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Effect of Mechanical Activation on the High-Temperature Synthesis of Fe_3Al and Its Catalytic Properties during the Carbon Dioxide Assisted Conversion of Natural Gas

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Abstract

Effect of mechanical activation of the powder mixture 3Fe + Al on the structure of mechanocomposites and their evolution during self-propagating high-temperature synthesis was investigated. It was shown that substantial decrease of the temperatures of heat evolution start typical for thermal explosion and the critical temperature of thermal explosion of preliminarily activated mixtures is connected with the presence of regions with fine layered structure in agglomerates, while the heterophase character of synthesis products is due to relatively low maximal synthesis temperature. It was established that mechanical activation of the systems Fe–Al leads to a substantial increase in the catalytic activity of Fe_3Al intermetallide during methane conversion into synthesis gas, and also to an increase in the conversion degree of CH_4 and CO_2 to 93 and 91 %, respectively. In the case of the sample without mechanical activation, these parameters are only 15 and 53 % for CH_4 and CO_2, respectively.

Key words: self-propagating high-temperature synthesis, mechanical activation, intermetallides, carbon dioxide conversion of methane

INTRODUCTION

Initial raw material for the production of diethyl ether as the alternative ecologically safe fuel is synthesis gas at the ratio $CO/H_2 = 1 : 1$. The latter is obtained by means of carbon-dioxide conversion of methane (CDMC) that provides equimolar component ratio:

$$CH_4 + CO_2 = 2CO + 2H_2$$

A broad implementation of this process is prevented by the absence of active, stable, inexpensive catalysts stable against carbon deposition. At present, CDMC catalysts are known that are the metals of iron sub-group deposited on oxide ceramics [1, 2]. Aluminides of Fe and Ni poses high catalytic activity in the CDMC process and are stable against carbon deposition; from the economical point of view, they exceed known active catalysts based on precious metals (Pt, Ru, Rh *etc.*) [3].

Self-propagating high-temperature synthesis (SHS) can be considered as the most promising method to obtain catalysts. This method is based on the use of the internal chemical energy of initial reagents and serves as an example of the most advantageous arrangement of synthesis process in the thermal sense. For many intermetallic systems with low heat of formation, the heat of chemical reaction alone is insufficient for combustion, so it is necessary to heat initial mixture before ignition. A logical continuation of the SHS method with preliminary heating of the mixture is the synthesis of intermetallides in the regime of gas-free thermal explosion. Diverse mechanisms of heat evolution are characteristic of the heterogeneous mixtures of metal powders under the conditions of thermal explosion. For example, melting of one of the components (or the appearance of eutectic melt) can lead to sharp acceleration of the reaction and its transition to the thermal explosion regime. In accordance with this, two stages of interaction were distinguished for Ni–Al and Fe–Al systems [5]: the solid-phase reaction leading to smooth self-heating, and prompt self-heating that occurs when the melting point of eutectics is achieved. If the size of particles is sufficiently small, thermal explosion can be initiated by the solid-phase reaction as it was demonstrated in [6] for Ni–Al system as example. For some systems (for example, Nb–Al [7]) it was discovered that thermal explosion occurs only after the sample is overheated at the temperature 200 K above the melting point of aluminium.

Mechanical activation (MA) of powdered reaction mixtures can principally broaden the possibilities for the application of SHS of inorganic materials. Mechanical treatment in planetary ball mills, vibratory mills or attritors with the acceleration of milling bodies reaching several ten *g* value allows substantial broadening of the concentration limits of combustion, decrease the temperature of reaction initiation and fully realize the solid-phase mode of combustion [8–13].

A combination of mechanical activation and SHS methods allows one to determine the ways for the synthesis of materials with required physical, chemical and mechanical properties.

In the present work we studied the effect of preliminary MA on the high-temperature synthesis of Fe_3Al compound in the thermal explosion mode. Interaction in activated mixtures can substantially differ from the interaction under usual conditions and provide high activity under the conditions of oxidative-reductive medium of the process of carbon-dioxide conversion of methane.

EXPERIMENTAL

Iron powder of carbonyl os. ch. grade TU 6-09-3000–78 (particle size <100 μm) and aluminium of ASD-4 grade were used in the work. The powder fraction of necessary size was obtained using the sieve method. The mixtures of powders with the stoichiometric composition 3Fe + Al (mass fraction of Al 13.87 %) were subjected to mechanical activation in a ball planetary mill M3 with the acceleration of 45*g*. Steel balls 5 mm in diameter, with the total mass 300 g, and powder mixtures with the mass 30 g, were loaded into the cylinders 1000 cm^3 in volume. The cylinders were filled with argon. Activation time varied from 10 s to 3 min. To avoid overheating, the mill was stopped every 30 s for 15–20 min. The activated mixture was placed into a cup made of thin steel net; the cup diameter was 15 mm, its height was 40 mm. The cup with powder and the tungsten-rhenium thermocouple (100 μm in diameter) in the centre was placed in a resistance tube furnace, the reaction chamber 5 L in volume was filled with argon ($P = 10^5$ Pa), and heated at a constant heating rate 200 °C/min up to the temperature of the start of thermal explosion. The thermocouple indications were recorded with the ADC (LA2m5PCI). The temperature of the start of heat evolution T_0, the critical temperature of thermal explosion T_0^c and the maximal temperature (T_{max}) were determined from the thermogram. The residual mixture (15–20 g) was separated using a set of standard sieves; the size distribution was plotted (histograms) for each activation time. The phase composition of activated mixtures and synthesized products was determined with DRON-UM-1 diffractometer using CoK_α radiation. The microstructure of samples was studied with the help of metallographic method (Axiovert 200M) and micro X-ray spectral analysis (Camebax). To reveal microstructure, we selected the granules 600–1000 μm in size and sealed them with epoxy resin. After hardening, the samples were polished, then a specially selected etching reagent $HNO_3/H_2O = 1 : 1$ was applied. Catalytic tests were carried out in a flow set-up with the quartz tubular reactor 5 mm in diameter, with the fixed catalyst layer. Analysis of the initial substances and reaction products was carried out with a Khromos GKh 1000.1 chromatograph. The Carbosieve S II sorbent was used to determine CH_4, C_2H_6, CO_2, C_2H_4,

C_3H_8, C_3H_6, H_2O, N_2, H_2, CO. Chromatographing conditions were: carrier gas (helium) flow 30 mL/min, steel column 3 m long and inner diameter 3 mm, analysis time 20 min, with programmed heating from 40 to 225 °C. The absolute calibration method was used to calculate the concentration of gaseous reaction products [14].

RESULTS AND DISCUSSION

In the opinion of the authors of [15], the maximal effect of preliminary mechanical activation of the reaction mixtures of metal powders is achieved in the case of the high level of plasticity of both components of the mixture. The early stages of mechanical activation of these systems involve selective formation of separate agglomerates containing ultrafine mixture of initial components in the form of thin layers. Further activation causes the growth of previously formed composite with simultaneous thickening of layers. This layered structure can be compared with a set of the diffusion pairs of different metals with good physical contact between the layers.

Iron and aluminium powder grades chosen by us, as well as their mixtures, were characterized by the necessary level of plasticity.

The thermograms of the thermal explosion of non-activated and activated mixtures after mechanical treatment for different time intervals are shown in Fig. 1. One can see that the pressed sample prepared from the initial (non-activated) mixture burst into fire at a temperature slightly above 700 °C (see Fig. 1, curve *1*). The maximal temperature of thermal explosion in this case was 1150 °C. The critical temperature of thermal explosion for the sample is somewhat higher than the eutectic (655 °C) and the melting point of aluminium (660 °C) [16]. The starting point of chemical reaction and the critical temperature of thermal explosion almost coincide. Overheating, which is 50 °C, can be explained by the presence of the oxide film on the powders and by relatively small area of contact between the particles. The inflection at 800 °C and some decrease in the rate of the chemical reaction provide evidence that the process includes several stages, which can be connected with large scatter of particle size in iron powder and with the diffusion braking through the product layer.

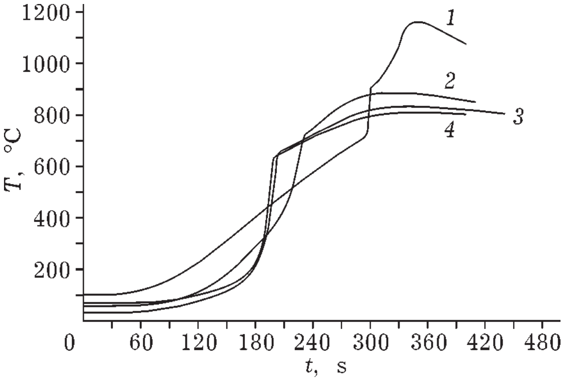

Fig. 1. Thermograms of thermal explosion of the initial (*1*) and mechanically activated samples 3Fe + Al (*2*–*4*). Time of mechanical activation, s: 10 (*2*), 60 (*3*), 140 (*4*).

Mechanical activation for 10 s causes a change of thermogram profile (see Fig. 1, curve *2*) and a decrease in all the characteristic temperatures of thermal explosion. Thus, the temperature of the start of chemical reaction is T_0 = 350 °C, and the critical temperature of thermal explosion is T_0^c = 500 °C. The maximal temperature of thermal explosion in this case is equal to 900 °C. At T = 750 °C, a break is observed on the curve, which is the evidence of the transfer from the rapid stage of chemical reaction into after burning. Further increase in activation time to 15, 30 and 60 min causes a decrease in all the characteristic temperatures of thermal explosion. Thermograms corresponding to activation time 60 s and more (till 2.5 min) are almost identical (see Fig. 1, curves *3*, *4*). After activation for 60 s T_0 = 200 °C, T_0^c = 350 °C, T_{max} = 820 °C. The points of inflection on curves *3*, *4* correspond to 660 °C, that is, the melting point of aluminium. Subsequent slowing down of the chemical reaction is connected with the diffusion braking in the product layer.

According to the data of X-ray phase analysis (Fig. 2), MA for 150 s does not cause the formation of any phases. Only the lines of Fe and Al are present in the diffraction patterns (see Fig. 2, curve *1*). The synthesis products in activated and non-activated mixtures contain many phases (see Fig. 2, curves *2*, 3). In addition to the lines of the major phase Fe_3Al, the lines of α-Fe phase are present in the diffraction patterns.

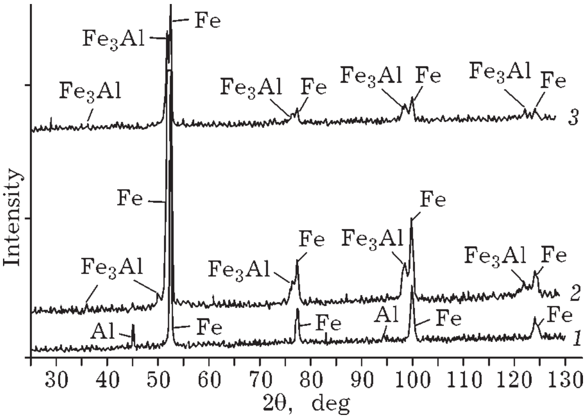

Fig. 2. X-ray diffraction patterns of reaction mixtures: *1* – Fe + 13.87 mass % Al after MA for 2.5 min before SHS; *2* – 3Fe + Al after SHS without MA; *3* – 3Fe + Al mechanically activated of 2.5 min after SHS.

The formation of agglomerates during MA, or, as they are often called, mechanocomposites, in two-component systems has been described in detail in [9, 13, 15]. As a rule, from the first second of the mechanical action, agglomerates composed of the smallest particles of initial composites are formed in the system; the size of some of them does not exceed 100–200 μm. The agglomerates get larger with an increase in the time of mechanical activation; layered pore-free structure is formed inside them. Metallographic studies of the layered mechanocomposites of the system (3Fe + Al) reveals some structural features. For example, due to rather broad scattering of particle size for iron (5–100 μm) in the centre of mechanocomposites (Fig. 3, *a*, *b*) the layered structure is especially clearly pronounced, and the layers themselves have minimal thickness. At the same time, the neighbouring regions contain rather large agglomerations of iron and aluminium particles in which the formation of thin-layered structure has not been finished yet; residual porosity is seen. On the other hand, MA for 150 s becomes critical for many formed agglomerates because rather long and well pro-

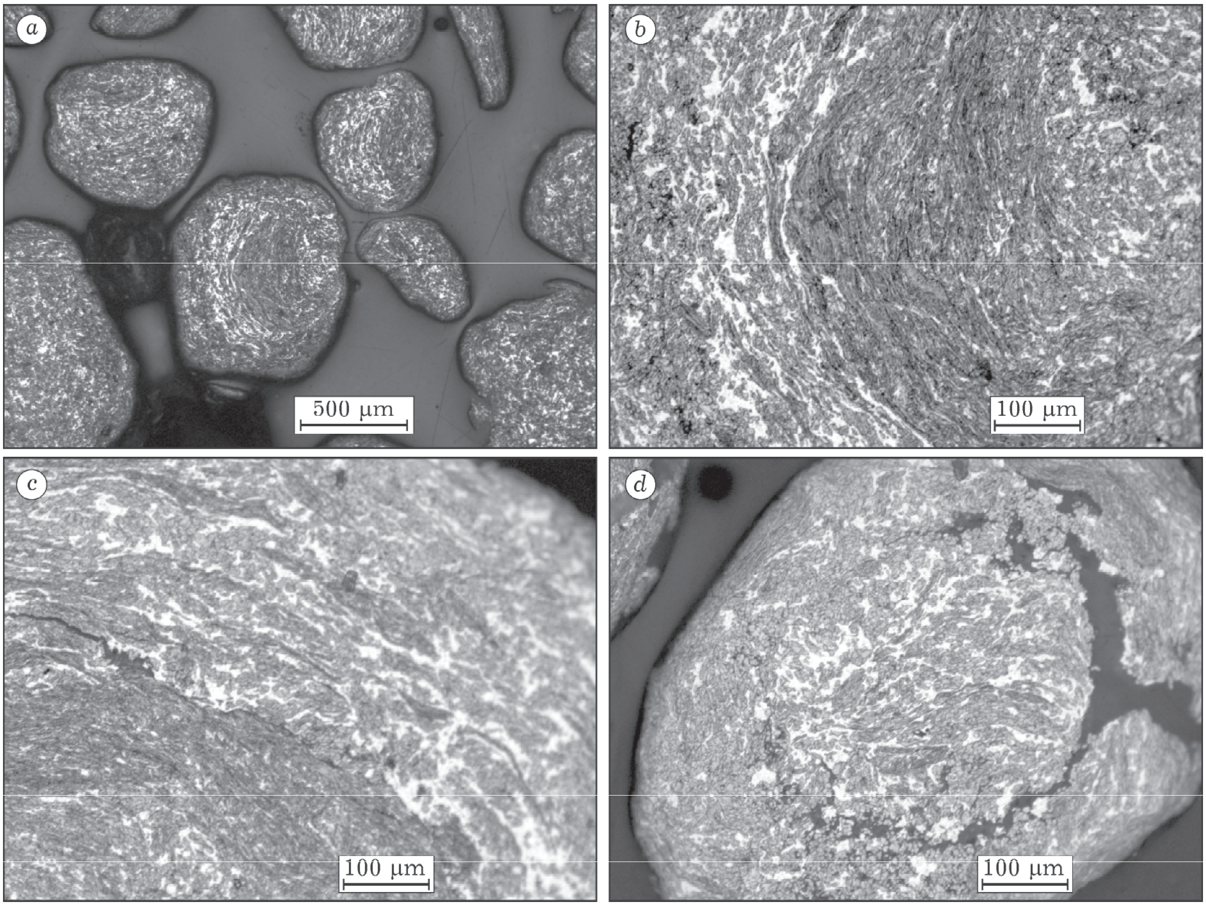

Fig. 3. Microstructure of mechanocomposites activated for 150 s: *a* – general view, *b* – layered structure, *c* – long cracks, *d* – intensive formation of cracks as a result of the application of MA.

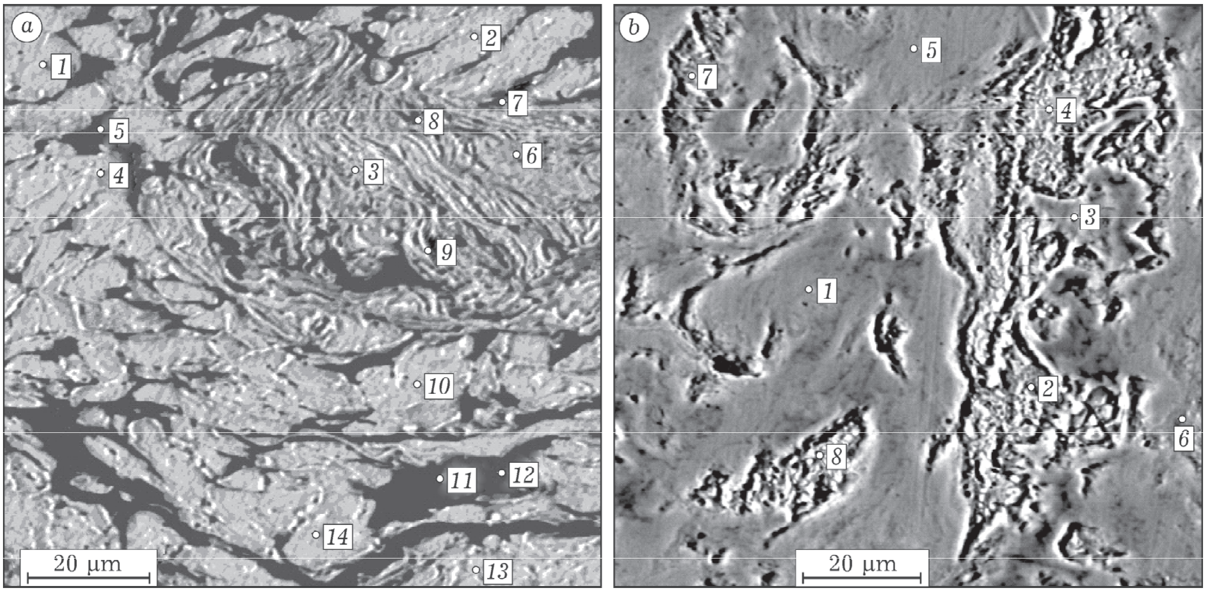

Fig. 4. REM image of the inner microstructure of samples after MA (*a*) and SHS products (*b*).

TABLE 1

Results of local X-ray structural analysis of mechanocomposite (Fe + 13.87 mass % Al), MA for 2.5 min

Point	Elemental composition, at. %	
No	Fe	Al
1	99.270	0.730
2	99.819	0.181
3	59.203	40.797
4	99.642	0.358
5	8.095	91.905
6	68.889	31.111
7	39.100	60.900
8	67.761	32.239
9	92.366	7.634
10	99.818	0.182
11	8.330	91.670
12	1.442	98.558
13	99.771	0.229
14	99.849	0.151

TABLE 2

Results of local X-ray structural analysis of the products of SHS (Fe + 13.87 mass % Al), MA for 2.5 min

Point	Elemental composition, at. %	
No.	Fe	Al
1	77.014	22.986
2	99.933	0.067
3	77.366	22.634
4	100.00	0
5	75.818	24.182
6	81.024	18.976
7	86.339	13.661
8	97.580	2.420

nounced cracks are observed in the structure of some mechanocomposites (see Fig. 3, *c*, *d*).

The presence of structural differences in the volume of separate mechanocomposites is connected with polydispersity of iron and with the phase composition of the product. The images of the inner structure of mechanocomposite, obtained using the detector of inversely reflected electrons, are presented in Fig. 4, *a*. According to the data of local micro X-ray spectral analysis (Table 1), the mechanocomposite under investigation having the composition Fe + 13.87 mass % Al (mechanically activated for 150 s) contains initial components Fe (points 1, 2, 4, 9, 10, 13, 14) and Al (5, 11, 12). The regions marked as points 3, 6, 7, 8 contain both iron and aluminium, which is due to the fact that several alternating Fe and Al layers get into the beam diameter (2–3 μm).

The microstructure of synthesis products in reflected electrons is shown in Fig. 4, *b*. It follows from the data of local micro X-ray spectral analysis (Table 2) that the synthesis product is composed mainly of the coarse-grained phase Fe_3Al (see Fig. 4, *b*, points *1*, *3*, *5*) and small-meshed branched substructure composed of pure iron (points *2*, *4*, *8*) and the solution of aluminium in iron (points *6*, 7). The regions of solution are located along the boundaries separating Fe_3Al and α-Fe phases.

The catalytic activity of the samples synthesized from non-activated (initial) and activated mixtures was studied. The sample of massive iron was used for comparison. Before crushing this sample was pressed in different molds with a hydraulic press. The fraction with particle size 400–1000 μm was chosen for investigation.

The mixture activated for 2.5 min is composed of agglomerates of different sizes. After SHS the agglomerates conserved their shape, were not fused and not welded with each other. It was established that the maximal catalytic activity at a temperature of 950 °C is exhibited by Fe_3Al intermetallide after MA for 2.5 min, obtained on the basis of the mixtures of iron and aluminium treated mechanically till the mechanocomposite of definite size was obtained, and then subjected to SHS (Fig. 5). In addition, in the case of this intermetallide, the degree of CH_4 conversion into CO_2 increases sharply with an increase in temperature and reaches its maximum at a temperature of 850 °C.

The Fe_3Al sample obtained by means of SHS without preliminary MA of the mixture is characterized by the intermediate conversion degree and the yield of valuable products. In this case, according to XPA data, the sample undergoes carbidization with the formation of Fe_3C phase. This phase blocks up the active catalyst surface and thus deactivates it.

The degrees of CH_4 and CO_2 conversion in the case of the reference sample (massive iron) did not exceed 15 %, similarly to the yields of H_2 and CO (12 %). According to XPA data, this sample undergoes intensive oxidation of the α-Fe phase to oxide FeO with the formation of FeC carbide. So, deactivation of massive iron catalyst occurs as a consequence of screening the catalytically active centres (Fe^0) by the oxide and carbide phases.

On the basis of XPA data and the diagram of state of the Fe–Al system [16] with the mass concentration of aluminium 13–20 % at temperatures above 552 °C (higher than the temperature of Fe_3Al phase destruction) we can

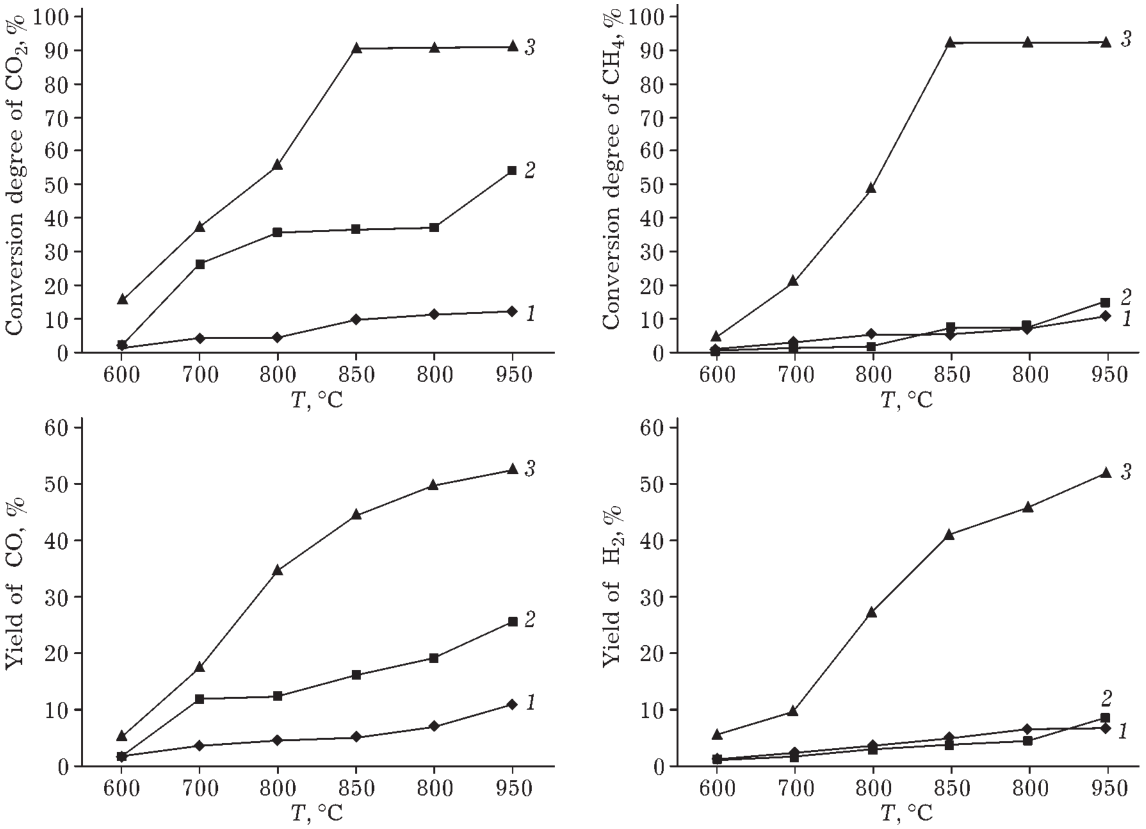

Fig. 5. Catalytic data obtained in the process of carbon-dioxide conversion of methane ($v(CO_2 + CH_4) = 100$ mL/min, catalyst volume 1 cm^3) for the samples having the composition Fe (*1*) and Fe + 13.87 mass % Al after SHS (*2*) and after MA for 2.5 min and SHS (*3*).

assume that directly during the catalytic process the Fe_3Al phase partially destroys and gets transformed into the solid solution of Al in α-Fe. Iron (Fe^0) formed in the fine dispersed state during the destruction of the major phase Fe_3Al can likely act as the catalytically active centre. In addition, at a temperature above 900 °C the polymorphous transition of the α-modification of iron with body-centred structure into the γ-modification of iron with face-centred structure occurs. This modification of iron is characterized by higher lattice parameter, which ensures good solubility of carbon in it and therefore causes deceleration of carbon formation processes according to the carbide cycle mechanism [1].

The favourable effect of MA on the catalytic characteristics of the process of methane conversion into synthesis gas can also be connected with the fact that two-dimensional (surface) defects and dislocations are formed during MA; they promote an increase in the catalytic activity of solids [1]. In addition (see Fig. 1), in the case of MA synthesis temperatures decrease substantially, which leads to the formation of the samples with higher porosity (unlike for the samples obtained at high temperatures of SHS without MA) and correspondingly higher specific surface. As a result, the number of active centres available for reagents per unit contact surface area increases.

CONCLUSION

Mechanical activation of the powder 3Fe + Al leads to the formation of mechanocomposites composed of structurally differing regions, which is due to the polydisperse character of iron particles. A substantial decrease in the temperatures characteristic of thermal explosion T_0, T_0^c, and T_{max} of preliminarily activated mixtures is connected with the presence of the regions with thin layered structure in the agglomerates. The heterophase character of synthesis products is due to relatively low T_{max}. The application of MA of Fe–Al systems promotes substantial increase in the catalytic activity of intermetallide Fe_3Al (the degrees of CH_4 and CO_2 conversion reach 93 and 91 %, respectively). For the samples without MA these parameters are 15 and 53 %, respectively) in the process of methane conversion into synthesis gas.

REFERENCES

1 Arutyunov V. S., Krylov O. V., Okislitelnye Prevrashcheniya Metana, Nauka, Moscow, 1998, p. 353.

2 Richardson J. T., Garriat M., Hung J.-K., *Appl. Catal.*, 255 (2003) 69.

3 RU Pat. No. 2351392, 2009.

4 FR Pat. No. 2088668, 1972; US Pat. No. 3726643, 1973; GB Pat. No. 1321084, 1974.

5 Itin V. I., Naiborodenko Yu. S., Vysokotemperaturny Sintez Intermetallicheskikh Soyedineniy, Izd-vo Tom. Un-ta, Tomsk, 1989, pp. 77–82.

6 Gasparyan A. G., Shteinberg A. S., *Fiz. Goreniya i Vzryva*, 24, 3 (1988) 67.

7 Kachemyer C. R., Rogachev A. S., Varma A. P., *J. Matter Res.*, 10 (1995) 2250.

8 Korchagin M. A., Grigorieva T. F., Barinova A. P., Lyakhov N. Z., *Int. J. Self-Propagating High-Temperature Synth.*, 9, 3 (2000) 307.

9 Bernard F., Gaffet E., *Int. J. Self-Propagating High-Temperature Synth.*, 10, 2 (2001) 109.

10 Grigorieva T., Korchagin M., Lyakhov N., *KONA Powder and Particles*, 20 (2002) 144.

11 Bernard F., Souha H., Gaffet E., Zenkouar M., Gillot B., Niepce J. C., *Int. J. Self-Propagating High-Temperature Synth.*, 9, 1 (2000) 1.

12 Korchagin M. A., Grigorieva T. F., Bokhonov B. B., Sharafutdinov M. R., Barinova A. P., Lyakhov N. Z., *FGV*, 39, 1 (2003) 51.

13 Korchagin M. A., Grigorieva T. F., Bokhonov B. B., Sharafutdinov M. R., Barinova A. P., Lyakhov N. Z., *FGV*, 39, 1 (2003) 60.

14 Galaktionova L. V., Arkatova L. A., Kurina L. N., Gorbunova E. I., Belousova V. N., Naiborodenko Yu. S., Kasatskiy N. G., Golobokov N. N., *Zh. Fiz. Khim.*, 82, 1 (2008) 1.

15 Merzhanov A. G., Kontseptsiya Razvitiya SVS kak Oblasti Nauchno-Tekhnicheskogo Progressa, Territoriya, Chernogolovka, 2003, p. 188.

16 Lyakishev N. P. (Ed.), Diagrammy Sostoyaniya Dvoynykh Metallicheskikh Sistem, Mashinostroyeniye, Moscow, 1996, vol. 1, p. 144.