phase) = -35 kJ/mole, critical bulk concentration of carbon dissolved in a-iron = 0.0015 mole/mole, adsorption rate constant 1.5 $\times$ 10$^{-9}$ (mole g)/(m$^2$ s Pa).

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