

## The Effect of Mechanical Activation on High-Temperature Synthesis and Phase Formation Low-Calorie Intermetallic Compounds

YURY S. NAYBORODENKO, NIKOLAY G. KASATSKY, ELENA G. SERGEEVA and OL'GA K. LEPAKOVA

*Department for Structural Macrokinetics, Siberian Branch of the Russian Academy of Sciences, Pr. Akademichesky 10/3, Tomsk 634055 (Russia)*

*E-mail: maks@fisman.tomsk.su*

### Abstract

The effect of mechanical activation on high-temperature synthesis in the regime of thermal explosion in Fe – Ti, Fe – Al systems is investigated. It is shown that preliminary mechanical activation of metal systems provides the decrease of temperature at which thermal explosion is realized. The extent to which the critical temperature decreases depends on the composition of mixture and activation time. It is demonstrated that mechanical alloying accompanied by phase formation promotes contact melting during the synthesis, which leads to the eutectic liquid phase. Phase composition and structure of the synthesized products are investigated.

### INTRODUCTION

Self-propagating high-temperature synthesis (SHS) of intermetallic compounds characterized by low heat of formation in most cases requires additional energy input, which is usually provided by heating the system [1]. Extensive investigations of the processes involved in the mechanical activation (MA) of metal systems demonstrated substantial increase in their reactivity after MA, which allows one to conduct SHS in wave regime under usual conditions [2]. Foreign investigators called such a SHS process preceded by MA “mechanically activated SHS (MASHS)” [3, 4].

However, high-temperature synthesis of inorganic compounds can also be conducted in the regime of heat explosion with temperature increasing within the whole volume of the reaction system from an external source, which leads to self-heating and to heat explosion when critical temperature is achieved. As shown in [5, 6], this synthesis regime has several advantages since it is characterized by more uniform temperature field which helps one to obtain more uniform macro- and microstruc-

ture of products and allows synthesizing compounds from low-energy mixtures.

Investigation of the regularities of heat evolution in heterogeneous metal systems under the conditions of dynamic heat explosion [7] shows that thermographic method is one of the most suitable ones to investigate the macrokinetics of high-temperature processes, because it allows investigating the main macrokinetic stages of non-isothermal SHS processes.

In the present work we investigate the effect of preliminary MA on high-temperature synthesis of low-calorie intermetallic compounds in the regime of heat explosion, since chemical interaction in activated mixtures under non-isothermal conditions can differ substantially from the interaction under usual conditions.

### EXPERIMENTAL

Titanium PTM powder (particles size <50 mm), carbonyl iron of special purity grade (“os. ch.”, particle size <50 mm) and of radiotechnical grade (R-10), aluminium of ASD-4 grade. Mixtures of powders of the stoichiometric com-

position Fe + Ti (46.17 mass % Ti), 3Fe + Al (54.71 mass % Al) were activated mechanically in a ball planetary mill M3 with a 45g acceleration. Steel balls 5–7 mm in diameter, their mass being 300 g, and 30 g of powder mixture were placed in steel cylindrical drums with a volume of 1000 cm<sup>3</sup>. Then the drum was filled with argon. Activation time was varied from 30 s to 10 min. After activation, samples 15 mm in diameter and 20 mm high, with the initial porosity of 45–50 %, were pressed out of the mixtures.

The synthesis of products of all the composition was carried out in a constant-volume set-up ( $V = 5$  l) in argon in the regime of heat explosion. Samples were heated with resistance furnace; temperature in the centre of a sample was measured with a Chromel-Alumel thermocouple 100 mm in diameter. The dependence of temperature *vs.* time was recorded with a KSP-4 recorder.

Phase composition of activated mixtures and synthesized products was determined using DRON-UM 1 diffractometer with Co radiation. Micro- and macrostructure of the samples under investigation were studied by means of metallography (MIM-8, Unimet) and micro-X-ray spectral analysis (Camebax).

## RESULTS AND DISCUSSION

### Iron – titanium system

Thermodynamic analysis of the Fe – Ti system shows that the adiabatic combustion temperature of the FeTi composition is 1110 K (830 °C), while its melting point is 1500 °C. Heating by about 700 °C is necessary to perform the synthesis in the wave regime. For comparison, in the Ni – Ti system, adiabatic temperature of the formation of NiTi compound is 1280 °C, melting point is 1310 °C, while the heating neces-

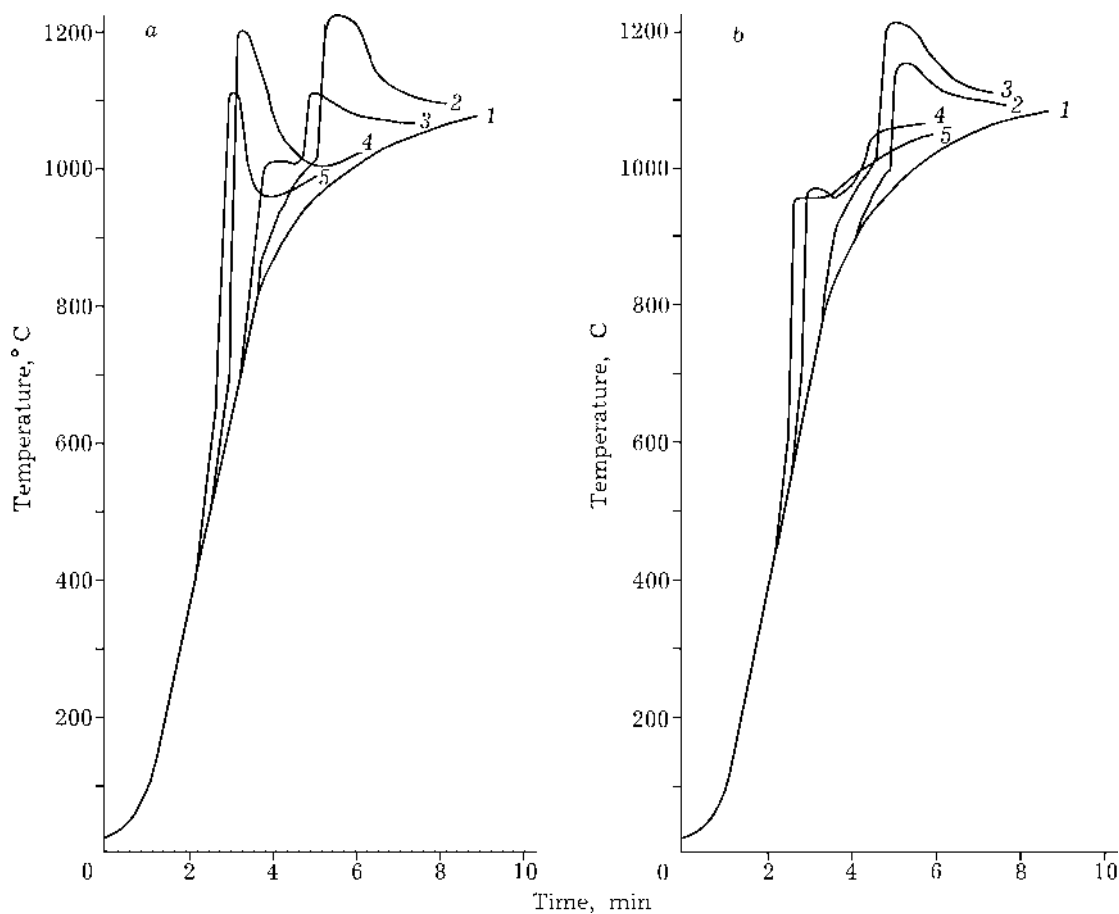


Fig. 1. Thermograms of FeTi samples containing Fe r. t. (a) and Fe "os. ch." (b) with content of Ti 46.17 mass %: 1 – heating of furnace; 2 – initial mixture; 3–5 – activated mixture,  $t_{MA}$ , min: 2.5 (3), 5 (4), and 10 (5).

TABLE 1

Thermographic analysis of the mechanically activated Fe + Ti system

MA time, min	Fe(r. t.) + Ti				Fe("os. ch.") + Ti			
	$T_1$ , °C	$T_{cr}$ , °C	$T_{max}$ , °C	$T_{p. t.}$ , °C	$T_1$ , °C	$T_{cr}$ , °C	$T_{max}$ , °C	$T_{p. t.}$ , °C
0	800	1000	1240		890	980	1150	
1.0	750	1000	1250		840	1000	1150	
2.5	700	1020	1100	1010	780	1000	1200	
5.0	500	700	1200		550	700	1050	970
10.0	400	640	1100		420	600	950	950

Note.  $T_1$ ,  $T_{cr}$ ,  $T_{max}$  and  $T_{p. t.}$  are temperatures of the start of reaction, critical, maximal and phase transition, respectively.

sary for SHS in wave regime is only ~30 °C. Such an insignificant heating can be successfully replaced by MA for several minutes, as it was demonstrated in [2]. However, for the Fe – Ti system, high-temperature synthesis in the heat explosion regime is most preferable.

Figure 1 shows results of thermographic studies of different Fe + Ti mixtures containing radiotechnical-grade iron (see Fig. 1, a) and carbonyl iron of special purity (see Fig. 1, b). A feature of the Fe – Ti system is that melting points of the compounds FeTi and Fe<sub>2</sub>Ti (1500 and 1480 °C, respectively) are lower than those for initial iron (1539 °C) and titanium (1665 °C). The formation of three eutectics is also possible in this system. Among them, the most low-temperature eutectics is formed at 1100 °C between Ti and FeTi.

The analysis of thermograms of initial mixtures (without preliminary MA) (see curves 2 in Fig. 1) showed that temperature of the start of reaction, determined as a smooth deviation of the heating curve of the furnace (curve 1), corresponds to 800 °C (radiotechnical iron, see Fig. 1, a) and to 890 °C (iron of special purity, see Fig. 1, b). Further smooth increase of temperature of the mixture reacting in the solid state is accompanied by a sharp temperature jump causing an angularity on the curve at  $T_c = 1020$  °C and to an increase of temperature to 1220 °C ( $\Delta T \sim 200$  °C) for the radiotechnical iron, and at 990 °C with temperature raise to 1150 °C for the iron of special purity (see Fig. 1, b, curve 2).

This character of temperature change can be connected with a sharp change of the reactivity of titanium and iron during the contact

melting of these elements, accompanied by the formation of eutectics (1100 °C). Contact melting in initial mixtures leading to an inflection on the temperature dependence, is the evidence of possible realization of Stephan's regime [8] when the interaction is determined by the maximal temperature.

Further thermographic investigations were carried out using mixtures after preliminary MA. Mechanical activation of mixtures for 2.5 min (radiotechnical iron, see Fig. 1, a, curve 3) and 5–10 min (special purity Fe, see Fig. 1, b, curves 4, 5) shows that changes of temperature during the interaction in the activated mixtures are substantially different from those in the initial mixtures. The first difference is that the stars of solid-phase reaction in activated mixtures, determined by the temperature of deviation  $T_1$ , decreased to 700 °C (Fe r. t.) and to 780 °C ( $t = 2.5$  min, Fe "os. ch.") (Table 1).

The second difference is that a region of constant temperature appears on the plot of temperature *vs.* time, which is the evidence of phase transition that occurs at 1000 °C (Fe r. t., see Fig. 1, a, curve 3) and 950 °C (Fe "os. ch.", Fig. 1, b, curves 4, 5) and corresponds to the region of contact melting with the formation of eutectics. However, the temperature of the formation of eutectics is somewhat lower than 1100 °C of the equilibrium diagram of state. The presence of a plateau of phase transition ( $T = \text{const.}$ ) at the temperature curve is the evidence that in this case the interaction can proceed according to a model with phase transitions when the process will be determined by the temperature of phase transition ( $T_{p. t.}$ ) [8].

Further activation of a mixture with radio-technical iron for 5 and 10 min provides substantial changes of the character of temperature behaviour and hence of the interaction process (see Fig. 1, *a*, curves 4, 5). We observe a substantial decrease of temperature at which the interaction starts (400 °C,  $t = 10$  min); in fact, at this temperature critical conditions are achieved and thermal explosion occurs in the system. This means that in this case the interaction is determined by the maximal temperature but not the temperature of phase transition (temperature of eutectics).

Thus, non-isothermal interactions in activated systems occur in regimes differing from those occurring in usual mixtures.

The analysis of synthesis products in the Fe – Ti system shows that the materials synthesized with the use of iron of different grades (r. t. and “os. ch.”) contain three phases (Fig. 2). Three phases clearly identified in the microstructure of product obtained using the radiotechnical iron are (see Fig. 2, *a*). According to the data of microanalysis, there are also small regions with increased titanium content (up to 92 %).

In the microstructure of product obtained from the carbonyl iron (“os. ch.”, see Fig. 2, *b*) the  $\text{Fe}_2\text{Ti}$  phase looks not like separate grains as in the case of radiotechnical iron but like continuous areas. The FeTi phase has a stripped structure. The phase  $\text{Ti}_2\text{Fe}$  was also detected in the final product; however, its amount is insignificant.

### Iron – aluminium system

Large number of investigations is dealing with the mechanical activation of the Fe – Al system [9–11]. The energy threshold of phase appearance during mechanical alloying has been determined. However, investigated were only the composition close to FeAl, while the  $\text{Fe}_3\text{Al}$  composition was not studied though, according to literature data, it possesses a complex of useful properties. Because of this, we studied the effect of MA on high-temperature synthesis of  $\text{Fe}_3\text{Al}$  and  $\text{Fe}_2\text{Al}_5$ . Thermodynamic analysis of the system Fe – Al [1] shows that the adiabatic temperature of the formation of  $\text{Fe}_2\text{Al}_5$  is 1284 K (1011 °C), melting point is 1165 °C.

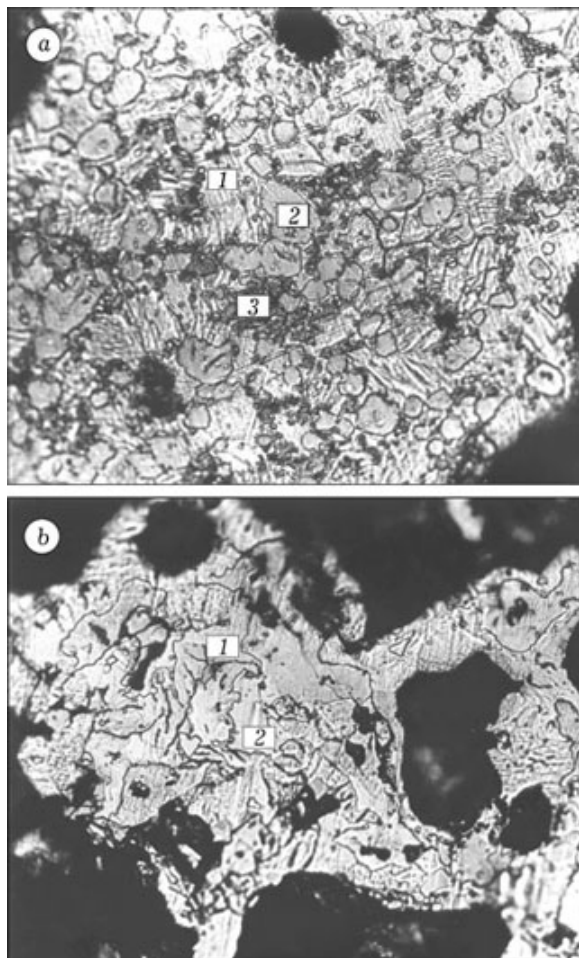


Fig. 2. Microstructure of the synthesis products in the Fe + Ti system with Ti content of 46.17 mass %. Magnification: 400: *a* – Fe (r. t.) – Ti; *b* – Fe (“os. ch.”) – Ti; 1 – light-coloured striped crystals of the FeTi phase; 2 – light-coloured rounded  $\text{Fe}_2\text{Ti}$  crystals; 3 – small gray crystals corresponding to  $\text{FeTi}_2$  composition.

Adiabatic temperature of the formation of  $3\text{Fe} + \text{Al}$  compound is only ~600 °C, a substantial energy input (heating) is necessary to carry out high-temperature synthesis. Preliminary investigations of the effect of MA showed that usual MA regimes did not provide the possibility to realize wave SHS regime, while the synthesis is possible only in the regime of thermal explosion [12].

Figures 3 and 4 show the results of thermographic investigation of the compositions:  $2\text{Fe} + 5\text{Al}$  and  $3\text{Fe} + \text{Al}$ . It should be noted that eutectics exists in the Fe – Al system at the Al content of 98.2 mass % and temperature 655 °C, which nearly coincides with Al melting point (660 °C). The curves of temperature changes in initial mixtures (see curves 2 in Figs. 3 and 4)

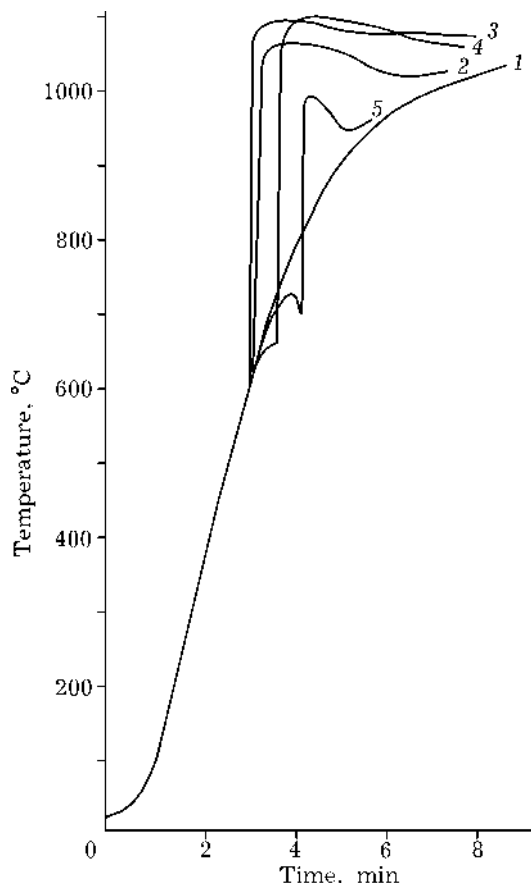


Fig. 3. Thermograms of the  $\text{Fe}_2\text{Al}_5$  samples with the Al content of 54.71 mass %: 1 - heating of the furnace; 2 - initial mixture; 3-5 - activated mixture,  $t_{\text{MA}}$ , min: 0.5 (3), 1 (4), and 5 (5).

look practically identical, but for an insignificant difference in temperature  $T_1$ . For the  $2\text{Fe} + 5\text{Al}$  composition, it is 610 °C, while for the  $3\text{Fe} + \text{Al}$  composition, it is 630 °C, which can be connected with higher aluminium content of  $2\text{Fe} + 5\text{Al}$  and larger area of the reactive surface in initial mixtures, providing solid-phase interaction.

A common feature for both compositions is also the further behaviour of temperature curves which go through an inflection reaching maximum at 1070 °C ( $2\text{Fe} + 5\text{Al}$ ) and 980 °C ( $3\text{Fe} + \text{Al}$ ).

MA of the  $2\text{Fe} + 5\text{Al}$  composition for 0.5 min (curve 3 in Fig. 3) has practically no effect on temperature change.  $T_1$  decreases by several degrees; then, a sharp raise of temperature to  $T_{\text{max}} = 1120$  °C is observed, similarly to thermal explosion. However, further activation for 1 and 5 min (curves 4, 5 in Fig. 3) reveals the features of reactivity of the activated mix-

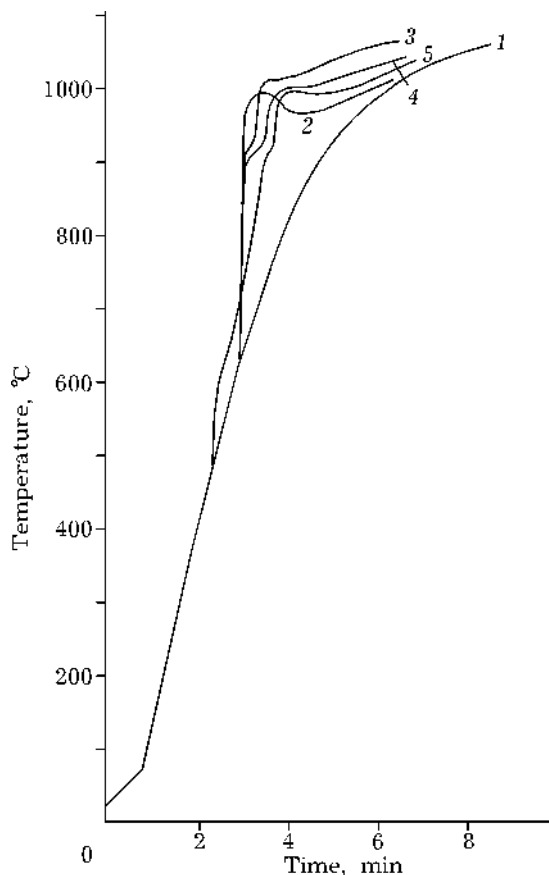


Fig. 4. Thermograms of the  $\text{Fe}_3\text{Al}$  samples with the Al content of 13.87 mass %: 1 - heating of the furnace; 2 - initial mixture; 3-5 - activated mixture,  $t_{\text{MA}}$ , min: 1 (3), 2.5 (4), and 10 (5).

ture. After the temperature of 610–620 °C is achieved, instead of sharp raise we observe a decrease, which means a deviation from the line of furnace heating. This behaviour can be connected only with the phase transition; in the case under consideration, this phase transition will be contact melting and the formation of eutectics. This is especially clearly exhibited in activation for 5 min. In this case, due to small differences in melting points of the eutectics and aluminium, the melting of aluminium is prevailing process, followed by its reaction with iron, which results in a sharp increase of temperature (curve 5 in Fig. 3). Thus, the activated mixture in the  $2\text{Fe} + 5\text{Al}$  system, similarly to the  $\text{Fe} + \text{Ti}$  system, can interact in the regime of phase transition, when temperature in the combustion wave will be determined by the temperature of phase transition, which in this case will be close to the melting point of aluminium (660 °C).

This effect of contact melting on chemical transformation is absent in the case of MA of the 3Fe + Al composition because of very low mass fraction of aluminium (13 %). However, in this case, the sequence of reaction stages in the solid state affects the character of interaction. For example, activation for 1 min (curve 3 in Fig. 4) leads to an inflection on the temperature curve at 900 °C. An increase of activation time to 2.5 min (curve 4) does not change the character of temperature behaviour.  $T_1$  corresponds to 620 °C, while the inflection corresponds to the solid-phase stage at 900 °C. One can see in Fig. 4 (curve 5) that the activation of this composition for 10 min causes a substantial decrease of the temperature of start of interaction in the activated mixture (480 instead of 630 °C).

The investigation of phase composition of the synthesis products in the systems 3Fe + Al and 2Fe + 5Al shows that the products obtained in the regime of thermal explosion are single-phase compounds  $\text{Fe}_3\text{Al}$  and  $\text{Fe}_2\text{Al}_5$ . Finer dispersed structures have materials obtained with the help of MA. A feature of the  $\text{Fe}_3\text{Al}$  compound is the presence of a broad region of homogeneity in which the atomic fraction of aluminium changes within a wide range from 22.2 to 36.5 %, which is in good agreement with the recent data on the diagram of state of this system [13].

## CONCLUSIONS

1. Mechanical activation of metal systems intensifies the solid-phase interaction and leads to self-acceleration (thermal explosion) at low temperatures.

2. Mechanical activation of metal eutectic systems for a definite time provides conditions for contact melting and the formation of eutectics.

3. Synthesis in the regime of thermal explosion leads to the single-phase compounds  $\text{Fe}_3\text{Al}$  and  $\text{Fe}_2\text{Al}_5$  in the Fe – Al system.

4. The product of the synthesis of FeTi compound is multi-phase. Besides the major compound FeTi, the phases  $\text{Fe}_2\text{Ti}$  and  $\text{Ti}_2\text{Fe}$  are present.

## REFERENCES

- 1 V. I. Itin, Yu. S. Nayborodenko, *Vysokotemperaturnyy sintez intermetallicheskikh soyedineniy*, Izd-vo Tom. un-ta, Tomsk, 1989.
- 2 M. A. Korchagin, T. F. Grigorieva, A. P. Barinova, N. Z. Lyakhov, *DAN*, 372, 1 (2000) 40.
- 3 F. Charlot, F. Bernard, D. Klein *et al.*, IV Intern. Symp. on SHS: Book of Abstr., Toledo, Spain, 1997, p. 138.
- 4 C. Gras, E. Gaffet, F. Bernard, J. C. Niepce, *Mater. Sci. Eng. A. Struct. Mater.*, 264, 1/2 (1999) 94.
- 5 A. G. Merzhanov, E. B. Pismenskaya, V. I. Ponomarev, A. S. Rogachev, *DAN*, 363, 2 (1998) 203.
- 6 E. B. Pismenskaya, A. S. Rogachev, V. I. Ponomarev, N. V. Sachkova, V Intern. Symp. on SHS (SHS-99): Book of Abstr., Moscow, 1999, pp. 64–65.
- 7 A. G. Gasparyan, A. S. Steinberg, *Zakonomernosti teplovydeleniya i teplovoy vzryv v smesyakh poroshkov nikelya i alyuminiya*, Prepr. No. 469, Chernogolovka, 1986.
- 8 A. P. Aldushin, A. G. Merzhanov, *DAN SSSR*, 236, 5 (1977) 1133.
- 9 P. F. Relushko, I. V. Berestetskaya, L. I. Trusov *et al.*, *Kinetika i kataliz*, 30, 3 (1989) 624.
- 10 V. E. Grinev, I. V. Berestetskaya, N. N. Platonov, XI Vsesoyuz. simp. po mekhanokhimii i mekhanoemissii tverdykh tel: Tez. dokl., vol. 1, Chernigov, 1990.
- 11 F. Charlot, E. Gaffet, B. Zeghmattiel, *Mater. Sci. Eng. A. Struct. Mater.*, 262, 1–2 (1999) 279.
- 12 E. G. Sergeeva, E. B. Pashko, A. A. Akimenko *et al.*, *Fizicheskaya mezomekhanika materialov: III Vseros. konf. molodykh uchenykh*, Tomsk, 2000. pp. 133–134.
- 13 Diagrammy sostoyaniya dvoynykh metallicheskh sistem, in N. P. Lyakishev (Ed.), *Mashinostroyeniye*, Moscow, 1996, vol. 1, p. 144.