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Solid−Gas Reaction with Adsorption as the Rate Limiting Step

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The model of nucleation where adsorption of reactant is a rate-limiting step has been considered. Assuming the adsorption range model, a numerical simulation has been made. The dependency of bulk concentration and surface coverage versus time and thermogravimetric curves are presented. The crystallite size is suggested to be the key factor of the nucleation rate. Theoretical considerations have been compared with the experimental results of the iron nitriding reaction.

1. Introduction

The processes between gaseous and solid phases can be divided with respect to the rate-limiting step (rls) of the process as a diffusion driven process (*diffusion range*) or a surface reaction driven process (*adsorption range*). There are several models assuming diffusion as the rls:

The shrinking core model assumes that during reaction the layer of product is produced on the core of the solid reactant. The gaseous reactant has to diffuse throughout the layer to react with a core.[2]

The crackling core model is similar to the shrinking core model, but during reaction the solid reactant cracks to smaller grains, and after this stage the process runs according to the shrinking core model.[3]

In the epitaxial growth model, product grows as a layer or islands on the surface of the substrate depending on the magnitude of misfits between the crystal lattice of the substrate and the product.[4] The rls of this model can be either diffusion or surface reaction.

In Figure 1 the typical TG curve (thermogravimetric curve) observed during carburization[5] and nitridation[1,5] of nanocrystalline materials is shown. Three characteristic stages of the curve (denoted as 1, 2, 3) can be discerned. The rate of the process in the stage 1 is connected with adsorption of the reactant. Therefore, at the beginning of the first stage the rate of the process is high and successively decreases. In stage 2 the dominant process is the dissolution of reactant in the bulk of solid material. Stage 3 begins when the nucleus of the new phase appears as a result of oversaturation. The new phase is a solid product of the reaction between gaseous reactant and solid. With the beginning of nucleation, the process rate increases to a certain value and then a constant reaction rate is observed. In general, after formation of the new phase, other phases can be formed. After saturation during the 2′ stage, the successive phase can be formed in stage 3′ analogously to stage 3. In other words, in Figure 1 region A corresponds to the existence of pure reactant A. In region B reactant A undergoes phase transition to product B. Analogously, in region C phase B is transformed to phase C. None of the models mentioned above explains the experimental curves of this kind. It leads to the conclusion that curves of this kind are not a result of a diffusion range process and, therefore, have to result from an adsorption range process. There is a vast amount of literature concerning reactions limited by diffusion, but there is a lack of literature describing reactions limited by adsorption. In the recent book of gas−solid reactions there is no description of TG curves in the adsorption range.[6] Only in the work of Rhodin et al.[7] was it mentioned that the nucleation of the new phase facilitates an adsorption in the neighborhood of the nucleus of the new phase. However, this paper gives only a phenomenological description of the process.

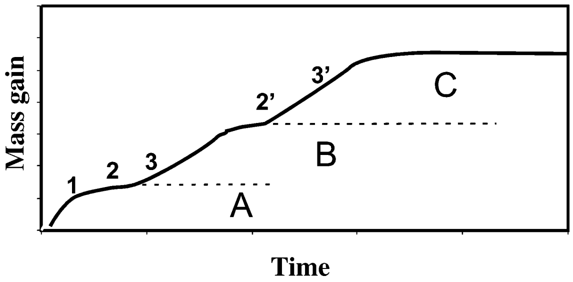

Figure 1. TG dependence of the process in adsorption range. Phase A in the course of reaction with gaseous reactant undergoes phase transition to product B and subsequently product B undergoes phase transition to product C.

The main objective of this paper is description of the process of solid-phase reaction with gas, occurring in the adsorption range**.** It will be shown by the example of the nanocrystalline iron nitriding reaction that numerical modeling for such processes is possible and gives good agreement between theoretical and experimental results.

Investigation of the processes governed by adsorption is of importance because it reveals phenomena that occur in diffusion governed processes, but their influence is indirect and thus much more difficult to investigate.

The adsorption range may occur when crystallites of the reactant are very small and/or partial pressure of the gaseous reactant is low and/or the sticking coefficient of the gaseous reactant is low. Such conditions cause the diffusion in the grains of the material to be faster than adsorption and hence adsorption is the rls.

Assumptions of the adsorption range model[1] make possible a numerical calculation of many dependencies and give insight into many factors that are impossible or very difficult to measure directly. Among them worthy of mention are surface and bulk

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concentration, mass gain, the influence of crystallite size, and crystallite size distribution on the rate of the nucleation.

2. Principles of the Adsorption Range Model

The adsorption range model is a model developed for reactions between gaseous and solid phases where the product is of solid state and the rls is adsorption or the reaction on the surface. If this condition is fulfilled, the rate of the whole process is the adsorption rate. After adsorption, the reactant dissolves in the bulk of the crystallite. It is assumed that when the critical bulk concentration of the reactant is exceeded, the phase transition of the whole crystallite occurs. If the reaction runs in the adsorption range and then between reactants on the surface and dissolved in the bulk, the thermodynamic equilibrium holds. Therefore, the other stages of the process, both in the solid and in the gaseous phases, are in a state of thermodynamic equilibrium too. As a consequence, there is no concentration gradient of the reactant in the bulk. Therefore, the assumption that the whole crystallite undergoes phase transition in the same time is justified.

The rate of adsorption for a single crystallite can be expressed by the Langmuir isotherm equation[8]

$$r = pk_{\mathrm{ads}}S(1-\theta)^n - k_{\mathrm{des}}S\theta^n \text{ [mol/s]} \tag{1}$$

where r is the rate of adsorption, p is the partial pressure of the adsorbate, k_{ads} is the adsorption constant, k_{des} is the desorption constant, S is the surface area of the crystallite, n is the number of adsorption sites occupied by one adsorbed molecule, and θ is the surface coverage.

As observed earlier, the state of the thermodynamic equilibrium is held between the substance on the surface and the one dissolved in the bulk of the crystallite. This is shown by the McLean−Langmuir equation[9]

$$\frac{\theta}{1-\theta} = \frac{X_{\mathrm{b}}}{1-X_{\mathrm{b}}} \mathrm{e}^{-\Delta G/RT} \tag{2}$$

where X_{b} is the bulk concentration, ΔG is the Gibbs free energy of segregation of the reactant, R is the gas constant, and T is the temperature.

In a more general approach, the Gibbs free energy of segregation is dependent on the bulk concentration (X_{b}). The approach given by Fowler and Guggenheim[10] assumes that ΔG is a linear function

$$\Delta G(X_{\mathrm{b}}) = \Delta G_0 + \alpha X_{\mathrm{b}} \tag{3}$$

where α is a factor considering change of the Gibbs free energy of segregation with a change in bulk concentration.

This approach is limited to cases when no phase transition takes place. In the case considering the phase transition, the point of maximal concentration in the bulk phase before the phase transition is a point of critical concentration (X_{bcr}). If this critical concentration is exceeded, then phase transition occurs. The phase transition at the point of the critical concentration (X_{bcr}) causes the ΔG function to change sharply; i.e., the ΔG function is not continuous at this point. The Fowler and Guggenheim approach was derived on the assumption that the interaction occurs between the molecules adsorbed on the surface. In this paper it is assumed that such an interaction does not exist and, therefore, the Langmuir isotherm equation (eq 1) can be applied. On the other hand it is assumed that the Gibbs free energy of segregation depends on the bulk concentration and it is a linear function of X_{b}. These different assumptions lead to the same equation (eq 3).

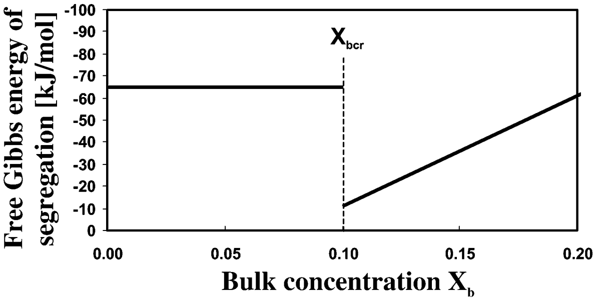

Figure 2. Dependence of the Gibbs free energy of segregation on concentration X_{b} for the single crystallite. Discontinuity corresponds to the phase transition of the crystallite.

3. Simple Example of Modeling

Let us apply the above reasoning for a single crystallite made of metal atoms. For typical metal elements it can be assumed that each surface atom is one adsorption site. Therefore, the total number of adsorption sites on average can be 15×10^{18} m^{-2}. The surface coverage θ is a ratio of occupied adsorption sites to all available adsorption sites. If the shape and size of the crystallite is assumed, then the value of the surface and the volume of crystallite can be calculated. Having the volume and density of the material, one can calculate the number of atoms per crystallite. Assuming the atomic and/or molar masses of the reactants, one can calculate the mass change in time. The mass change in time corresponds to experimental TG dependence. The calculations can be performed according to eqs 1−3, and to the defined or assumed parameters of those equations. Additionally, dependencies such as surface coverage and bulk concentration as a function of time can be modeled.

For the sake of simplicity in the remaining part of the paper it is assumed that the rate of desorption is negligible in comparison to the adsorption rate, but it is also possible to make calculations with introduction of the desorption process. If the desorption process is not negligible, then such an assumption will cause smaller values of the adsorption constant and sticking coefficient. It is also assumed that the molecule/atom of the reactant can occupy one adsorption site; therefore, n is equal to 1 (eq 1).

The modeling is performed as follows: At the beginning the coverage θ is set as zero. The amount of adsorbed reactant in the finite period of time for the crystallite of a given surface from eq 1 can be calculated. In next step the coverage θ and the molar fraction X_{b} for a crystallite of surface S and volume V from eqs 2 and 3 can be calculated. In this way the adsorbate is distributed in the surface and in the bulk. The whole procedure is then iterated.

Let us consider two cases of modeling of single isolated spherical crystallites of diameters 10 and 20 nm. An arbitrarily assumed ΔG function for those crystallites is presented in Figure 2. This function has one point of discontinuity (X_{bcr}) corresponding to the phase transition. After the point of discontinuity (X_{bcr}), the ΔG function has to be of higher value to enable the phase transition to be possible due to thermodynamic reasons. According to eqs 1−3 and assumed ΔG function, the modeling was performed and results are presented in Figure 3. The dashed line denotes the value of the critical bulk concentration X_{bcr}. It can be seen that the bulk concentration X_{b} increases with time faster if the crystallite is smaller. Therefore, a smaller crystallite achieves a point of critical concentration X_{bcr} earlier. When X_{b}

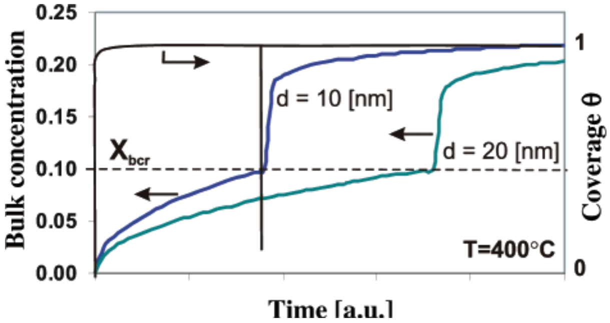

Figure 3. Bulk concentration dependence on time for the two single crystallites of different diameters. The black curve corresponds to the coverage dependence on time of the smaller crystallite.

reaches X_{bcr}, the process increases. A smaller crystallite has a higher surface-to-volume ratio and the crystallite of smaller size undergoes phase transition earlier than the bigger one. If the shapes of the crystallites are different, then the spherical surface-to-volume ratio is the crucial parameter. In Figure 3 the dependence of surface coverage θ on time for a crystallite of diameter 10 nm is also presented. It can be seen that the coverage increases quickly and achieves a value close to 1. However, the coverage is not significantly close to 1 only at the beginning of the process and in the moment of phase transition. In the point of phase transition the coverage sharply decreases because at this point the ΔG function is not continuous. After phase transition the value of coverage increases again to 1.

The real materials usually do not consist of crystallites of the same size but of crystallites of size distribution. Let us introduce this parameter. The reasoning made for one isolated crystallite can be made for the set of isolated crystallites. In the case of a set of isolated crystallites, the convenient way of expressing the process progress is dependence of mass gain on time (TG curve). To simulate the TG curve for a single crystallite, the time dependence of total mass dissolved in the bulk and present on the surface is required. The calculated TG curve for the set of crystallites is a sum of weighted calculated TG dependencies for single isolated crystallites of a given size. The set of isolated crystallites has a certain grain size distribution (GSD). It was assumed that this distribution can be of normal kind and, therefore, can be described by

$$\mathrm{GSD}(d,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(\bar{d} - d)^2}{2\sigma^2}\right) \qquad (4)$$

where GSD is the grain size distribution function, σ is the standard deviation, d is the size of the crystallite, and $\bar{d}$ is the average crystallite size.

In general, any kind of distribution can be taken, but in the case of normal distribution, it is easy to present clearly the influence of its parameters on the shape of the TG curves, because there can be materials of the same average crystallite size but different standard deviations and vice versa.

The simplest approach assumes the lack of transition; thus the ΔG function is constant. The calculated TG curves and dependence of coverage θ on time for such a case are presented in Figure 4. The full coverage is reached quickly. The coverage is virtually independent of ΔG. However, the maximal concentration of reactant in the bulk is dependent on ΔG. For large values of ΔG, the solubility in the bulk is negligible and the total mass gain is caused by reactant adsorbed on the surface. In the case of the TG line corresponding to $\Delta G = -80$ kJ/mol, the maximal total mass gain is about the calculated mass of the monolayer of adsorbed reactant denoted by ML on the ordinate axis.

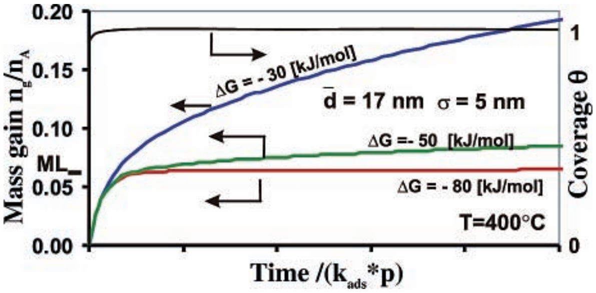

Figure 4. TG curves (no phase transition) for polycrystalline materials of different Gibbs free energies of segregation.

TABLE 1: Parameters of Function of the Gibbs Free Energy of Segregation

	$\Delta G = \Delta G_0 + \alpha X_b$ [kJ/mol]					
	(A) $X_b = 0-0.012$		(B) $X_b = 0.0012-0.20$		(C) $X_b > 0.2$	
no.	ΔG_0 [kJ/mol]	α	ΔG_0 [kJ/mol]	α	ΔG_0 [kJ/mol]	α
1	−55	0	−42	−400	71	−400
2	−60	0	−37	−400	66	−400
3	−65	0	−32	−400	61	−400
4	−60	0	−2	−200	13	−200
5	−60	0	−37	−400	66	−400
6	−60	0	−77	−600	120	−600
7	−90	0	−27	−57	120	−610

To consider the case when the phase transition occurs, the set of ΔG functions was assumed as discontinuous and characterized by parameters given in Table 1.Identical distributions of crystallites are assumed.

Each ΔG function consists of three regions: A, B and C. Each ΔG function has also two points of discontinuity corresponding to the critical bulk concentrations (X_{bcr}) and to the borders between regions A−B and B−C. The values of the factors of functions (nos. 1−6 Table 1) were taken arbitrarily, but the following considerations were taken into account: The order of magnitude for the ΔG_0 parameter in region A corresponds to the values of the Gibbs free energy of segregation of nitrogen and carbon from metals. The point of discontinuity corresponds to the phase transition; therefore, the Gibbs free energy of segregation has to change in this point to make the phase transition process thermodynamically favorable. After phase transition, the ΔG_0 parameter is of a higher value and the segregation process is less thermodynamically favorable. Therefore, the crystal is more stable. Finally, the variations in values of parameters were taken to check their influence on the shape of TG curves.

Regions A, B and C of the ΔG function correspond to the characteristic stages of *adsorption range* indicated in Figures 5 and 6. The limits (dashed horizontal lines) were calculated as a sum of mass of species adsorbed on the surface and dissolved in the bulk, which corresponds to the critical concentration (X_{bcr}). Stage A corresponds to the adsorption and dissolution without phase transition, as described above (Figure 4). The increase (inflection of the TG curve) of the rate of the process after stage A is related to the phase transition of the smallest crystallites. The second phase transition occurs analogously in stage C. In the large part of stage B, the TG line is straight. This fact denotes a constant reaction rate. To show the influence of the ΔG_0 parameter on the shape of TG curve, the three curves were calculated by varying ΔG_0 (Figure 5). The higher the ΔG_0 value,

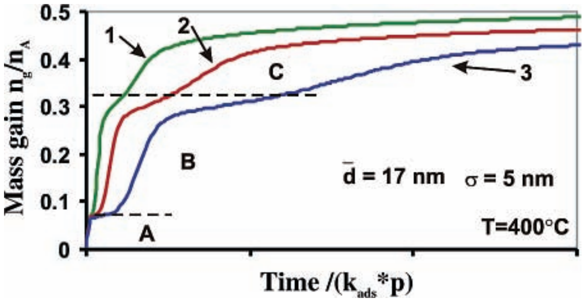

Figure 5. TG curves (two phase transition) for polycrystalline materials with different values of ΔG_0.

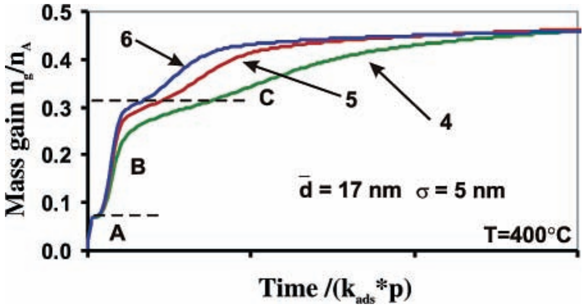

Figure 6. TG curve (two phase transition) for polycrystalline materials with different values of α.

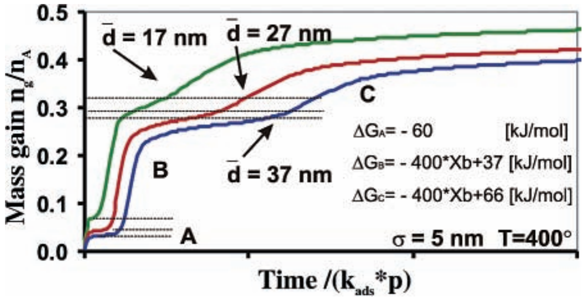

Figure 7. Influence of average crystallite size on the TG curve shape for polycrystalline material.

the earlier the nucleation process occurs and the higher the reaction rate corresponding to the linear region.

In Figure 6 three curves with various α parameters are presented. The corresponding ΔG functions are characterized by parameters given in Table 1. The reaction rate corresponding to the linear region and the onset of the phase transition of the smallest crystallites are not dependent on the value of α parameter. The higher the value of the α parameter, the earlier the TG curves become nonlinear.

Assuming a normal distribution of the crystallite's size, the influence of average crystallite size and standard deviation (σ) parameters were considered for a given ΔG (Table 1, position 5). In Figure 7 simulated TG curves for various average crystallite sizes are presented. The critical bulk concentrations (X_{bcr}) between stages A and B are identical because they are calculated for the same material for all curves. Therefore, the mass gain corresponding to the critical concentration in the bulk is different for each curve (dashed lines) due to different specific surface areas for materials of different average crystallite sizes. In regions B and C the first derivatives of each curve are approximately identical; therefore, the same reaction rate can be supposed. The smaller the crystallite's size, the earlier the onset of phase transition occurs. The smaller crystallites have a higher part of the total adsorbed mass remaining on the surface due to the larger specific surface area.

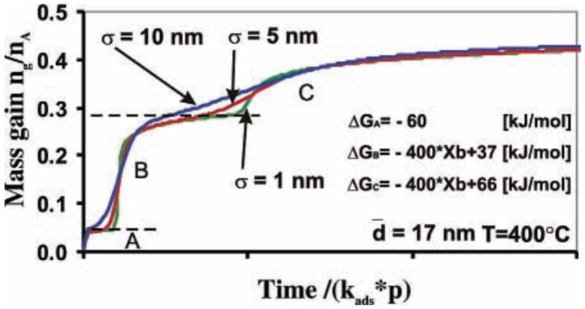

Figure 8. Influence of σ on the TG curve shape for polycrystalline material.

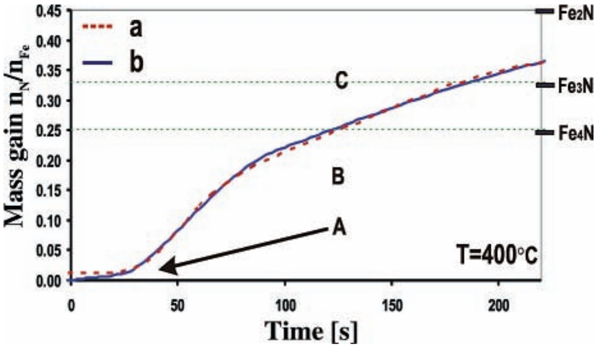

Figure 9. TG curve of α-Fe nitriding process: (a) theoretical; (b) experimental. In region A there is only α-Fe. Region B corresponds to the phase transition of α-Fe to the Fe_4N nitride. In region C nitride Fe_4N undergoes phase transition to the nitride Fe_3N.

The other parameter characterizing normal distribution is the standard deviation σ. The influence of σ on the shape of TG curve is presented in Figure 8. The specific surface area is independent of σ; therefore, the mass gain corresponding to the critical concentration in the bulk is the same for each curve (dashed lines). The smaller the σ parameter, the steeper the slope of the TG curve is.

4. Modeling of Real System

Understanding the influence of each parameter of eqs 1−4 on a TG curve, one can compare theoretical data with experimental ones. The TG curve of the nitriding process of nanocrystalline iron is presented in Figure 9 (curve b). The process was carried out at 400 °C under 1 bar of ammonia. The average iron crystallite size was 17 nm. The specific surface was 11 m^2/g according to the BET (Brunnauer−Emmet−Teller) method. It was previously[1] shown that the process meets the assumptions of the *adsorption range model*. The three characteristic stages can be distinguished on the curve. The mass gain in stage A is due to adsorption of ammonia on the iron surface and dissolution of atomic nitrogen in the bulk of the α-iron. The critical bulk concentration of nitrogen in iron is very low (400 °C, $X_{bcr} = 0.0012$[11]), and the total mass gain in stage A is caused by mass adsorbed on the surface. The gain of mass in stage A is lower in comparison with TG curves presented before (e.g., Figure 6) due to the lower specific surface of the sample. This gain of nitrogen corresponds to the monolayer of nitrogen atoms on the iron surface. It indicates that the process of ammonia adsorption on the whole surface of the sample occurs.

The inflection of the experimental TG curve indicates the end of stage A. After exceeding critical concentration X_{bcr}, the phase transition of iron to Fe_4N occurs and the rate of the process increases. Formation of Fe_4N corresponds to stage B. After formation of Fe_4N, the formation of Fe_3N begins. Formation of

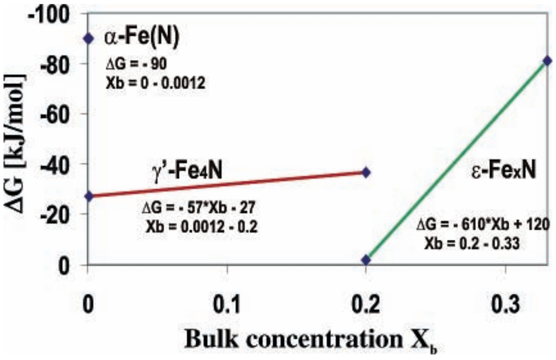

Figure 10. Dependence of the Gibbs free energy of nitrogen segregation on bulk concentration X_b determined as a result of the fitting process of the modeled curve to the experimental one.

the Fe_3N phase corresponds to stage C (linear part of TG curve). The remaining nonlinear part of the TG curve in stage C is the saturation of the Fe_3N phase till Fe_2N is formed.

The following initial factors were taken from literature to carry out modeling: The Gibbs free energy of segregation of nitrogen from iron is −110 kJ/mol.[12] For this value and for critical bulk concentration of nitrogen in α-iron (400 °C, $X_{bcr} = 0.0012^{11}$) the critical coverage was calculated ($\theta_{cr} = 0.999998$) according to eq 2. The Gibbs free energy of segregation of nitrogen from iron was set to −90 kJ/mol to obtain a better fit of the theoretical TG to the experimental one. The corresponding critical coverage is $\theta_{cr} = 0.999914$.

The parameters characteristic for investigated material were as follows.

The average size of iron crystallites was 17 nm according to Scherrer's method.[13] The spherical shape and Gaussian distribution of the crystallites were assumed. Upon those assumptions the standard deviation σ was derived according to the method[14] and amounts to 4 nm. Hence for spherical crystallites the calculated specific surface area is 44 m^2/g. The experimentally measured specific surface is 11 m^2/g according to the BET method. The apparent discrepancy of those measurements is the result of sticking of the crystallites and thus of blocking part of the surface to the adsorption process. The comparison of values denotes that only 25% of the whole surface of crystallites participate in adsorption process. Therefore, the factor 0.25 was used to limit the surface area.

The ΔG function and the adsorption constant k_{ads} were varied during the fitting process. The result of the fitting is presented as curve a in Figure 9. In Figure 10 the dependence of ΔG on bulk concentration obtained by fitting is presented. The values of parameters of the ΔG function are also presented in Table 1 (seventh line).

The obtained fitting process constant factor $pk_{ads}S$ was 0.0033 [mol/s]. Taking into account that the ammonia pressure p in the experiment was 1 bar and the measured specific surface S was 11 m^2/g, the adsorption constant k_{ads} was evaluated to be 0.0003 [mol g bar^{-1} m^{-2} s^{-1}]. The parameter $pk_{ads}S$ from the kinetic theory of gases can be predicted

$$pk_{ads}S = zs_0S = \frac{1}{N_a}\cdot\frac{p}{\sqrt{2\pi MkT}}s_0S \text{ [mol/s]} \qquad (5)$$

where N_a is Avogadro's number, k is the Boltzmann constant, s_0 is the sticking coefficient for $\theta = 0$, S is the active surface, M is the molar/atomic mass of particle hitting on the surface, and z is the number of collisions per second.

The calculated collision number z of ammonia molecules with an iron surface in the nitriding process is 130 [mol/(s m^2)]. The specific surface area S of nanocrystalline iron is 11 [m^2/g]. So the total number of collision amounts 1430 [mol/s]. Having those values and the number of collision of ammonia molecules evaluated in the fitting process the sticking coefficient was calculated and is $s_0 = 0.000002$ at 400 °C (eq 5). The corresponding literature values are $s_0 = 0.16$ on the Fe(100) surface at −153 °C[15] and 0.03 for Fe(111) surface contaminated with oxygen at 27 °C.[16]

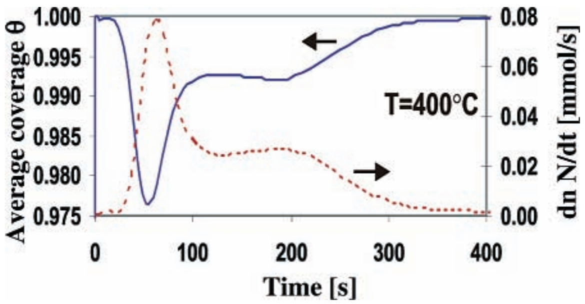

Figure 11. Change of average coverage θ and nitriding reaction rate with time. The coverage was determined from modeling and the nitriding reaction rate is an experimental result.

In Figure 11 the calculated change of average coverage in time corresponding to the a curve from Figure 9 is presented. The process occurs with coverage near 1 except for the initial stage. The shape of the negative first derivative of TG curve a in Figure 9 is identical to that in Figure 11. Therefore, the rate of the nitriding reaction should be proportional to the average coverage. The rate of an adsorption process is proportional to the number of unoccupied adsorption sites (eq 1). As a consequence, dependence of average coverage on time determines the whole shape of the TG curve of the nitriding process. Hence the assumption raised at the beginning of this paper that adsorption is the rls of the whole process is proved.

It would be tempting to perform further experiments with respect to particle diameter and standard deviation of the particle distribution to check the predictions of the simulations. But there are experimental difficulties, e.g., the synthesis of materials of equal average crystallite sizes but different standard deviations or of equal standard deviations but different average crystallite sizes. Moreover the state of the surface that influences the surface reaction rate is dependent on the method of preparation of the material. Therefore, the experimental investigation of the influence on the kinetics of only one of the parameters, such as the adsorption rate constant, the standard deviation or average crystallite size, with fixed other parameters is impossible to perform with the present level of knowledge.

5. Conclusions

Based on assumptions of *adsorption range model*, it is possible to numerically model the iron nitriding reaction process limited by adsorption.

The numerically obtained TG curve was successfully fitted to the real one.

Successful fitting allows estimation of the Gibbs free energy function of segregation and adsorption constant.

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