UDC 542.9+544.463

Mechanical Activation of the Mixture for Self-Propagating High-Temperature Synthesis of Iron Aluminides

A. I. LETSKO[1], T. L. TALAKO[1], A. F. ILYUSHCHENKO[1], T. F. GRIGORIEVA[2] and N. Z. LYAKHOV[2]

[1]Powder Metallurgy Institute, National Academy of Sciences of Belarus,
Ul. Platonova 41, Minsk 220005 (Belarus)

E-mail: letsko@tut.by

[2]Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: grig@solid.nsc.ru

Abstract

Effect of mechanical activation in attritor in the structure and reactivity of powdered mixture Fe–45 mass % Al for self-propagating high-temperature synthesis (SHS) of powders based on iron aluminide was studied. It was established that the decisive influence on the change of the mechanisms of phase formation during SHS has the level of microheterogeneity of reaction mixture and the formation of nanosized iron aluminides B2–FeAl and/or Fe_2Al_5.

Key words: mechanical activation, self-propagating high-temperature synthesis, iron aluminide

INTRODUCTION

Due to the unique combination of properties (high mechanical strength at elevated temperatures, excellent resistance to corrosion, lower density than that of the majority of iron- and nickel-based alloys, and the low cost of the raw material for production) iron aluminides belong to the promising materials for operation under the conditions of increased temperature and corrosive atmospheres [1] in such branches of industry as transport, aerospace and automobile industry, and in energy-generating systems as the candidates to replace light alloys, stainless steel, or nickel superalloys.

It is known that the formation of iron aluminides from elements is an exothermal reaction [2]. In this connection, self-propagating high-temperature synthesis (SHS) may be considered as a promising and cost-effective method of obtaining the powder of iron aluminides. It may be used to obtain various refractory compounds, intermetallides and compositions based on them, using the energy of the exothermal reaction between the reagents. Due to unusual synthesis conditions characterized by short-time chemical and physical processes, high rate of internal self-heating, and sharp temperature gradient during the process, the formation of non-equilibrium structure of the material is possible. In addition, high temperature developed during the process provides the synthesis of the high-purity materials with respect to admixtures. However, insufficiently high exothermal effects of the formation of iron aluminides restrict the possibilities of obtaining the required structures and phase compositions of synthesized products in the system Fe–Al in the classical version of the SHS process [3]. These problems can be solved using mechanically activated SHS (MASHS) [4–6]. During MASHS, the mixture of the components of reacting mass is treated in a high-energy mill for a short time and then used as a reaction mixture for SHS. The stage of mechanical activation (MA) is necessary to initiate the combustion of some weakly exothermal systems, and also to modify the basic parameters of SHS.

The MASHS process in the system Fe–Al was studied in [7–10]. It was shown that this process can result in the formation of homogeneous iron aluminide with the specified grain size. It was reported that MA leads to a substantial decrease in the temperature of initiation (by 10–150 °C) and a substantial increase in the velocity of the front (from 2.5 to 12 mm/s) in comparison with the classical SHS process (without MA). Moreover, analysis of heat evolution during the SHS reaction showed that the rate of heat evolution in activated mixture increases by a factor of 3–3.5. Authors explained this fact by the evolution of mechanical energy accumulated during joint grinding in powder grains and/or by a decrease in diffusion routes due to the existence of chemical gradients at the nanometre level.

However, the approach based on optimization of MA mode with respect to the maximum of heat evolution appears to be of low efficiency from the viewpoint of obtaining SHS materials with required structure and properties. It is known that the decisive part in the formation of the microstructure, crystal structure and phase composition of the target product of synthesis is played by the processes of secondary structure formation that take place behind the front of the combustion wave and depend to a higher extent on the duration of the process and on the mode of sample cooling [11]. The problem of optimization of the activation mode is obviously reduced to the determination of the optimal state of the mixture to provide subsequent synthesis under the required combustion conditions and therefore to obtain the required structure and properties of the synthesized product.

The authors of [7] proposed to carry out preliminary MA in the system Fe–Al in such a manner that a homogeneous mixture of reagents is formed but the interaction between them is avoided.

On the other hand, the authors of [12, 13] demonstrated that the formation of a definite amount of the products of interaction during MA can have a positive effect. The products of the mechanochemical interaction distributed uniformly inside the grains of mechanocomposites act as the centres of heterogeneous crystallization during subsequent SHS. During this process, due to a decrease in the chemical energy of the system, combustion temperature decreases, thus providing the possibility to obtain nanostructured product.

The goal of the present work was to study the effect of MA on the structure and reactivity of powdered mixture for SHS of powders based on iron aluminides.

EXPERIMENTAL

The object under investigation was a powdered mixture having the composition Fe–15 mass % Al corresponding to the two-phase region of eutectoid FeAl–$FeAl_2$ in the diagram of state of Fe–Al, which must provide improved mechanical properties of the material due to the formation of eutectoid structure, as well as an increase in corrosion stability and the stability against hydrogen embrittlement due to the high aluminium content [14].

The powders of reagents (iron powder PZhRV2, State Standard GOST 9849–86, fraction <100 μm, aluminium powder ASD-1 TU 6-02-848–74, as supplied) were mixed in a four-jar mixer for 6 h. Mechanical activation was performed in attritor A-4.5 (Powder Metallurgy Institute, Minsk) in argon environment, with the ratio of ball mass to sample mass 20 : 1 (the frequency of impeller shaft rotation was 350 min^{-1}). The balls made of ShKh15 steel, 5 mm in diameter, were used as the milling tools. The duration of treatment was varied from 30 to 180 min.

Sampling was performed by means of quartering according to GOST 23148–98. The structure of powders was studied by means of optical microscopy (Polyvar, Austria; Neophot-20, Germany) and transmission electron microscopy EM-125.

X-ray phase analysis was carried out on a DRON-3.0 diffractometer in monochromatized radiation of CuK_α and CoK_α within the angle range $2\theta = 20–120°$. Collection, processing and analysis of the recorded data were made with the help of X-ray (versions 1.0 and 2.0) and AIST software packages, as well as the automated program for separation of superimposed lines Split Line. To calculate the function of the physical line broadening (FPB, $\beta_{1/2}$, rad), we used MIC2L program from the GOR software package. Recording was performed in the continuous mode with the rate of counter rotation 1°/min., and in the discrete mode with a step of $2\theta = 0.05°$ and the time of pulse accumulation per point from 40 to 200 s. Precise X-ray studies were performed with CuK_α radiation using a D8 ADVANCE diffractometer (Bruker AXS GmbH Co., Germany) with the DIFRAC^{plus} software. The profile of line shape was analysed using TOPAS software. Calculation of the average size of crystallites was performed by means of the complete decomposition of diffraction patterns according to Pouly procedure. Arithmetic mean values of three measurements for which the calculated error did not exceed 10 % were used to build the plots.

Differential thermal analysis (DTA) was made with a Q-1500D instrument (MOM, Hungary) in argon medium. Measurements were performed within temperature range 20 to 100 °C under heating at a rate of 10 °C/min. The heat of reaction was determined as the area of the peak on the DTA curve reduced to unit mass.

RESULTS AND DISCUSSION

The microstructure of powder particles depending on MA time is presented in Fig. 1. One can see that in all the cases mechanically activated powders are agglomerates based on aluminium particles with iron inclusions inside. With an increase in treatment time, we observe enhanced homogeneity of the distribution of iron inclusions over the volume of powder particles, a decrease in the thickness of layers and jitter of their boundaries. Due to the formation of coarse aggregates during MA of powders because of the presence of plastic aluminium in the reaction mixture, one should not expect that activation would cause of effects connected with a decrease in the size and change of the specific surface of powders.

Comparative analysis of diffraction patterns did not reveal monotonous accumulation of defects in the crystal volume and microdeformation of grains during MA. Non-systematic variations of angular positions, shape and width of diffraction reflections, as well as the integral intensity of diffraction patterns with an increase in the time of MA provide evidence of periodical formation and annihilation of the defects of crystal structure. Changes of these parameters depending on the time of MA have a complicated character depicting the variety of processes that take place and their mismatch in time (Fig. 2).

Nevertheless, analyzing the results of the determination of the parameters of the crystal structure of separate phases, we can state the following general regularities.

A sharp increase in lattice parameters, both for iron and for aluminium, was observed after MA for 90 min. With further increase in

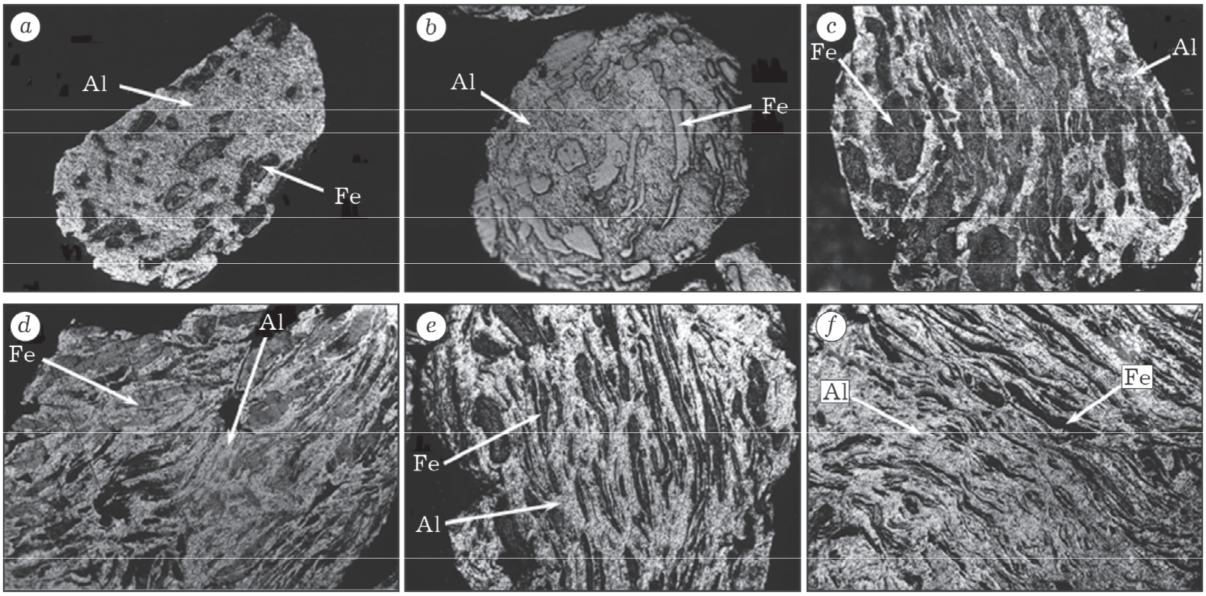

Fig. 1. Microstructure of powder particles depending on the time of mechanical activation, min: 30 (*a*), 60 (*b*), 90 (*c*), 120 (*d*), 150 (*e*), 180 (*f*). × 500 Magn.

the duration of MA to 120 min this parameter decreased, especially for aluminium (a sharp drop of the parameter to the values close to the initial ones). A qualitative similarity in the behaviour of the lattice periods of α-iron and aluminium, in spite of the differences in the plastic properties of these metals, in their relations to inserted impurities, and the absence of evident correlations between the dynamics of changes in lattice parameters, crystallite size, and broadening of the lines related to basic reflections, may provide evidence that changes of lattice period values are due not to chemical processes but to deformation.

Another common regularity is a decrease in crystallite size to the nanometre scale after MA for 120 min, followed by the achievement of dynamic equilibrium.

The absence of noticeable changes of the substructure of phases after MA for more than 120 min is likely to be connected with the fact that these conditions brings about the structural

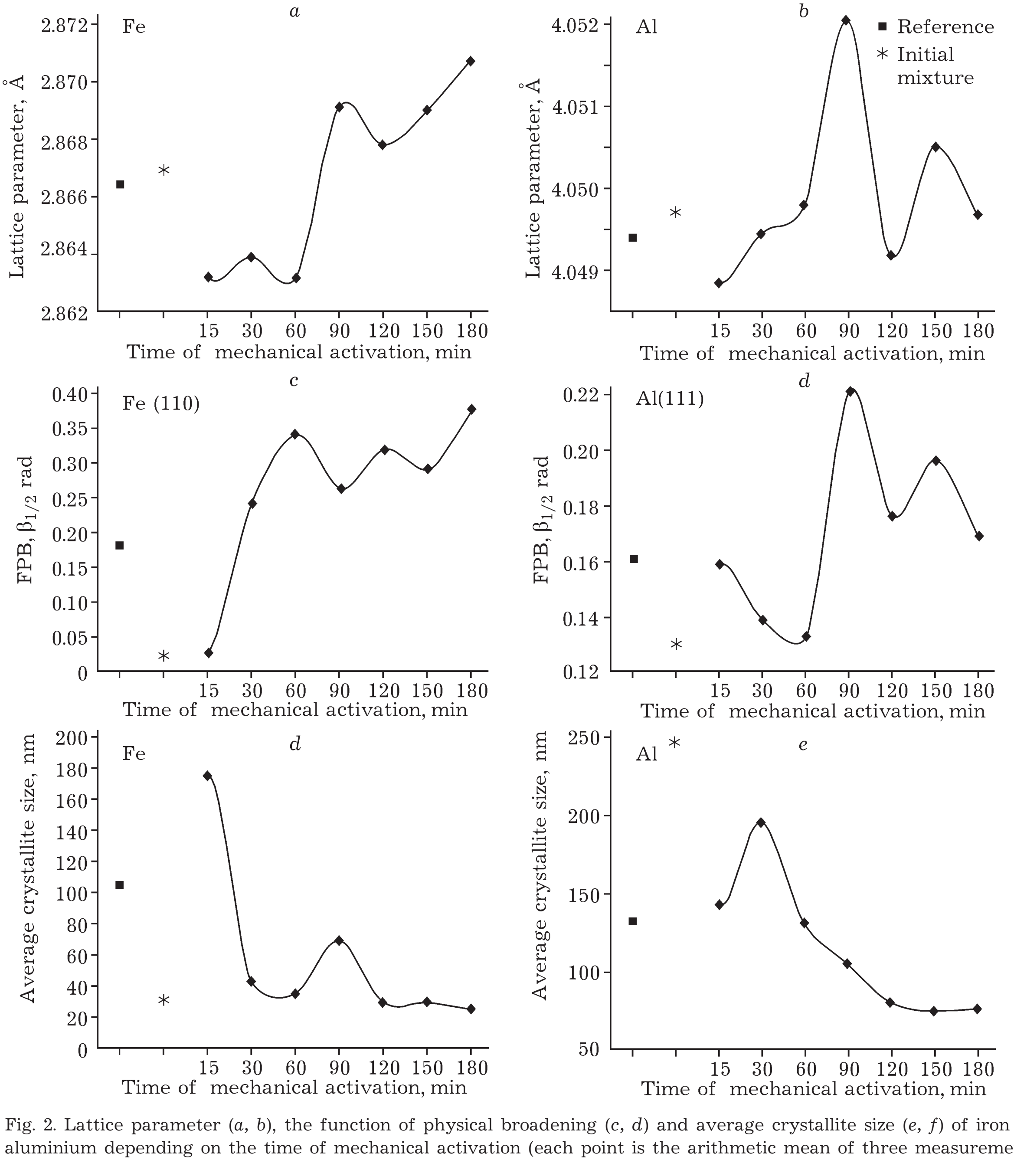

Fig. 2. Lattice parameter (*a*, *b*), the function of physical broadening (*c*, *d*) and average crystallite size (*e*, *f*) of iron and aluminium depending on the time of mechanical activation (each point is the arithmetic mean of three measurements).

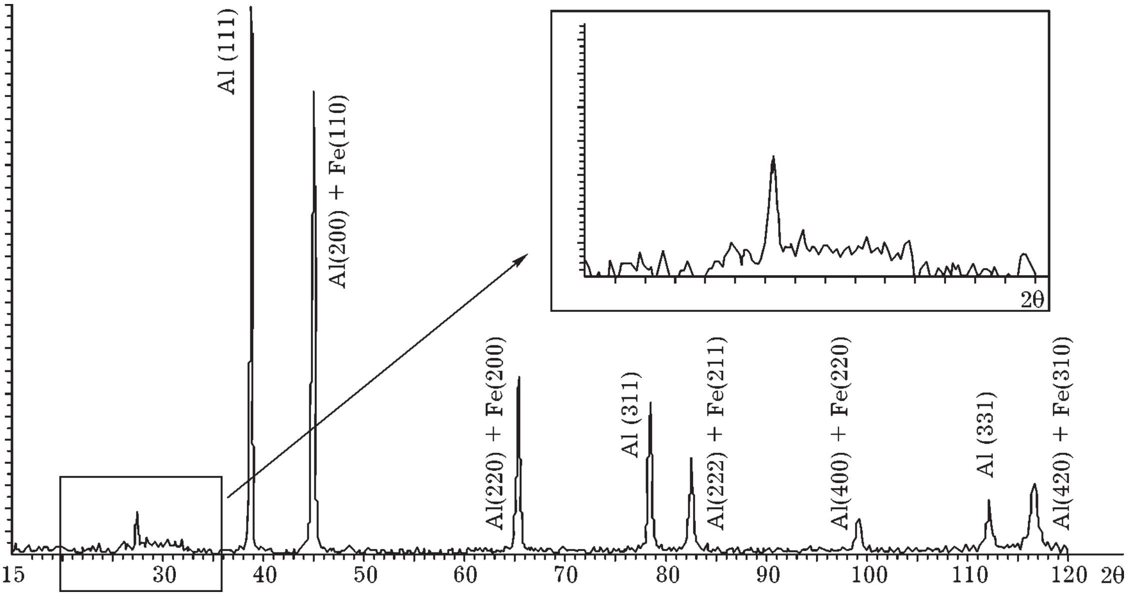

Fig. 3. Diffraction patterns of the reaction mixture after mechanical activation for 120 min in attritor, with record in the high-resolution mode.

state in which the limiting (for this kind of deformation) saturation with dislocations is achieved, and dislocation itself is accompanied by relaxation processes (dynamic return) [15].

The dynamic relaxation of dislocations before 120 min of MA is likely to proceed through annihilation. With the achievement of a definite critical density of dislocations (after MA or 90 min) we observe the relaxation process connected with plastic deformation. The latter is accompanied by the formation of nanocrystalline structure (the relaxation of dislocation structure occurs through the formation of off-orientation boundaries both with small angles and with large ones).

It may be assumed that the nature of defect accumulation is different for iron and for aluminium. For instance, the major type of defects for iron is likely to be dislocations, exhibited as broadening of X-ray lines, while for aluminium, most probably; point defects prevail at the first stage. They manifest themselves in the changes of lattice period. However, this question, similar to the question concerning the quantitative estimation of defect concentration, requires additional investigation.

It is interesting that it was the sample subjected to MA for 120 min for which, unlike for all the other cases, during recording in the high-resolution mode, in the diffraction spectrum we observed the appearance of a small peak at $2\theta = 27.3°$ and a small halo of low intensity within the angle range $2\theta = 25–32°$ (Fig. 3). This may be the evidence of the possible formation of non-equilibrium intermetallide phases. Unfortunately, it is impossible to identify these lines precisely by means of XSA. Within the error, the reflections may belong to $Al_{13}Fe_4$, Al_5Fe_2 and Al_3Fe. In addition, the presence of the halo may also be connected with the presence of B2 phase of FeAl for which the superstructural reflection in the region of 30–32° is characteristic, and other lines coincide within

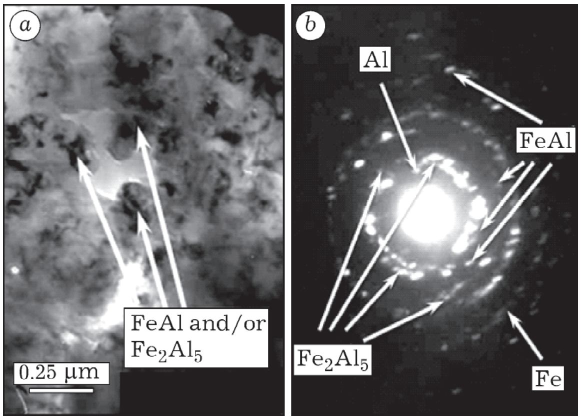

Fig. 4. TEM image of the reaction mixture Fe–45 mass % Al after mechanical activation for 120 min in attritor (*a*) and electron diffraction patterns of the region with loop dislocations (*b*).

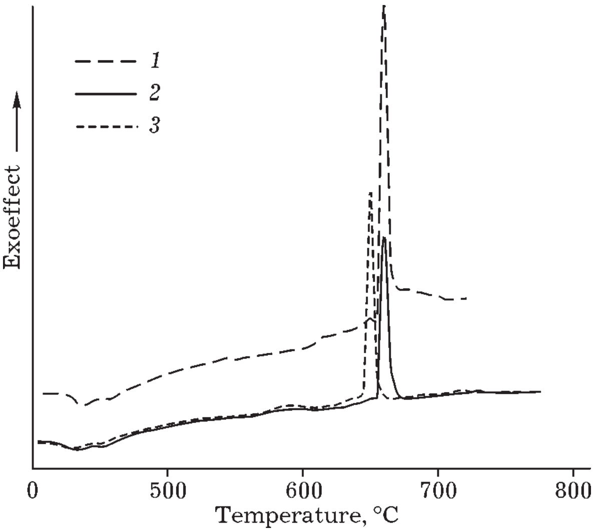

Fig. 5. Changes of the DTA curves of reaction mixture Fe–45 % Al depending on the time of mechanical activation: *1* – initial; *2, 3* – activated for 90 and 120 min, respectively.

the error limit with the lines related to iron. The absence of reflections with further increase in MA time can be connected either with the decomposition of non-equilibrium intermetallides as a result of subsequent MA or with disordering and comminution of their structure. Taking the data of metallography into account, the latter assumption appears to be more probable.

Investigating the structure of the reaction mixture Fe–Al after MA for 120 min in attritor by means of transmission electron microscopy (Fig. 4) we discovered the regions 50 to 300 nm in size with different light contrast, and loop dislocations inside which there were inclusions with the average diameter about 50 nm. Analysis of the electron diffraction patterns of the corresponding regions allowed us to interpret these inclusions as fine segregated B2–FeAl and/or Fe_2Al_5 with orthorhombic lattice. They may be formed as a result of low-temperature reactions proceeding in the nanosized diffusion pairs formed during mechanical activation [16].

The DTA curves of powdered mixture Fe–45 mass % Al during heating in the derivatograph depending on the time of MA are shown in Fig. 5. During the combustion of the initial mixture without activation, a sharp exothermal peak of thermal explosion is observed at 647 °C, which is due to the appearance of the liquid phase. Starting from the MA time of 90 min we observe the disappearance of the endothermic effect that provided the evidence of the start of melting, and then the exothermal reaction starts. It should be noted that for this MA time the size of the crystallites of both components of the reaction mixture becomes less than 100 nm. The obtained results agree with the statement of the authors of [17] that with the achievement of ultrafine size (about 100 nm) by the reagents of SHS mixtures the mode of solid-phase combustion becomes possible.

With further increase in the duration of MA, the exothermal effect on DTA curves increases; however, for all the investigated activation modes, the heat effect of reactions reduced to the unit mass turns out to be lower than that for non-activated state (Fig. 6, *a*). This somewhat unexpected fact can be easily explained by comparing the values of heat effect

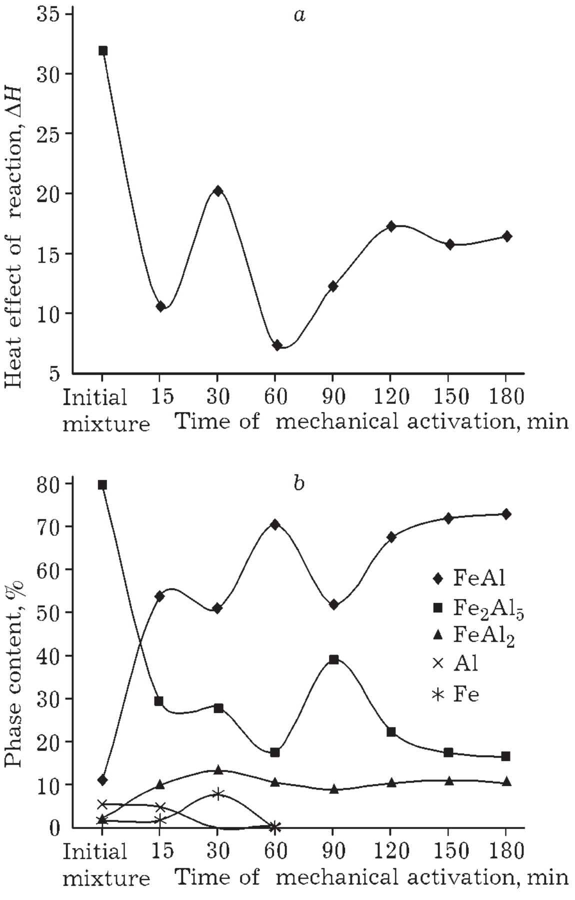

Fig. 6. Value of heat effect of reactions (*a*) and phase composition of the products of SHS (*b*) depending on the time of mechanical activation.

with the results of the phase analysis of synthesis products (see Fig. 6, *b*). One can see in Fig. 6 that a decrease in the heat effect is connected with the change of the leading synthesis reaction. Unlike for non-activated mixture for which the formation of Fe_2Al_5 with the heat effect of 27 kJ/mol is preferential, the reaction predominant for all the activation modes is the formation of iron monoaluminide; its heat effect is lower (25.1 kJ/mol). The change of reactions is evidently due to a decrease in its activation energy (the energy barrier necessary for the reaction onset) due to an increase in the concentration of non-equilibrium defects of structure during activation. The occurrence of one exothermal peak on the DTA curve is the evidence of the fact that the reactions of the formation of different intermetallides proceed simultaneously, and the heat effect is a sum of the heat effects of separate reactions. These results agree with the data obtained in [17]. The authors of that work studied the features of the behaviour of activated Ni–Al mixtures during heating the samples in the column of electron microscope and observed the simultaneous presence of several phases of intermetallides. The simultaneous formation of several intermetallides is likely due to a decrease in the energies of activation of the reactions leading to the formation of FeAl and $FeAl_2$.

For MA time 120 min and more, a stable character of the system behaviour during SHS is established, which provides the stable composition of synthesis products. To remind, similar dynamics was observed by us when we studied the parameters of the crystal structure of reaction mixture. The coefficient of the completeness of transformation in the mixture activated for 120 min and longer is close to unity in spite of relatively small total heat effect if the reactions (in comparison with non-activated mixture). This is likely to be connected with the formation of nanosized iron aluminides in the structure of the material, and they play the part of additional crystallization centres at the early stage of structure formation thus promoting the process of heterogeneous nucleation during SHS.

The results obtained in the work provide evidence of the decisive role of the level of micro-heterogeneity of reaction mixture for the change of the mechanism of SHS and the necessity to take into account the potential centres of the crystallization of new phases with optimized modes of mechanical activation for subsequent SHS.

CONCLUSION

The effect of mechanical activation on the structure and reactivity of powdered mixture Fe–45 mass % Al for SHS of iron aluminides was studied.

The investigations showed that among many parameters of the structure of mechanically activated reaction mixture the level of microheterogeneity has the decisive effect on the change of the mechanisms of phase formation during SHS in the system Fe–45 mass % Al. With the achievement of nanosized state of reagents, solid-phase interaction starts in nanosized pores. As a result of this interaction, nanosized iron aluminides B2–FeAl and/or Fe_2Al_5 are formed; they have the decisive effect on subsequent SHS causing the change of the leading reaction in SHS and providing the completeness of transformation under the conditions of decreased heat evolution.

REFERENCES

1 D. Pocci, O. Tassa, and C. Testani, in: Processing, Properties, and Applications of Iron Aluminides, in H. Schneibel and M. A. Crimp (Eds.), The Minerals, Metals & Materials Society, 1994. pp. 19–30.

2 V. I. Itin, Yu. S. Nayborodenko, Vysokotemperaturny Sintez Intermatallicheskikh Soyedineniy, Izd-vo Tom. Un-ta, Tomsk, 1989.

3 D. L. Joslin, D. S. Easton, C. T. Liu, S. S. Babu, S. A. David, *Intermetallics*, 2 (1995) 467.

4 F. Charlot, C. Gras, F. Bernard, J. C. Niepce, E. Gaffet, *Acta Materialia*, 47, 7 (1999) 2113.5 V. Gauthier, F. Bernard, E. Gaffet, Z. A. Munir, J. P. Larpin, *Intermetallics*, 9, 7 (2001) 571.

6 C. Gras, N. Bernsten, F. Bernard, E. Gaffet, *Intermetallics*, 10, 3 (2002) 271.

7 D. Klein, J. C. Niepce, F. Charlot, E. Gaffet, F. Bernard, *Acta Materialia*, 47, 2 (1999) 619.

8 F. Bernard, F. Charlot, E. Gaffet and Z.A. Munir, *J. Am. Ceramic Soc.*, 84, 5 (2001) 910.

9 O. El Kedim, S. Paris, C. Phigini, F. Bernard, E. Gaffet, Z. A. Munir, *Mat. Sci. Eng.*, A 369, 1–2. (2004) 49.

10 F. Charlot, E. Gaffet, F. Bernard, J. C. Niepce, *Mat. Sci. Eng. A*, 262 (1999) 279.

11 E. A. Levashov, A. S. Rogachev, Yu. Yukhvid, I. P. Borovinskaya, Fiziko-Khimicheskiye i Tekhnologicheskiye Osnovy Samorasprostranyayushchegosya Vysokotemperaturnogo Sinteza, Binom, Moscow, 1999.

12 V. Gauthiera, F. Bernarda, E. Gaffet, D. Vrelc, M. Gailhanoud, J. P. Larpina, *Intermetallics*, 10 (2002) 377.

13 F. Bernard, E. Gaffet, *Int. J. Self-Prop. High-Temp. Synth.* 2 (2001)109.

14 A. I. Letsko, Polucheniye Poroshka na Osnove Alyuminidov Zheleza Metodom Mekhanoaktiviruyemogo Samorasprostranyayushchegosya Vysokotemperaturnogo Sinteza dlya Naneseniya Gazotermicheskikh Pokrytiy, Stoykikh k Iznosu i Vozdeystviyu Vysokotemperaturnoy Korrozii (Author's Abstract of Candidate's Dissertation in Technical Sciences), Minsk, 2008, p. 24

15 Yu. A. Skakov, N. V. Edneral, M. R. Kataeva, *Fizika Metallov i Metallovedeniya*, 2 (1992) 111.

16 D. L. Zhang, D. Y. Ying, *Mat. Sci. Eng.*, A 301 (2001) 90.

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