doi.org/10.15407/tpwj2017.09.06

STRUCTURE AND PROPERTIES OF ALLOYED POWDERS BASED ON Fe_3Al INTERMETALLIC FOR THERMAL SPRAYING PRODUCED USING MECHANOCHEMICAL SYNTHESIS METHOD

Yu.S. BORISOV[1], **A.L. BORISOVA**[1],
A.N. BURLACHENKO[1], **T.V. TSYMBALISTAYA**[1] and **C. SENDEROWSKI**[2]
[1]E.O. Paton Electric Welding Institute, NASU
11 Kazimir Malevich Str., 03150, Kiev, Ukraine. E-mail: office@paton.kiev.ua
[2]Military University of Technology in Warsaw
Warsaw, Poland. E-mail:csenderowski@wat.edu.pl

Physical-chemical processes taking place in formation of particles of iron intermetallics based on Fe_3Al alloyed with Cr, Zr, Mg, La and Ti under mechanochemical synthesis conditions were investigated. It is determined that the process of synthesis of alloyed powders passes a range of sequential stages with formation of solid solutions and finishes with formation of single-phase Fe_3Al(Cr, Zr), Fe_3Al (Mg), Fe_3Al (Mg, La) and $(Fe, Ti)_3Al$ products with nanodispersed structure (size of CSA = 10–30 nm). The powders are designed for deposition of heat-resistant FeAl-coatings using thermal spraying and electric arc metallizing methods. 12 Ref., 2 Tables, 10 Figures.

Keywords: *iron-based intermetallics, alloying, mechanochemical synthesis, powders, structure, properties, thermal spraying*

Intermetallics of transition metals (Ni, Fe, Ti) find wide distribution in industry. They are characterized with a complex of such physical, mechanical and corrosion properties as high melting temperature, high heat conductivity, small specific gravity, high strength-to-density relationship, oxidation resistance at high temperatures (up to 1000 °C and above) including in aggressive sulfur-containing media [1–3].

The special attention is focused on iron-based aluminides. They are considered as substitutes of heat-resistant nickel alloys and their competitiveness is provided by availability and low prices of base component iron [3].

However, the disadvantages of iron aluminides are their low ductility and impact resistance at room temperature, insufficient creep resistance in area of moderate temperatures [2, 3]. One of the methods for improvement of mechanical and physical-chemical characteristics of Fe–Al intermetallics is introduction in their composition of alloying components with formation of ternary compounds as well as transfer of these materials in nanostrucutral state [4–6]. The main reason of low strength of iron-aluminum intermetallics is formation in them of interlayers. The latter consist mainly of $FeAl_3$ binary compounds and, in particular, Fe_2Al_5. It is determined that introduction of some metals in Fe–Al intermetallic composition can prevent formation of these two phases and provide positive effect on their strength [4].

A method of mechanochemical synthesis (MCS) takes a special place among the methods of iron aluminides production. This method has no limitations in production of intermetallic compounds of elements with large difference of melting temperatures and densities of initial components, phases with nanometric grain size, stable and metastable phases [7, 8]. The powders produced using MCS method have chemical and phase homogeneity. One of the ways of their practical application is deposition of iron-aluminum heat-resistant coatings using thermal spraying (TS) methods [9, 10].

Present paper studies a production process, structure and properties of alloying powders based on Fe_3Al intermetallic.

Objects for investigation and experiment procedure. A composition corresponding to Fe_3Al intermetallic was used as a basis for alloyed powders production, since such combination of components allows receiving a single-phase product in process of MCS without additional heat treatment [11].

The alloying elements were selected based on carried material analysis of multicomponent Fe–Al–X systems as well as available results of investigation of effect of the third element (or several elements) on mechanical, corrosion and other properties of Fe–Al system alloys [4, 5, 12].

Following the reference data [4] the improvement of properties of iron-aluminum alloys at high temperatures can be realized as a result of such mechanisms as formation of Fe–Al–X solid solution with increased hardness, strengthening of Fe–Al alloy with dispersed

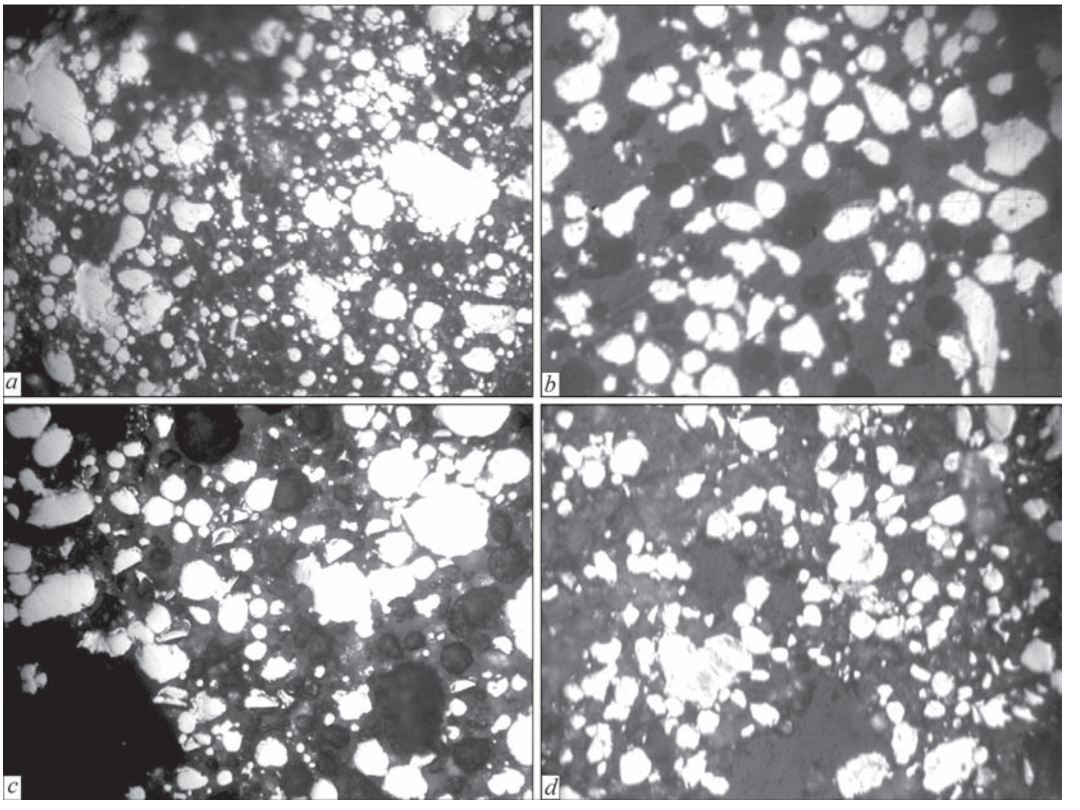

Figure 1. Microstructure (×400) of particles of aluminum alloy powders: Al1.5Cr1Zr (*a*), Al5Mg (*b*), Al5Mg1La (*c*), Ti35Al (*d*)

precipitations or development of ordered structure in Fe–Al–X compound.

«Solid solution strengthening» is carried out in the wide ranges of concentrations in the case of Fe–Al–Cr system.

Strengthening with incoherent precipitations is realized in Fe–Al–X systems, where solubility in solid state of the third element in Fe–Al phases is limited (for example, in Fe–Al–X systems, where X is the Ti, Zr, Nb and Ta). A significant strengthening effect can be generated by coherent precipitations, for example in Fe–Al–Ni system.

Titanium is of the highest interest as an alloying element. Its application allows realizing several mechanisms of iron intermetallic strengthening, namely structure ordering, strengthening with dispersed inclusions, formation of coherent microstructures. Titanium differs by significant solubility in solid state in Fe–Al phases that results in Fe_3Al structure stabilizing in relation to FeAl structure at high temperatures. Strengthening with dispersed precipitations of hexagonal Laves phase $(Fe, Al)_2Ti$ or $\tau_2$cubic phase of $Mg_{23}Th_6$ type can take place in addition to strengthening due to structure ordering in Fe–Al–Ti system. Besides, there is a specific range of composition in Fe–Al–Ti system where coherent structures [4] are formed. Such elements as chromium and zirconium with possibility of solid solution strengthening as well as magnesium and lanthanum, where strengthening with incoherent compounds can be expected, were used in present work in addition to titanium for alloying of Fe_3Al intermetallic based powder.

Powders of iron and aluminum alloys: (wt.%) Al1.5Cr1Zr, Al5Mg and Al5Mg1La, produced using melt nitrogen sputtering as well as powder of Ti35Al (T65Yu35) intermetallic, produced by calcium-hydrate recovery of oxides, were used as initial materials.

Shape of the particles of aluminum alloy powders produced by melt nitrogen sputtering as well as method of calcium-hydrate recovery is close to spherical one and their structure differs by homogeneity and absence of inner pores (Figure 1). Fraction of 40–100 μm size was used for feeding the powder mixture in MCS process.

Method of X-ray structural phase analysis (XSPA) determined that all initial aluminum alloys, except for titanium-aluminum, has a material structure representing itself aluminum lattice with insignificant variation of its parameter. This can indicate presence in them of solid solutions based on aluminum (Figure 2, *a*–*c*, Table 1). In the case of titanium-aluminum intermetallic (Figure 2, *d*) one phase, namely TiAl (γ-phase), was found in the powder.

MCS process was performed in planetary-type mill «Aktivator 2SL». Relationship of mass of balls to mass of powder made 10:1. The central axis of mill triboreactor was rotated with 100 rmp rate, drums rotated around their axis with 1500 rmp rate. Parts of the drum and milling agents were manufactured of steel ShKh15. MCS process was performed in air medium. Surface-active substances (SAS), namely oleic acid was

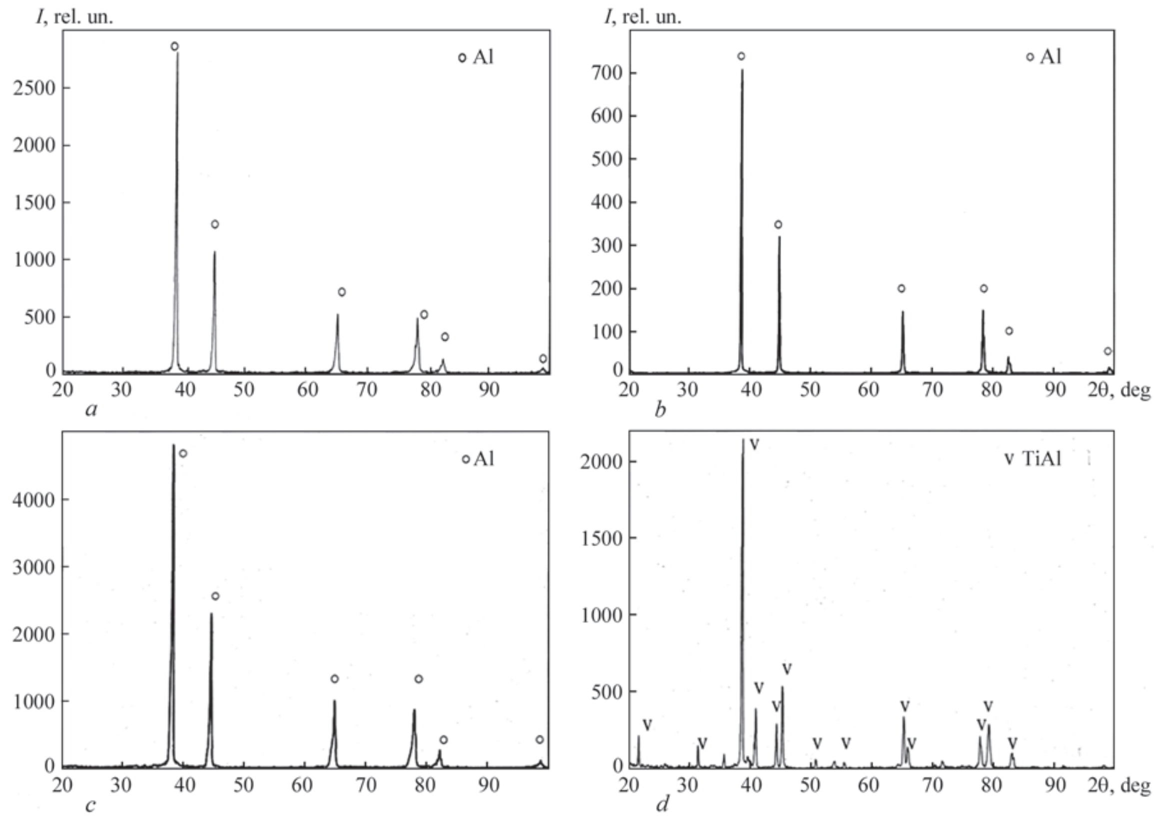

Figure 2. X-ray patterns of powders of aluminum alloys: *a* — Al1.5Cr1Zr; *b* — Al5Mg; *c* — Al5Mg1La; *d* — Ti35Al

added to the mixture to prevent pickup of processed charge on the milling agents and drum wall as well as intensification of process of new phases synthesis.

Amount of aluminum alloy powder, introduced in the mixture with iron powder was selected for the purpose of formation in MCS of $Fe_3(Al, X)$ intermetallics in the case of AlCrZr, AlMg and AlMgLa that corresponds to 14 wt.% of Al-alloy and $(Fe, Ti)_3Al$ in the case of TiAl intermetallic. In the latter variant amount of introduced TiAl made 39.2 wt.%.

Results and discussion. Structural and phase transformations, taking place in process of MCS, were examined on powder particles taken out of the drum with determined time intervals.

The metallographic examinations of powder mixtures showed that similar to non-alloyed powders of Fe–Al system [9], there is breaking of coarse particles and formation of conglomerates consisting of initial components at MCS process initial stages. Refinement of the formed conglomerates takes place next and in 5 h of processing the particles obtain awakward, chipped shape of < 40 μm particle size (Figure 3).

Examination of grain-size composition of the powders, carried using a device for dispersion determination ASOD-300, showed that 1.5 h processing promotes refinement up to < 30 μm size of more than 50 % of particle weight, and approximately 76 % of particles have size < 20 μm (Figure 4) after 5 h.

Examination of appearance of powder-products of MCS on scanning electron microscope (Figure 5) showed that coarse as well as most of fine (< 20 μm) particles represent themselves the conglomerates consisting of 1–2 μm size particles.

Examination of internal structure in all powders, produced by MCS method, determined the particles of three types, namely insufficiently dense particles of conglomerate type with distinguished intergrain boundaries (Figure 6, *a*); particles with dense lamellar structure, but non-uniform on coloring, and, probably, on composition (Figure 6, *b*) and monolithic, homogeneous on composition particles (Figure 6, *c*).

Particles of the first type prevail in the powders at the initial (0.5–1.5 h of processing) stages of synthesis. MCS products after five hours processing consist

Table 1. Characteristics of initial powders

Initial powder	Composition, wt.%	Microhardness, MPa	Phase composition, lattice parameter*
PZhR	99 Fe; 0.05 C; 0.05 Si	1500±230	Fe
Al1.5Cr1Zr	97.5 Al; 1.5 C; 1.0 Zr	3550±470	Solid solution Cr and Zr в Al, *a* = 0.4052 nm
Al5Mg	95.0 Al; 5.0 Mg	4920±510	Solid solution Mg in Al, *a* = 0.4072 nm
Al5Mg1La	94.0 Al; 5.0 Mg; 1.0 La	5780±1220	Solid solution Mg and La in Al, *a* = 0.4068 nm
Ti35Al	62.5 Ti; 37.5 Al	4400±1400	TiAl, *a* = 0.3986 nm; *c* = 0.4085 nm

*Parameter of aluminum lattice *a* = 0,4050 nm.

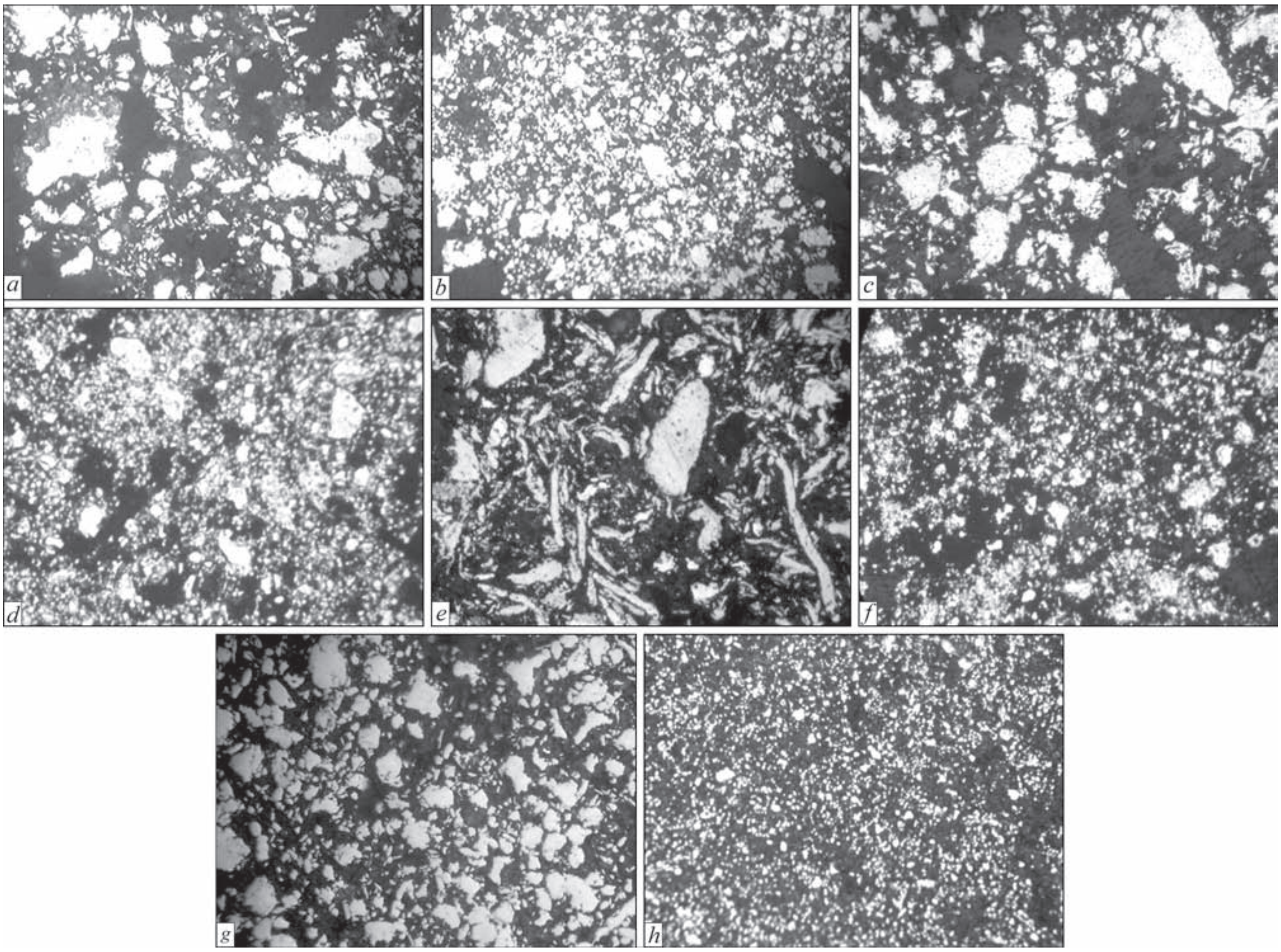

Figure 3. Microstructure (×400) of particles of alloyed powders produced from charge: 86 Fe+14 Al1.5Cr1Zr (*a*, *b*), 86 Fe + 14 Al5Mg (*c*, *d*), 86 Fe + 14 Al5Mg1La (*e*, *f*), 60.8 Fe + 39.2 TiAl (*g*, *h*), in planetary mill during 0.5 (*a*, *c*, *e*, *g*) and 5.0 h (*b*, *d*, *f*, *h*)

of monolithic, homogeneous on structure and composition particles.

Method of X-ray structural phase analysis (Figure 7, Table 2) determined that MCS process after 5 h of processing forms the particles in the mixtures of iron with aluminum alloys AlCrZr, AlMg and AlMgLa. These particles represent themselves solid solutions of alloying elements in Fe_3Al intermetallic lattice.

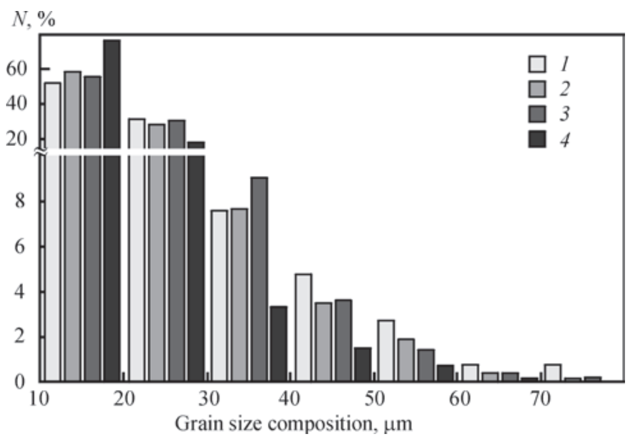

Figure 4. Histogram of distribution (*N*) of size of particles of MCS powder-products of Fe_3Al composition depending on processing time: *1* — 0.5; *2* — 1.5; *3* — 3.0; *4* — 50 h

Complex iron-titanium aluminide — $(FeTi)_3Al$ [12] is formed in the case of MCS in the mixture of iron with titanium-aluminum intermetallic.

Microdurometer examinations of the MCS produced products showed that increase of their microhardness takes place in process of powder processing. At that the maximum growth of microhardness value takes place at powder mixture processing during first 1.5 h (Table 2, Figure 8). It is related with change of structure dispersion that is indicated by decrease of particle size and area of coherent dissipation.

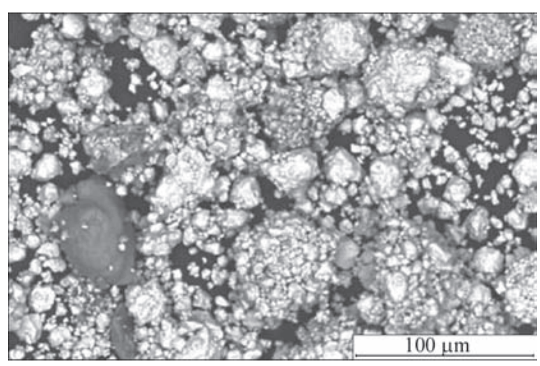

Figure 5. Appearance of particles of MCS powder-product perceived after five hours processing of Fe + TiAl charge in planetary mill

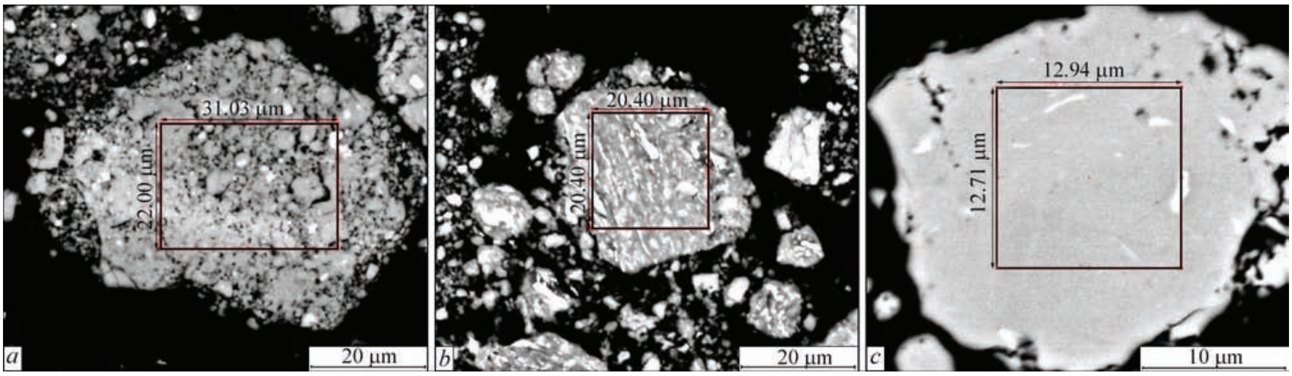

Figure 6. Types of powder structures at initial (*a*), intermediate (*b*) and final stages of MCS process

Earlier carried investigations of phase and structural transformations in synthesis of Fe–Al system intermetallics using MCS method [11] showed that the process consists of a range of sequential stages, namely *1* — refinement of particles of initial Fe and Al powders and formation of the conglomerates; *2* — interphase interaction of the components with formation of Al solid solution in Fe; *3* — formation of Fe(Al) solid solution mixture and intermetallic phase Fe_3Al; *4* — formation of single phase Fe_3Al product. Analysis of XSPA data, received in the present work, showed that such a mechanism takes place in the synthesis of alloyed Fe_3Al(Cr, Zr), Fe_3Al(Mg), Fe_3Al-(Mg, La) powders. All three cases have a Fe_3Al lattice with somewhat different values of the parameter and increased microhardness (Table 2) that is related with formation of solid solutions of alloying elements in Fe_3Al lattice. In Fe–TiAl system the phase transformations in MCS process are accompanied by gradual decrease of TiAl in the charge, formation of ferrotitanium and solution of Al in its lattice (Figure 9) up to formation of $(Fe, Ti)_3Al$ intermetallic. Except for increase of parameter of solid solution lattice from 0.2870 till 0.2937 nm, there is an broadening of the lines of $(Fe, Ti)_3Al$ as well as TiAl intermetallics up to complete disappearance of the latter in five hours processing of the charge.

Breaking of the powder particles as well as their deformation take place in MCS, therefore broadening of the reflection lines on X-ray patterns can be a consequence of both these reasons. Division of these effects, as it well known, is based on different dependence of

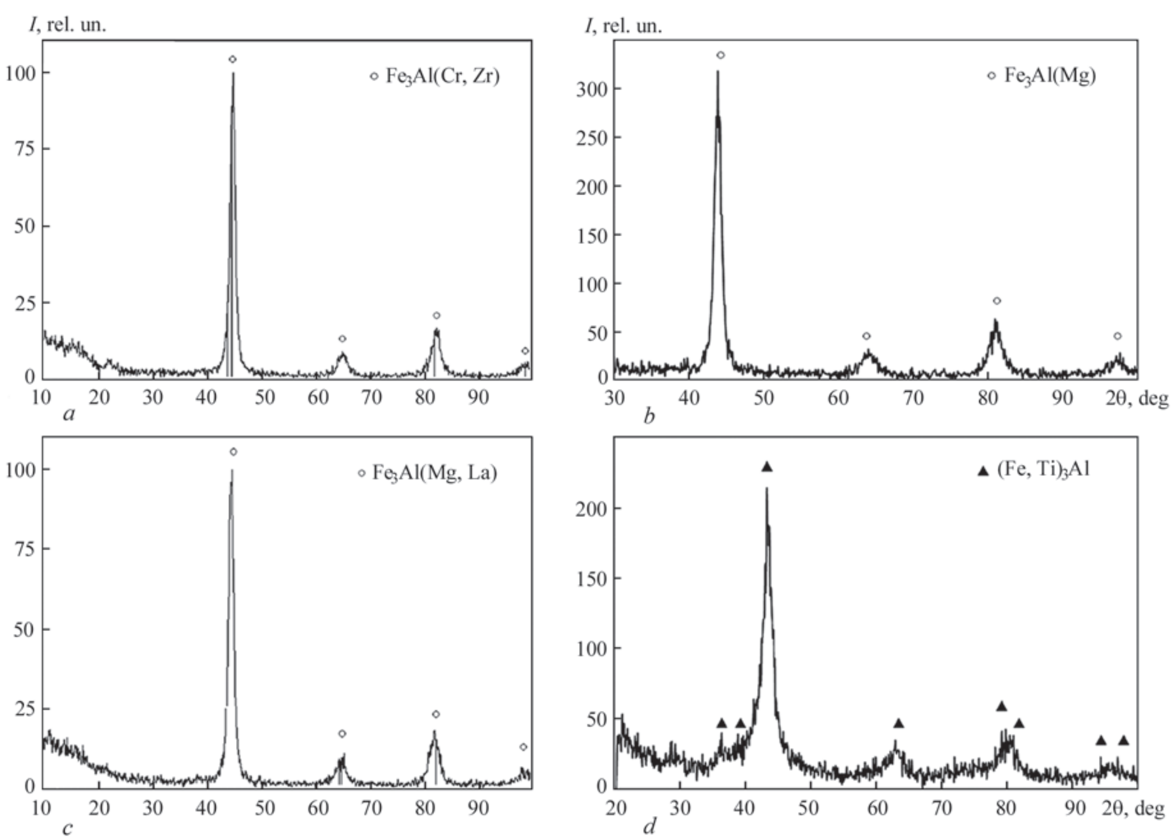

Figure 7. X-ray patterns of powders produced by MCS method in planetary mill during 5 h of mixtures (wt.%): *a* — 86 Fe + 14 Al1.5Cr1Zr; *b* — 86 Fe + 14 Al5Mg; *c* — 86 Fe + 14 Al5Mg1La, *d* — 60.8 Fe + 39.2 TiAl

Table 2. Characteristics of alloyed powders based on Fe_3Al intermetallic produced by MCS

Mixture content, wt.%	Time of milling, h	MCS product		
		Microhardness* HV 0.01. MPa	Phase composition	Lattice parameter a^*, nm
86 Fe + 14 Al1.5Cr1Zr	0.5	1680±440	Fe, solid solution Cr and Zr in Al	–
	1.5	3490±1040	–	–
	3	3550±710	–	–
	5	3840±800	Solid solution Cr and Zr in Fe_3Al	0.5974
86 Fe + 14 Al5Mg	0.5	2300±400	Solid solution Mg in Al	–
	1.5	5320±730	–	–
	3	4590±1050	–	–
	5	4630±950	Solid solution Mg in Fe_3Al	0.5812
86 Fe + 14 Al5Mg1La	0.5	980±240	Fe, solid solution Mg and La in Fe_3Al	–
	1.5	3860±500	–	–
	3	3950±1120	–	–
	5	5580±840	Solid solution Mg and La in Fe_3Al	0.5792
60.8 Fe+39.2 TiAl	0.5	4400±1400	FeTi. FeAl	–
	1.5	7830±2070	–	–
	3	7170±1960	–	–
	5	7600±2190	$(Fe, Ti)_3Al$	0.2937

*In the case of MCS product with Fe_3Al composition, HV0.01-4060 ± 1010 MPa, a = 0.5787 nm.

increment of lines broadening on value of Bragg angle θ. Evaluation of coherent scattering area (CSA) of MCS products after processing of powders of Fe–TiAl system during 0.5–5.0 h was carried out in present work. The width of reflection lines was measured at half of their height with their doubling correction.

A template was made for taking into account an instrumental line broadening under similar conditions. It was produced of powder of superpure carbonyl iron. Then, real β broadening of X-ray lines of specimen makes

$$\beta = \sqrt{B^2 - b^2},$$

where B is the experimental width of lines of examined specimen; b is the template line width.

CSA value was determined on Scherrer formula $D = \kappa\lambda/\beta\cos\theta$, where $\kappa \approx 1$ is the Scherrer constant; λ is the wave length of used radiation (for Cu-K_α λ = 0.15418 nm); θ is the reflection angle.

Carried evaluations showed that a product with nanodispersed structure (CSA 10-40 nm) is formed at all stages of synthesis of Fe–Ti–Al intermetallics, made using MCS method. Approximately the same CSA values, namely 10–30 nm, were received using a program for harmonic PDXL analysis, which is included in Rigaku X-ray unit (CSA at MCS time increase from 0.5 to 5 h decreased from 30 to 10 nm).

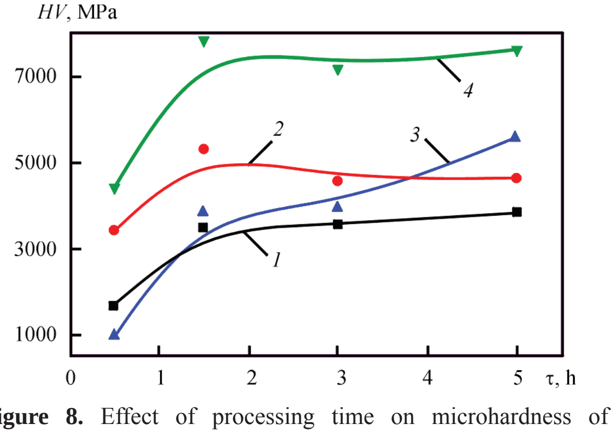

Figure 8. Effect of processing time on microhardness of MCS product — powders produced of mixtures *1* — 86Fe + 14Al1.5Cr1Zr; *2* — 86Fe + 14Al5Mg; *3* — 86Fe + 14 Al5Mg1La; *4* — 60.8Fe + 39.2TiAl

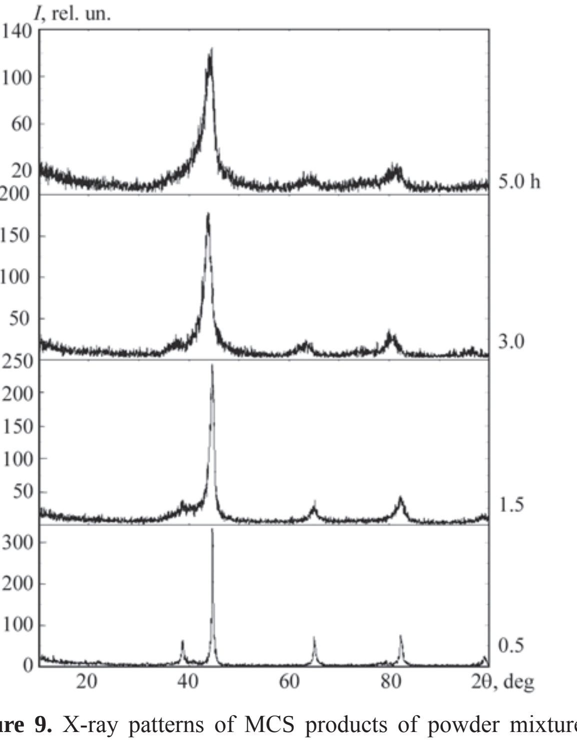

Figure 9. X-ray patterns of MCS products of powder mixture (wt.%) 61Fe + 39TiAl depending on processing time

Thus, it can be stated that a product with nanodispersed structure is formed when producing alloyed powders based on Fe_3Al intermetallic by means of MCS technology.

Effect of alloying on heat resistance of Fe_3Al intermetallic powders was investigated on derivatograph of Q-1500 D grade (Hungary) in air atmosphere at heating rate 10 deg/min to 1000 °C temperature. Powder weight was located in preliminary burnt to necessary temperature crucible of ZrO_2, cross-section area of which made $1\cdot10^{-4}$ m^2, and continuously weighed during all thermal cycle with $5\cdot10^{-4}$ g accuracy.

One of the peculiarities of powders oxidation as a result of their sintering is decrease of free surface in process of thermal cycle. Since there is no mathematical dependence of its change for investigated materials, the value of specific weight increment was determined as relationship of specimen mass increase to initial weight value.

Comparing the thermal gravimetric curves of alloyed powders with unalloyed Fe_3Al (Figure 10), we can evaluate effect of alloying elements on temperature of process start and its intensity in all temperature interval in comparison with Fe_3Al. Such elements as Mg, Mg + La, Cr + Zr rise the temperature of oxidation start from 300 to 500–540 °C, at that oxidation intensity decreases. Titanium alloying in contrast reduces the temperature of oxidation start, and significantly rises its intensity. Thus, investigated powder on oxidation resistance parameter should be ranged as $(Fe, Ti)_3Al \rightarrow Fe_3Al \rightarrow Fe_3Al(Mg) \rightarrow Fe_3Al(Cr, Zr)$.

Conclusions

1. Iron aluminide powders, alloyed with Ti, Mg, Cr, Zr, La, were produced by mechanochemical synthesis method by means of introduction of aluminum alloys (Al5Mg, Al1.5Cr1Zr, Al5Mg1La) or titanium aluminide (TiAl) in the charge.

2. Mechanism of formation of particles alloyed with powders based on Fe_3Al as well as non-alloyed particles Fe_3Al consists of a series of subsequent stages, namely formation of conglomerates of mixture of initial powders of Fe and Al-alloys, formation of solid solutions of alloying elements Mg, Cr, Zr and La in Fe_3Al lattice or solid solution of Al in FeTi lattice, transformation of solid solutions in single-phase products $Fe_3Al(Cr, Zr)$, $Fe_3Al(Mg)$, $Fe_3Al(Mg, La)$, $(Fe, Ti)_3Al$ having nanodispersed structure (CSA size = 10–30 nm).

3. Magnesium, lanthanum and, in particular, titanium alloying of Fe_3Al powder provokes increase of their microhardness. Powder resistance to oxidation, measured in non-isothermal conditions in heating on air to 1000 °C, rises for all alloying elements except for titanium.

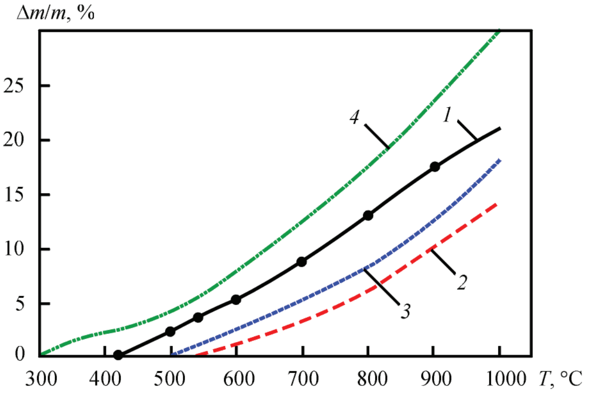

Figure 10. Specific increase of weight of powders in heating on air: *1* — Fe_3Al; *2* — $Fe_3Al(Cr, Zr)$; *3* — $Fe_3Al(Mg)$; *4* — $(Fe, Ti)_3Al$

4. Developed powders of alloyed iron aluminide, produced by mechanochemical synthesis method, are designed for deposition of heat-resistant thermal coatings, including for applications in sulfur-containing media (in form of powders or filler for powder wire).

1. Sinelnikova, V.S., Podergin, V.A., Rechkin, V.N. (1965) *Aluminides*. Kiev: Naukova Dumka.
2. Deevi, S.C., Sikka, V.K. (1996) Nickel and iron aluminides: An overview on properties, processing and applications. *Intermetallics*, **4**, 357–375.
3. Stoloff, N.S. (1998) Iron aluminides: present status and future prospects. *Mater. Sci. Eng., A*, **258**, 1–14.
4. Palm, M. (2005) Concepts derived from phase diagram studies for the strengthening of Fe–Al-based alloys. *Intermetallics*, **13**, 1286–1295.
5. Hadef, F. (2016) Solid-state reactions during mechanical alloying of ternary Fe–Al–X (X = Ni, Mn, Cu, Ti, Cr, B, Si systems: A review. *J. Magn. Magn. Mater*., **419**, 105–118.
6. Guilemany, J.M., Cinca, N., Cassas, L., Molins, E. (2009) Ordering and disordering processes in MA and MM intermetallic iron aluminide powders. *J. Mater. Sci*., **44**, 2152–2161.
7. Borisova, A.L., Adeeva, L.I., Tunik, A.Yu. et al. (2009) Investigation of powders of Al–Cu–Fe–Ti–Cr–Si system for thermal spraying produced by mechanochemical synthesis with subsequent annealing. *Poroshk. Metallurgiya*, **9–10**, 31–42.
8. Borisov, Yu.S., Borisova, A.L., Adeeva, L.I. et al. (2010) Production of powders for thermal coatings by methods of mechanical alloying and mechanochemical synthesis. *Svarochn. Proizvodstvo*, **12**, 18–22.
9. Magnef, A., Offergeld, E., Leroy, M., Lefort, A. (1998) Fe–Al intermetallic coating application to thermal energy conversion advanced systems. In: *Proc. of 15th ITSC* (Nice, France), 1091–1096.
10. Xiao, Ch. (2006) Sulfidation resistance of CeO_2-modified HVOF sprayed Fe-Al coatings at 700 °C. *Surf. Coat. Technol*., **201**, 3625–3632.
11. Borisova, A.L., Timofeeva, I.I., Vasilkovskaya, M.A. et al. (2015) Phase and structure transformations in formation of powders of FeAl system intermetallics using mechanochemical synthesis method. *Poroshk. Metallurgiya*, **7–8**, 135–143.
12. Rafiei, M., Enayati, M.N., Karimzadeh, F. (2009) Caracterization and formation mechanism of nanocrystalline $(Fe, Ti)_3Al$ intermetallic compound prepared by mechanical alloying. *J. of Alloys and Compounds*, **480**, 392–396.

Received 18.05.2017