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STUDIES OF THE INITIAL STAGE OF THE CARBURISATION OF NANOCRYSTALLINE IRON WITH METHANE

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Abstract. The aim of the study was to investigate the initial stage of the carburisation of nanocrystalline iron with methane at low temperature (500 °C). The nanocrystalline iron samples contained small amounts of additives (Al_2O_3, K_2O, CaO) applied as structural modifiers. The carburisation process was controlled by thermobalance – a differential reactor. After carburisation, the samples were characterised using XRD method and Mössbauer spectroscopy. The mass increase at the beginning of carburisation did not correspond to the determined iron carbide content. A formation of a thin carbon layer on the iron crystallite surface, accompanied by diffusion of iron atoms to this layer, was proposed for the initial stage of the process.

1. INTRODUCTION

The carburisation of coarse-grained iron and its alloys is well known as a process carried out to improve the hardness of steel. The carburisation of nanocrystalline iron has been also studied and described, mainly in view to obtain such products as carbon fibres or nanotubes [1-7]. There are many papers published by Grabke's group concerning the kinetics of iron carburisation [8-10], but they deal with coarse-grained iron and with the low range of carbon concentration (below the solubility limit of carbon in iron). In our previous papers the kinetics of the carburisation of nanocrystalline iron at low temperatures (500-600 °C) has been studied [11-13]. The kinetics equation for the rate of iron carbide formation has been proposed. The apparent activation energy for this process has been determined as 150 kJ/mol. The modification of the iron surface with other elements, as potassium or sulphur, has been found to influence the reaction rate, but not the reaction mechanism [11, 13].

The presented work deals with the initial stage of carburisation when the maximal solubility of carbon in iron is reached but the conversion of iron into carbide is not yet completed.

2. EXPERIMENTAL

The nanocrystalline iron used in experiments was prepared by fusion of magnetite with small amounts of promoter oxides (Al_2O_3, K_2O, CaO) in electric furnace. The obtained alloy was crushed, sieved and reduced with hydrogen. After reduction the nanocrystalline iron was obtained and the promoters remained in the oxidised state. The role of promoter oxides was to stabilise the nanocrystalline iron structure at elevated temperatures. In order to avoid a dramatic oxidation, after reduction the sample was passivated by means of nitrogen containing traces of water vapour.

The chemical composition of the reduced and passivated samples was determined using AES-ICP method (Yvon-Jobin equipment). Besides the iron

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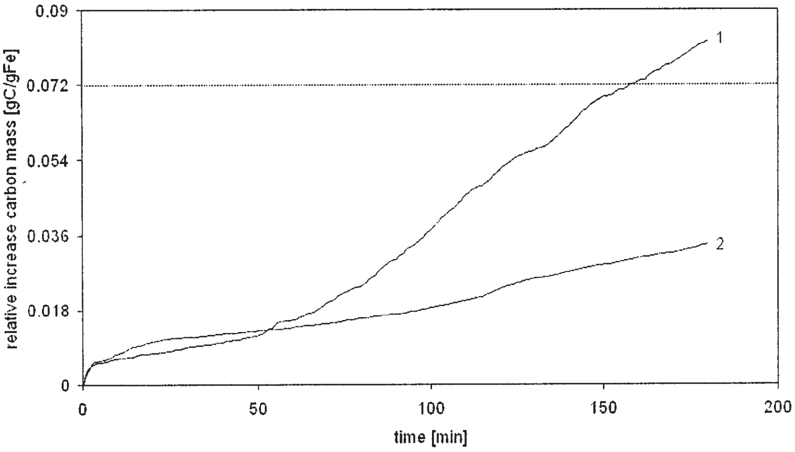

Fig. 1. TG curves of carburisation process of nanocrystalline iron at 500 °C. TG 1- represents sample of iron without addition of potassium, TG 2 – represents sample of iron with addition of potassium.

the samples contained 2.92 % of Al_2O_3, 2.97 % of CaO, 0.65 % of K_2O, 0.31 % of SiO_2 and 1 % of other metal oxides (Mg, Ni, Cr, Ti, V).

The carburisation process was investigated in a spring thermobalance equipped with cathetometer, that gives the accuracy of $1 \cdot 10^{-4}$ g.

The mean crystallite size of iron crystallites determined by X-ray diffraction method (Philips X'Pert equipment) and calculated using the Scherrer equation, was equal to 17 nm. The phase composition of the samples after carburisation was determined using X-ray diffraction (λ = 1,79026 Å) and Mössbauer spectroscopy (conventional spectrometer with a source ^{57}Co/Rh).

3. RESULTS AND DISCUSSION

The interaction of methane with iron results in the formation of iron carbide Fe_3C and carbon deposit. The composition of reaction products depends on temperature and gas composition, according to the equilibrium diagram of the system Fe-CH_4-H_2 [14-15].

According to our earlier studies [11-13] on the reaction of nanocrystalline iron with methane in the temperature range of 500-600 °C, at the beginning of carburisation the iron carbide is formed at first followed by carbon deposition. It was found that the carburisation rate depended on temperature, gas composition and on the iron surface modification (for example with potassium or sulphur). The relative mass increase of two samples with different set of promoters, as a function of carburisation time at 500 °C is shown in Fig. 1. Line 1 in this figure corresponds to the iron sample promoted with Al_2O_3 and CaO, line 2 – to the sample containing additionally K_2O. The horizontal dashed line represents the stoichiometric content of carbon in Fe_3C. The rate of carburisation is shown in Fig. 2 as DTG curves corresponding to the TG lines from Fig. 1. The reaction rate is maximal at the beginning of the process and decreases rapidly, reaching a minimum at about $1 \cdot 10^{-4}$ gC/gFe·min. Taking into account the specific surface area of the iron sample containing 3 promoter oxides (Al_2O_3, CaO and K_2O) measured using BET method (~12 m^2/g) and the number of iron atoms on the polycrystalline iron surface equals to $15 \cdot 10^{18}$ atoms per m^2 [16], one can determine the number of carbon atoms for one iron atom on the surface as being equal to 10. Depending on the package density, the number of carbon atoms adsorbed on one iron atom can vary from 1 [17] to 3 for the most dense graphite structure. The maximum of the mass increase before the cementite formation corresponds to the surface coverage by three carbon monolayers. However, the carbon atoms can be also located in subsurface region [18]. After the minimum some increase of the reaction rate is observed, which can be due to the diffusion of iron atoms into carbon layer on the surface.

The shape of TG and DTG lines for both iron samples (with potassium and without potassium) is similar. However, the rate of carburisation is higher for the sample without potassium. In this sample the minimum of reaction rate is reached at lower content of carbon in the sample. The steady state is established for sample with potassium at lower carbon content that equals about 0.02 gC/gFe, while for sample without potassium it is equal to about 0.04 gC/gFe.

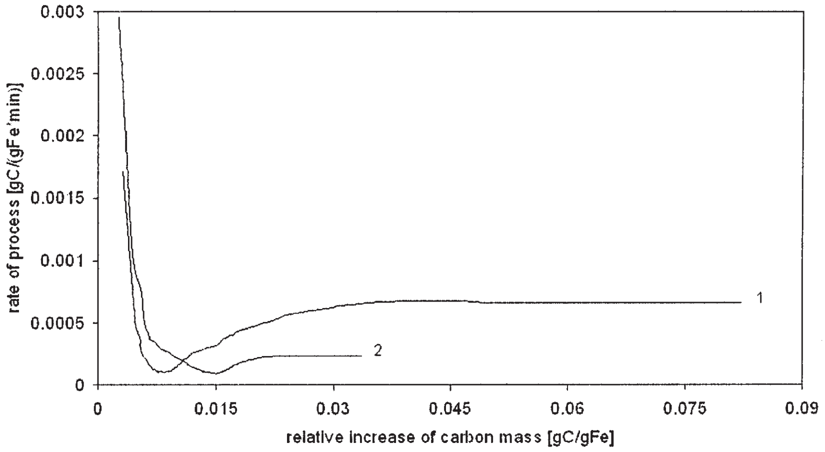

Fig. 2. DTG curves corresponding to TG curves in Fig. 1.

The phase composition of both samples after carburisation was studied using XRD method. The obtained diffraction patterns are shown in Fig. 3. The diffraction pattern No1 corresponds to the triply promoted (Al_2O_3, CaO and K_2O) iron sample before carburisation. In this pattern only peaks characteristic for α-Fe can be identified. The diffraction pattern No 2 corresponds to the same sample after carburisation and pattern No 3 – to the doubly promoted sample (without potassium) also after carburisation. The additional peaks in these patterns correspond to cementite. The intensity of cementite peaks is greater in case of sample without potassium. This sample was carburised up to carbon content equal to 0.08 gC/gFe i.e. higher than a stoichiometric concentration of carbon in Fe_3C. In spite of this fact, the peaks corresponding to α-Fe can be still observed in the diffraction spectrum. If unconverted iron is still present in the sample, some part of carbon has to stay in form of carbon deposit.

On the basis of the obtained results it can be stated that in the first stage of the carburisation of nanocrystalline iron with methane only cementite (no other iron carbides) is formed and further – carbon deposit. According to TG and DTG lines, the carburisation rate is lower for the triply promoted

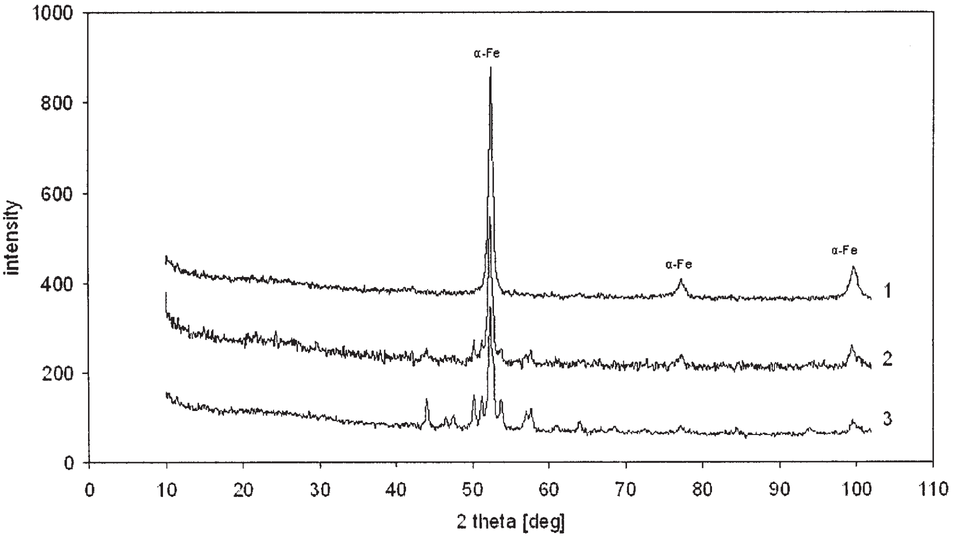

Fig. 3. The diffraction patterns:No 1 – triply promoted (Al_2O_3, CaO and K_2O) iron sample before carburisation, No 2 – the same sample after carburisation, No 3 – doubly promoted sample (without potassium).

Table 1. Results of XRD and Mössbauer spectroscopy measurement for the samples of nanocrystalline iron with addition of potassium after carburisation under methane at 500 °C.

sample	relative increase of carbon mass	XRD conversion Fe to Fe_3C	MÖSSBAUER SPECTROSCOPY											
			alpha iron (sextet)				graphite phase (doublet)				Fe_3C (sextet)			
	[gC/gFe]	—	IS [mm/s]	2Γ [mm/s]	H [kOe]	A [%]	IS [mm/s]	2Γ [mm/s]	H [kOe]	A [%]	IS [mm/s]	2Γ [mm/s]	H [kOe]	A [%]
1	0,007	0,00	0,00	0,27	331,3	97,2	0,38	0,96	0,71	2,8	—	—	—	—
2	0,012	0,00	0,00	0,27	331,6	95,0	0,29	0,72	0,80	3,3	0,21	0,22	209,4	1,7
3	0,020	0,00	0,00	0,28	331,2	96,7	0,29	1,17	0,76	2,2	0,15	0,24	207,0	1,2
4	0,024	0,39	0,00	0,28	332,3	65,5	0,30	0,98	0,60	4,4	0,19	0,34	211,1	30,3
5	0,029	0,42	0,00	0,27	332,6	57,8	0,28	0,93	0,65	5,5	0,19	0,32	211,4	36,8
6	0,034	0,46	0,00	0,27	331,3	57,6	0,29	0,81	0,64	6,0	0,19	0,32	210,4	36,4
7	0,054	0,61	0,00	0,27	333,2	36,8	0,21	0,92	0,36	4,1	0,19	0,35	211,6	59,1

The meaning of the parameters in the table are as follows:
IS – isomer shift
QS - quadrupole splitting
H – Zeeman's splitting
A – area of the subspectrum corresponding to the amount of the species
Γ – line width

iron sample and every subtle changes may be easier noticed, thus this iron sample was taken for further detailed studies of the beginning of carburisation.

Samples containing different amounts of carbon were prepared during carburisation under methane at 500 °C. The carburisation was stopped at a given conversion degree by cooling the reactor down to the room temperature under the flow of nitrogen. Traces of oxygen were added to the nitrogen in order to passivate the samples. Phase composition of samples obtained was determined X-ray diffraction. The obtained results are shown in Table 1.

The same samples were also studied using Mössbauer spectroscopy. The typical spectra are shown in Fig. 4 and the calculated Mössbauer parameters are setted in Table 1.

The obtained results reveal the presence of unconverted α-iron in all samples. The samples 2-7 contain also iron carbide Fe_3C. The satisfactory fits were get when in the middle part of spectra an additional doublet was taken into account. The contribution of this doublet is about a few percent. It is ambiguous to attribute this doublet to a given reaction phase. It can be ascribed to the thin passive oxide layer, because all the samples were passivated after the carburisation. Nevertheless, according to our earlier studies [19] the Mössbauer parameters for the thin passivation layer were: IS = 0.40–0.45 mm/s and QS = 0.96–1.08 mm/s. The comparison of these values with the parameters given in Table 1 reveals that only for sample 1 the parameters of the doublet belong to these ranges. In this sample the cemantite is not yet formed and the passivation layer has to be present. For other samples having greater mass increase the values of IS parameter are lower than that for the oxide layer. The values of QS parameter are also lower, except for samples 3 and 4. In case of the most carburised sample 7 Mossbauer parameters of the doublet suggest the presence of a very fine crystalline paramagnetic cementite besides coarse-crystalline bulk magnetic cementite (59%). The total amount of cementite in this sample is about 63 – 64% Fe_3C. Parameters of the doublet for samples 2-6 can indicate the existence of both phases: iron oxide and/or iron carbide (or intercalated graphite phase).

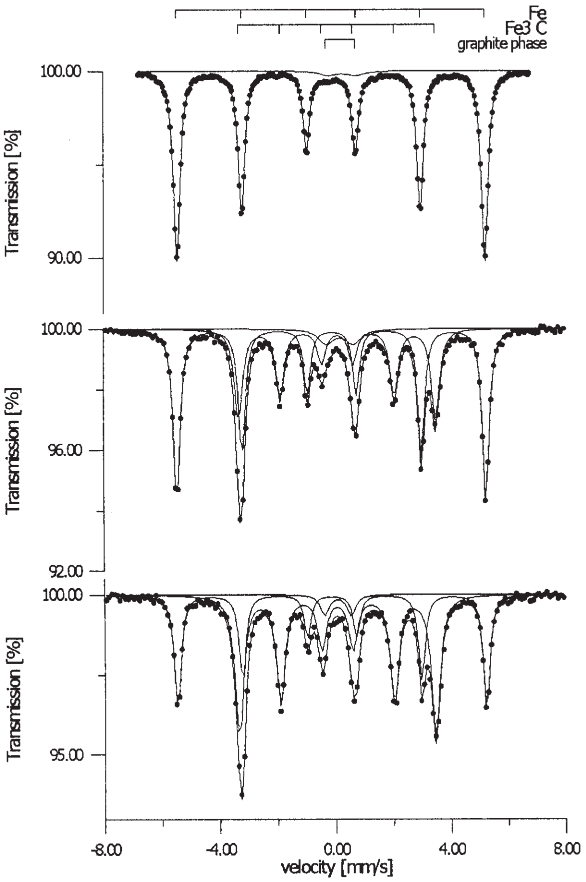

Fig. 4. Examples of the Mössbauer spectra of the carburised samples.

Dependence of the conversion degree of iron to iron carbide (calculated both on the basis of XRD and Mössbauer spectroscopy results) on the relative mass increase of the carburised samples is shown in Fig. 5. The diagonal corresponds to the formation of stoichiometric cementite. The plot can be divided into 3 parts, each attributed to a particular reaction area. At the beginning, in area I, dissolution of carbon in α-iron occurs. The solubility of carbon in iron at 500 °C was calculated from the equation given below [20]:

$$\log(\%C)_{\alpha}^{H} = -\frac{4509}{T} - 2.25 \cdot 10^{-4} T + 3.22 .$$

The calculated value of solubility equals 0.00002 gC/gFe and it is too low to be distinguished in the plot. However, after the solubility limit of carbon the formation of cementite is not observed, neither by XRD nor by Mössbauer spectroscopy. The experimental points in the area I are located on the X-axis, much below the line of cementite formation. If cementite is not formed in this reaction area, other possibilities should be taken into account. The formation of other iron carbides can be considered, but these carbides appear mainly in the presence of carbon monoxide. Niemantsverdriet *et al.* [21] studied the conversion of iron catalyst to carbides during Fischer-Tropsch synthesis. Depending on the reaction conditions (temperature, catalyst nature) the different iron carbides were found. According to these authors, in spite of Fe_5C_2, Fe_3C and $Fe_{2.2}C$ also some undefined iron carbide Fe_xC can be formed

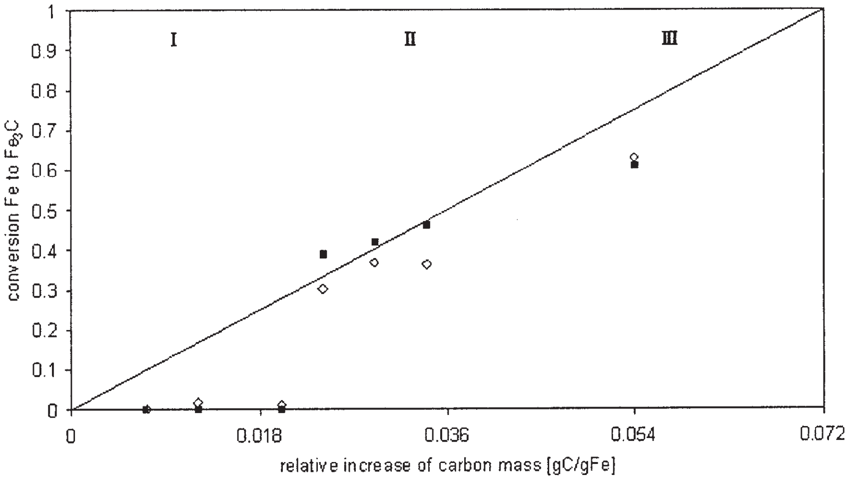

Fig. 5. The dependence of conversion degree of iron to Fe_3C on relative increase of carbon mass. I – formation of Fe - C structures. II – formation of the stoichiometric Fe_3C. III – formation of Fe_3C with simultaneous formation of carbon deposit.

at moderate temperatures. In the paper of Motjope [22] the increase of the formation of iron carbides $Fe_{2.2}C$ and $Fe_{2.5}C$ with increasing conversion of carbon monoxide is reported. As far as interaction of hydrocarbons with iron is concerned there are a lot of papers dealing mainly with the conditions of formation and morphology of carbon deposit in form of fibers or nanotubes [1-7] but the formation of other carbides (except cementite) was never reported.

Taking into account the literature information and the obtained results we can exclude the formation of iron carbides at the beginning of carburisation process (in area I). Our suggestion for this reaction area is the formation of thin carbon layer on the iron surface. The diffusion of iron atoms through this layer can occur and some species like graphite-intercalated compounds can be created.

Rajchel and Stanek [23], who studied the microscopic properties of carbon films interacting with transition metals, have prepared carbon layers, doped with ^{57}Fe ions on Ni/Si substrates using Ion Beam Assisted Deposition. They found a defective or even amorphous structure of carbon layers strongly doted with atoms originating from the substrate. The fast diffusion of iron atoms within carbon layer was detected, even at the moderate temperature of 500 °C.

In the area II in Fig. 5 the formation of cementite takes place, the experimental points fit with the stoichiometric line, starting from the value about 0.02 gC/gFe. It corresponds to the beginning of the steady state of the reaction rate observed in DTG lines (Fig. 2). Process of cementite formation does not occur according to the stoichiometry up to total conversion of iron to iron carbide. Before all iron is converted, the formation of carbon deposit starts, that can be observed in area III in Fig. 5.

4. CONCLUSIONS

A mechanism of the initial step of the carburisation of nanocrystalline iron with methane is proposed. After the overcoming the solubility limit of carbon in iron, a thin layer of carbon can be formed on the iron crystallites surface. Iron atoms can diffuse into this layer. When the amount of carbon in the sample is about 0.02 gC/gFe of carbon content in Fe_3C, the formation of Fe_3C starts. During carburisation under pure methane the formation of carbon deposit commences before a complete transformation of iron into iron carbide was over.

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