Rev.Adv.Mater.Sci. 8 (2004) 53-58

STUDIES OF THE KINETICS OF METHANE DECOMPOSITION ON THE NANOCRYSTALLINE IRON TO CARBON DEPOSITION FORMATION

U. Narkiewicz, W. Arabczyk, W. Konicki and I. Kucharewicz

Technical University of Szczecin, Institut of Chemical and Environment Engineering, Pulaskiego 10, 70-322 Szczecin, Poland

Received: November 20, 2004

Abstract. The kinetics of the formation of carbon deposit formed on Fe_3C in the result of the carburisation of nanocrystalline iron with methane has been studied. The experiments were carried out in the thermobalance (considered as an differential reactor), in the temperature range of 500-600 °C under atmospheric pressure. The kinetics of the carbon deposit formation was studied in the kinetic area of the reaction, where the rate of the carburisation process is limited by the dissociative adsorption of methane on the iron carbide surface. The rate of the process is proportional to the methane partial pressure. The determined apparent activation energy for the process of carbon deposit formation is about 150 kJ/mol, the same as the apparent activation energy of the iron carbide formation.

1. INTRODUCTION

The carburisation of transition metals and their alloys with hydrocarbons leads to the formation of carbon fibres or nanotubes [1-5]. The composition of the reaction products depends on the process conditions (temperature, composition of the carburisation mixture). In case of the carburisation with methane, according to the phase diagrame of the system Fe-CH_4-H_2 [6], depending on temperature and on methane partial pressure, the obtained products are: iron carbide and carbon deposit.

Despite numerous papers concerning interaction of hydrocarbons with iron [7-11], there are no information about the kinetics of the carbon deposit formation in the reaction of methane with iron below the temperature of 600 °C. There is only one paper of Pilipenko and Veselov [12] concerning the decomposition of methane on iron in this temperature range, but the character of this paper is descriptive only, there are no conclusions about the kinetics or the mechanism of carburisation of iron with methane. The authors state that in the temperature range 450-500 °C only iron carbide was formed, when above 500 °C the carbon deposit was also found. These results are controversial and against the phase diagram CH_4/H_2/Fe [6], according to which in the result of pure methane on iron above 300 °C both Fe_3C and carbon deposit are formed.

The kinetics of the methane decomposition on coarse-grained iron and its alloys has been studied extensively by the group of Grabke [13,14]. The studies concerned only the range of the solubility of carbon in iron. The authors concluded that in the initial step of carburisation the reaction was limited by the dissociative adsorption of methane on the surface. On the basis of the proposed kinetic equation for this process, the apparent activation energy of the carburisation of iron with methane was determined as E_a=213,7 kJ/mol for α-Fe and E_a =230,5 kJ/mol for γ-Fe.

The present paper is a continuation of former studies on carburisation of nanocrystalline iron to the formation of nanocrystalline Fe_3C in the gas-solid system at low temperatures [15].

Corresponding author: U. Narkiewicz, e-mail: un@ps.pl

© 2004 Advanced Study Center Co. Ltd.

The motivation of the present study is a lack of kinetics studies of the carbon deposit formation below 600 °C, as well as the interest in nanocrystalline Fe_3C as an intermediate phase influencing the formation of carbon deposit.

2. EXPERIMENTAL

The studies of the kinetics of the carbon deposit formation in the process of decomposition of methane on the nanocrystalline iron were carried out in a home-made electronic thermobalance – differential reactor. Nanocrystalline iron was obtained by the fusion of magnetite with a small amount of aluminum and calcium oxides. The obtained alloy was next reduced with hydrogen [16]. In order to avoid a dramatic oxidation in contact with air after the reactor opening, the iron samples after the reduction were passivated with nitrogen containing traces of oxygen.

The specific surface area of the samples determined using thermal desorption of nitrogen (ASAP Micromeritics) was 22 m^2/g.

The chemical composition of the samples of nanocrystalline iron was determined using the inductively coupled plasma atomic emission spectroscopy (AES-ICP) (Yvon-Jobin). After the reduction the samples contained in spite of iron 2.92 wt.% of Al_2O_3 and 2.97 wt.% of CaO.

The phase composition of the samples was determined using XRD analysis with CoK_α radiation (X'Pert, Philips). The mean crystallite size of iron calculated on the basis of the Scherrer formula was 17 nm.

The grains of the sample (fraction of 1.2-1.5 mm) were placed in a single layer in the platinum basket of thermobalance. Taking into account a low conversion degree of methane (below 2 %) during the experiments, the thermobalance can be considered as a differential reactor [17].

The iron samples were covered with a thin passivation layer and to remove this layer, each sample before the carburisation experiments was first reduced with hydrogen (0.2 $dm^3 \cdot g^{-1} \cdot min^{-1}$). The reduction process was carried out polythermally in the temperature raising from 20 °C to the carburisation temperature with a rate of 15 $°C \cdot min^{-1}$. After the reduction (the reduction was completed when a stable mass of the sample was reached) the carburisation process was carried out isothermally at a temperature in the range of 500-600 °C. The process was carried out under atmospheric pressure. As carburising gas pure methane was used or a mixture CH_4/N_2 or CH_4/H_2, at the constant velocity of 1.2 $dm^3 \cdot g^{-1} \cdot min^{-1}$. After the carburisation process each sample was cooled to the room temperature under nitrogen flow.

3. RESULTS AND DISCUSSION

An example of the results of thermogravimetric studies for the carburisation under pure methane at 580 °C is shown in Fig.1. The TG line presents a relative increase of the mass of carbon in time, referred to the mass of iron in the sample. A dashed line corresponds to the carbon/iron ratio corresponding to the stoichiometric composition of Fe_3C (0.072 gC/gFe). A DTG line, plotted on the basis of the TG one, shows the changes of the reaction rate in time.

The phase composition of the samples after the carburisation was determined using XRD method. Fig. 2 presents a dependence of the conversion degree of Fe to Fe_3C on the content of carbon in the sample, referred to the mass of iron. The conversion degree of iron to iron carbide was determined on the basis of the surface area of the XRD peaks of Fe_3C (121/210) and α-Fe (200). The dashed line corresponds to the stoichiometric composition of Fe_3C. The continous line was traced on the basis of the experimental points obtained from the carburisation process carried out under methane at 580 °C.

According to Fig. 2, at the beginning of the carburisation only Fe_3C is formed, however with increasing carbon content, the carbon deposit is also formed, before a complete transformation of iron to iron carbide takes place below the stoichiometric composition of Fe_3C. The complete transformation of nanocrystalline iron into iron carbide occurs for carbon content equal to 0.22 gC/gFe (17.72 wt.% C).

According to the results presented in Figs. 1 and 2 it can be concluded that after the initial induction stage, in which an increase of the reaction rate of the Fe_3C formation is observed, the reaction rate becomes constant (the horizontal segment of the DTG line in Fig. 1). In this area the rate of the decomposition of CH_4 to Fe_3C is controlled by dissociative adsorption of methane on the surface of the sample. The studies on the kinetics of the formation of Fe_3C from nanocrystallne iron were described in our former papers [18,19]. In the next step of the process a sudden increase of the reaction rate is observed, connected with a nucleation of a new phase – carbon deposit. During further carburisation a decrease of the reaction rate is observed, connected with a blocking of part of active sites for methane dissociative adsorption by carbon deposit.

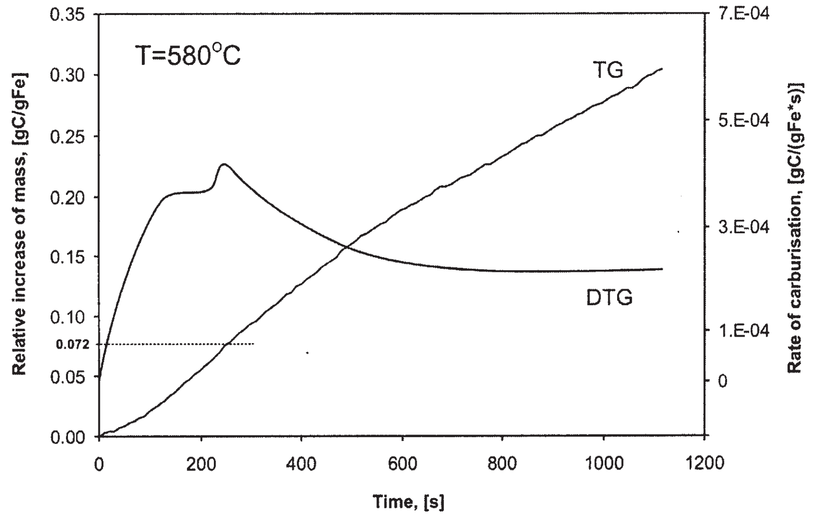

Fig. 1. TG and DTG curves for carburisation under methane at 580 °C.

The further increase of the carbon content in the sample leads to the complete transformation of iron into Fe_3C. The rate of the decomposition of methane on the iron carbide is constant, does not depend on the degree of carburisation of the sample.

The studies of the kinetics of the process of carbon deposit formation were carried out in the area where the reaction rate is constant (the last one, horizontal segment of the DTG line). The effect of the methane pressure on the rate of the carbon deposit formation was determined through the measurements of the carburisation rate under a CH_4/N_2 mixture at 580 °C. Fig. 3 presents a dependence on the rate of the formation of carbon deposit on the methane partial pressure in the reaction mixture. The quantity of hydrogen in the gas mixture created from the decomposition of CH_4 is very small and can be neglected, then the rate of the carbon deposit formation can be described using a following equation, similar as that for the reaction of Fe_3C formation [18]:

$$r = kp_{CH_4}, \qquad (1)$$

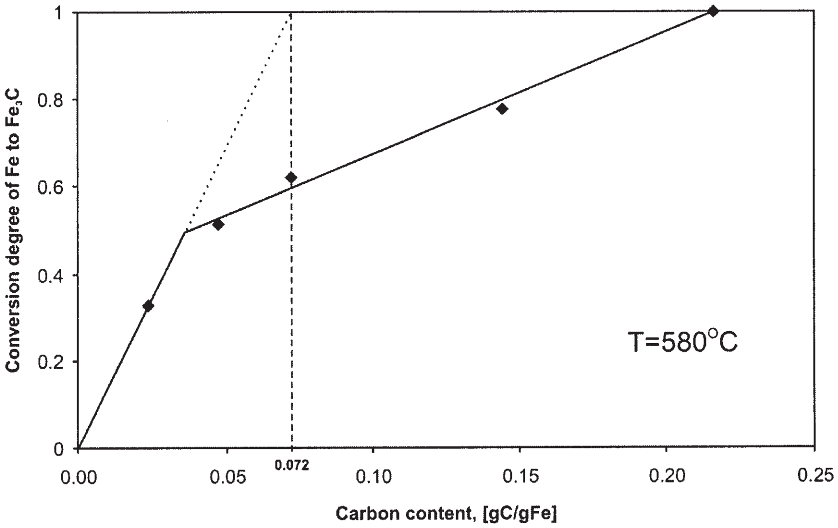

Fig. 2. Dependence of the carbon content in the sample after the carburisation on the conversion degree of iron to iron carbide.

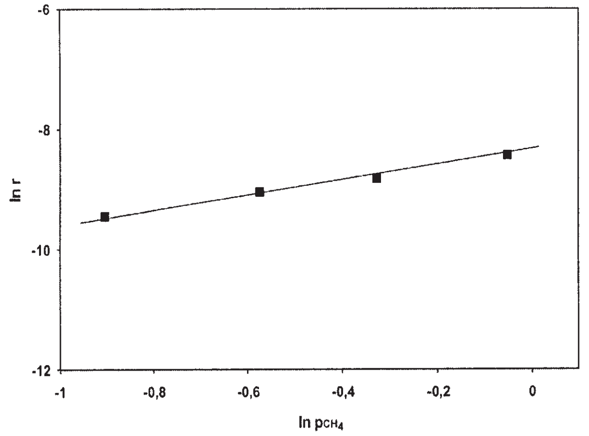

Fig. 3. Dependence of the rate of carbon deposit formation on the methane pressure in the reaction gas mixture.

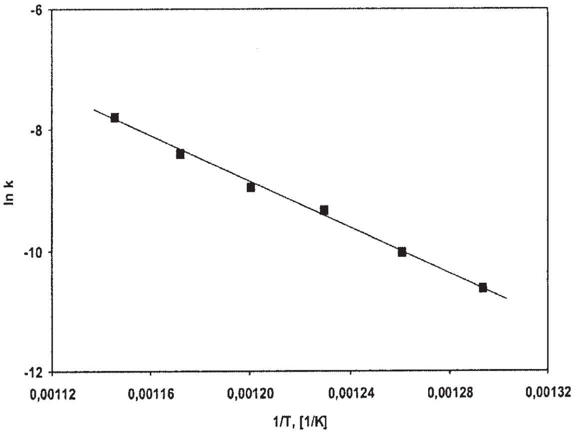

Fig. 4. Dependence of the reaction constant rate on the reciprocal temperature.

where: r is the rate of the formation of carbon deposit, k is the reaction constant rate, and p_{CH_4} is the methane partial pressure in the reaction mixture.

The dependence of the rate of carbon deposit formation on temperature was studied in the temperature range of 500-600 °C under pure methane. In Fig. 4 the linear dependence of the reaction constant rate k (determined from Eq. 1) on the reverse temperature is presented. On the basis of this Arrhenius dependence the apparent activation energy of the carbon deposit formation was determined as 150 kJ/mol. This apparent activation energy is the same as that determined before for the process of Fe_3C formation, which was 158 kJ/mol [18]. If the apparent activation energy is alsmost the same, it can be suggested that in the kinetics area of the reaction the mechanism of the process of the decomposition of methane on the nanocrystalline iron to carbon deposit is the same as the mechanism of the methane decomposition to Fe_3C on nanocrystalline iron.

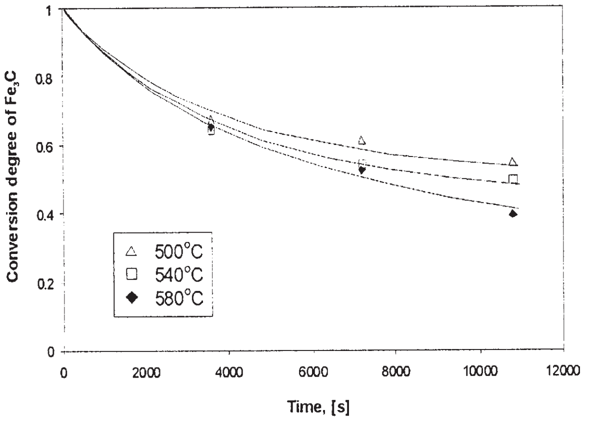

Fig. 5. Dependence of the conversion degree of iron carbide to the carbon deposit on the reaction time.

According to a *carbide cycle* mechanism [20], in the result of the reaction of methane with iron the iron carbide Fe_3C is formed, which, as a metastable phase, undergoes a thermal decomposition to carbon and iron. Carbon formed in this reaction segregates onto the surface and iron reacts again with hydrocarbon, forming Fe_3C. Such a *carbide cycle* mechanism assumes the formation of free iron. According to the results of the experiments presented here, the free α-iron is not formed.

In order to investigate the mechanism of the carbon deposit formation, studies of the thermal decomposition of nanocrystalline Fe_3C were carried out in the temperature range of 500-580 °C. At first the samples of nanocrystalline iron were carburised with a mixture methane-hydrogen ($CH_4/H_2=2$) at 580 °C to reach the ratio carbon/iron equal to 0.072 gC/gFe (corresponding to the stoichiometric composition of Fe_3C). The presence of iron carbide was confirmed using XRD. Under these conditions only iron carbide is formed as the solid product of the carburisation process, without carbon deposit. Other iron carbides were not detected. After the carburisation each sample was heated under nitrogen flow at different temperatures.

The conversion degree of Fe_3C to carbon deposit after the heating was determined on the basis of the surface area measurements of the Fe_3C (121/210) and α-Fe (200) peaks. An example of the dependence of the conversion degree of Fe_3C on

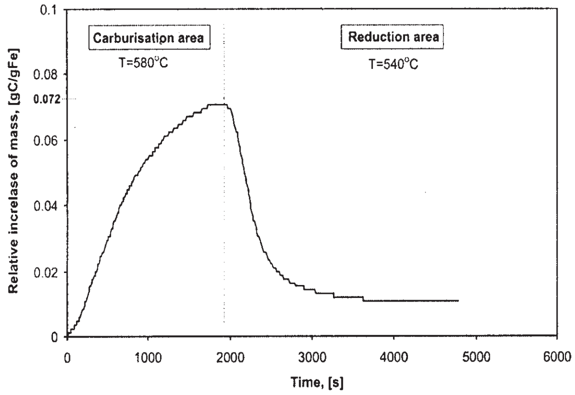

Fig. 6. Carburisation at 580 °C followed by reduction under hydrogen at 540 °C.

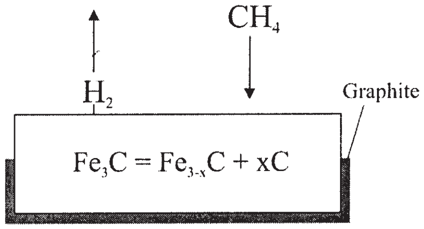

Fig. 7. Scheme of the methane decomposition to the carbon deposit formation.

time of heating for the temperatures of 500, 540, and 580 °C is shown in Fig. 5. During the heating a decomposition of nanocrystalline iron carbide was observed and the degree of decomposition slightly increases with temperature.

The reduction of nanocrystalline Fe_3C with hydrogen in the temperature range of 500-580 °C was also investigated. An example of the process of carburisation under the methane-hydrogen ($CH_4/H_2=2$) mixture at 580 °C to obtain Fe_3C and then the reduction under pure hydrogen at 540 °C is shown in Fig. 6. The reduction is not complete after the process the initial mass of iron sample is not reached. According to the XRD analysis results, in the samples after the reduction only the phase of α-iron was determined, the peaks corresponding to Fe_3C were not observed. It can be then concluded that the samples after the reduction are composed of iron and some carbon deposit, resistant against reduction. The decrease of mass observed during the reduction under hydrogen corresponds to two processes: reduction of iron carbide to iron and methane, and thermal decomposition of iron carbide with a formation of hardly reductible carbon deposit.

On the basis of the experiments described here above it can be concluded that under the applied conditions iron carbide does not decompose to pure α-iron, as it was suggested according to the *carbide cycle* mechanism. When carbon deposit starts to form on the surface of iron carbide, two reaction areas can be distinguished on the surface. A part of the surface is occupied by carbon deposit, and the other part of the surface is depleted with carbon and the dissociative adsorption of methane can still occur on this free part of the surface (see Fig. 7).

In the reaction area where iron is completely transformed into Fe_3C and where the process of the carbon deposit formation occurs with a constant rate (a last, horizontal segment of the DTG line in Fig.1), There is a steady state in the system Fe_3C/C. In this state the rate of the dissociative adsorption of CH_4 is equal to the rate of carbon deposition from Fe_3C. The limiting step of the carburisation process in this area is the dissociative adsorption of methane on the sample surface. A steady state is reached for some determined degree of surface coverage with carbon.

4. CONCLUSIONS

The dissociative adsorption of methane on the nanocrystalline iron in the temperature range of 500-600 °C results in the formation of the nanocrystalline Fe_3C, followed by the formation of carbon deposit, created as a result of thermal decomposition of iron carbide on the interface Fe_3C – C.

The mechanism of the process of decomposition of methane on nanocrystalline iron carbide to the formation of carbon deposit is the same as the mechanism of the process of decomposition of methane to Fe_3C on nanocrystalline iron.

REFERENCES

[1] M. A. Ermakova, D. Yu. Ermakov, G. G. Kuvshinov and L. M. Plyasova // *J. Catal.* **187** (1999) 77.

[2] Z. Li, J. Chen, X. Zhang, Y. Li and K. K. Fung // *Carbon* **40** (2002) 409.

[3] K. Hernadi, A. Fonseca, J. B. Nagy, A. Siska and I. Kiricsi // *Appl. Catal. A* **199** (2000) 245.

[4] N. M. Rodriguez, M. S. Kim, F. Fortin, I. Mochida and R. T. K. Baker // *Appl. Catal. A* **148** (1997) 265.

[5] M. S. Kim, N. M. Rodriguez and R. T. G. Baker // *J. Catal.* **131** (1991) 60.

[6] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, London, 1953).

[7] L. B. Avdeeva, T. V. Reshetenko, Z. R. Ismagilov and V. A. Likholobov // *Appl. Catal. A* **228** (2002) 53.

[8] K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts and A. A. Lucas // *Carbon* **34** (1996)1249.

[9] M. A. Ermakova, D. Yu. Ermakov, A. L. Chuvilin and G. G. Kuvshinov // *J. Catal.* **201** (2001) 183.

[10] A. Sacco, Jr., P. Thacker, T. N. Chang and A. T. S. Chiang // *J. Catal.* **85** (1984) 224.

[11] A. Peigney, Ch. Laurent and A. Rousset // *J. Mater. Chem.* **9** (1999) 1167.

[12] P. S. Pilipenko and V. V. Veselov // *Poroshk. Metall.* **6** (1975) 9, In Russian.

[13] H. J. Grabke and E. M. Martin // *Arch. Eisenhuttenwes.* **44** (1972) 837.

[14] H. J. Grabke // *Arch. Eisenhuttenwes.* **46** (1975) 75.

[15] W. Arabczyk, U. Narkiewicz, W. Konicki, R. Wrobel, B. Bay and R. Wozniak // *Przem. Chem.* **82** (2003) 207.

[16] W. Arabczyk, J. Ziebro, K. Kalucki, R. Swierkowski and M. Jakrzewska // *Chemik* **1** (1996) 22.

[17] C. Perego and S. Peratello // *Catal. Today* **52** (1999) 133.

[18] W. Arabczyk, U. Narkiewicz, W. Konicki and B. Grzmil // *Polish Journal of Chemical Technology* **4** (2002) 1.

[19] W. Arabczyk, W. Konicki and U. Narkiewicz // *Solid State Phenomena-Trans. Tech.* **94** (2003) 181.

[20] R. A. Buyanov, V. V. Chesnokov, A. D. Afanasev and V. S. Babenko // *Kinet. Katal.* **4** (1997) 1021.