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DETONATION COATINGS OF INTERMETALLIC POWDERS OF Fe–Al SYSTEM PRODUCED USING MECHANICAL ALLOYING

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Structure, composition and microhardness of detonation coatings were examined. They were received using Fe_2Al, FeAl and Fe_2Al_5 intermetallic powders, produced by mechanical alloying (MA) method, and mixtures of Fe and Al powders of equivalent compositions. An effect of «oxygen–combustible gas» relationship in the detonation mixture on oxidation process of material being sprayed was determined. The results of determination of phase composition of the coatings, deposited using different powders, show that in case of application of mechanical mixtures a layer mainly consists of the particles of Fe and Al initial mixture. A structure of coatings of MA Fe–Al-powders contains mixture of heating and oxidation products of these powders. Microhardness of the coatings varies from 4580 to 5710 MPa depending on composition. 21 Ref., 3 Tables, 8 Figures.

Keywords: *detonation spraying, iron aluminides, powders, mechanical alloying, composition of detonation mixture, coatings, phase composition, microhardness*

Due to low strength properties of iron aluminides, in particular at room temperature [1, 2], a reasonable way of practical application of their high wear and corrosion resistance in the aggressive high-temperature gas media is development of protective coatings, including ones received by thermal spraying (TS) of Fe-Al based powders [3, 4]. The main bulk of work in this area was carried out in the USA (Oak Ridge Nat. Lab., Idaho Nat. Lab) [5, 6] and Western Europe, namely France (University of Technology of Belfort-Montbéliard, Lille University) and Spain (Barcelona University) using plasma and HVOF spraying [7–11].

A range of investigations on examination of structure and properties of Fe–Al coatings, produced by detonation spraying method, was carried out at Military University in Warsaw [12, 13]. Fe–Al alloy powders, produced using Fe–28Al–2Cr and Fe–40Al–0.05Zr–0.01V at.%, melt spraying with inert gas, were applied as coating deposition materials at indicated operations fulfillment. The disadvantage of this method of Fe–Al powder production is the difficulties related with melting of such alloys, initial components of which are characterized with large difference in melting temperatures and high exothermicity of alloy forming.

Simpler and less cost-based method of intermetallic powder production is application of MA process, which is realized under conditions of high-energy treatment of powder mixtures in the ball planetary-type or vibration mills [14, 15]. This allows to significant extent remove limitations in compositions of developed intermetallics and provides the possibility of chemical and phase homogeneity of the synthesized powders. In MA all reactions are in solid phase, therefore, there is no problem related with appearance of fluctuations in a liquid phase concentration during remelting. Works [16–18] present practical application of powders of Fe–Al intermetallics, produced by MA, for deposition of thermal coatings, including with nanosized structure.

Investigation of formation of Fe_2Al, FeAl and Fe_2Al_5 intermetallic powders under conditions of MA process with examination of phase and structural transformations was carried out in work [19].

Aim of the present paper lied in examination of structure and phase composition of detonation coatings of Fe_2Al, FeAl and Fe_2Al_5 intermetallic powders, made by MA method, and of mechanical mixtures of Fe + Al powders meant for production of intermetallics of the same composition in process of their spraying.

Sampling of powder particles, which were treated using a jet of detonation products in a water pool with analysis of their shape, size and structure, was carried out for evaluation of effect of parameters of

Table 1. Characteristic of powders based on Fe–Al for TS

Composition	Production method	H_μ, MPa	Phase composition
86Fe + 14Al (wt.%)	Mechanical mixture	1500±230 (Fe), 330±50 (Al)	Fe, Al
Fe_3Al	MA	4060±1010	Fe_3Al c a = 0,5787 nm
67Fe + 33Al (wt.%)	Mechanical mixture	1500±230 (Fe), 330±50 (Al)	Fe, Al
FeAl	MA	2530±740	FeAl c a = 0,2928 nm
45Fe + 55Al (wt.%)	Mechanical mixture	1500±230 (Fe), 330±50 (Al)	Fe, Al
Fe_2Al_5	MA	2560±800	Fe_2Al_5, additive FeAl

detonation spraying (DS) on conditions of heating of Fe–Al powders and development of process of their oxidation. «Splat–test» was also used for analysis of shape and size of the particles, which were subjected to deformation at collision with the basis.

Effect of the following DS parameters, namely consumption of dilution gas (air) and relationship of oxygen to combustible gas (β) consumption, were investigated at that. The latter have impact on temperature and velocity of the jet and detonation products. MA process was carried out by means of processing of Fe + Al powder mixture in a planetary-type ball mill with crushing cylinder rate 1500 rpm, that of central axis was 1000 rpm during 5 hours. The mechanical mixtures were made in a laboratory attritor by mixing in course of 5 min. Powders of MA conglomerated products and mechanical mixtures of Fe + Al powders with particles of 40–80 μm size were used for coating deposition. Table 1 shows the characteristics powders for TS.

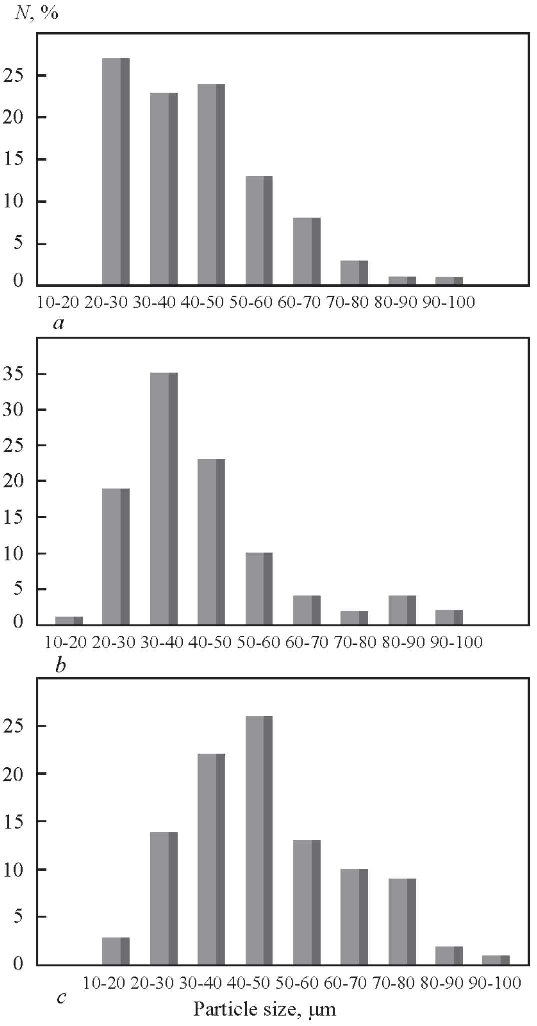

Figure 1. Block diagram of size distribution of particles of Fe_3Al powder, sprayed in water at air consumption: *a* — 0.4; *b* — 0.6; *c* — 0.9 m^3/h (consumption of propane-butane 0.45, oxygen 1.55 m^3/h, spraying distance 110 mm)

Spraying of the coatings was carried out on «PERUN-S» unit. The following was used as the main operation parameters:

Combustible gas composition	propane–butane mixture ($60C_3H_8 + 40C_4H_{10}$, vol. %)
Dilution gas	air
Transporting air, m^3/h	0.4
Shot frequency, min	400
Powder loading, mg/shot	120
Depth of powder loading, mm	250

Consumption of propane-butane made 0.45 and that of oxygen was 1.55 m^3/h. It was as a basic DS mode for investigation of effect of dilution air consumption on dispersion of powder being sprayed. Air consumption was varied in 0.4; 0.6 and 0.9 m^3/h range. Sampling of the particles in the water pool was carried out at 50 mm distance from unit shank edge. Figure 1 shows block diagrams of size distribution of treatment particle-products in a detonation jet of Fe_3Al powder (Table 1). It can be concluded that breakdown of a part of conglomerated particles takes place in process of powder feeding in the unit shank and as a result of effect of detonation product jet. This provokes appearance of powder fraction of particle size less than 40 μm, portion of which makes 40–55 % depending on dilution air consumption. The largest refining level, namely 55 %, was found in the case of its consumption equal 0.6 m^3/h (Figure 1, *b*).

Decrease of particle size, on the one hand, improves conditions of their heating, and, on the other hand, rises relative size of free surface that can effect a level of sprayed material oxidation.

Effect of β index on oxidability and microhardness of coatings of Fe_3Al powder was evaluated by measurement of oxygen consumption in 0.80 to 1.75 m^3/h

Table 2. Effect of relationship of consumption of oxygen and propane-butane content in detonation mixture β on amount of oxides and microhardness of Fe–Al coatings

Oxygen consumption, m^3/h	Relationship of oxidizer and combustion gas		H_μ, MPa	Content of oxides on XSPA data (vol.%)
	β	β`		
0.8	1.6	2.04	3900±520	<5
1.05	2.10	2.54	4230±790	~5
1.3	2.6	3.04	4520±610	~10
1.55	3.1	3.54	4620±680	40
1.75	3.5	3.90	5767±1280	~50

Note. Consumption of propane–butane 0.5; dilution air 0.65; transporting air 0.4 m^3/h; spraying distance 110 mm.

limits at constant consumption of propane-butane 0.5 m^3/h, dilution air 0.65 m^3/h and transporting air 0.4 m^3/h. This corresponds to β variation in 1.6–3.5 range, and taking into account air oxygen β' (relationship of total oxygen (oxygen + air) to combustible gas) made 2.04–3.90. Table 2 shows the experiment results.

Content of oxides in the coating was evaluated on the results of metallographic and X-ray structural phase analysis (XSPA). Figure 2 as an example shows the fragments of X-ray images of detonation coatings, received at different relationship of oxygen and propane-butane in the detonation mixture. On them the areas with numbers 1 and 2 refer to metallic constituent of the coating (intermetallic Fe_3Al and solid solution Al in Fe) and areas with numbers 3, 4 and 5 are the reflections from oxide phases (Fe_3O_4, $FeAl_2O_4$). Relative content of metallic and oxide phases in the coating (Table 2) was evaluated using the relationship of their X-ray reflection intensity.

Rapid increase of oxide content at transfer of oxygen consumption from 1.3 to 1.55 and β value from 3.0 to 3.5 can be explained by change of mode of combustible gas burning from incomplete (with formation of CO and H_2O) to complete one (CO_2 and H_2O). This results in rise of temperature and velocity of detonation products jet with overheating of the powder particles [20, 21].

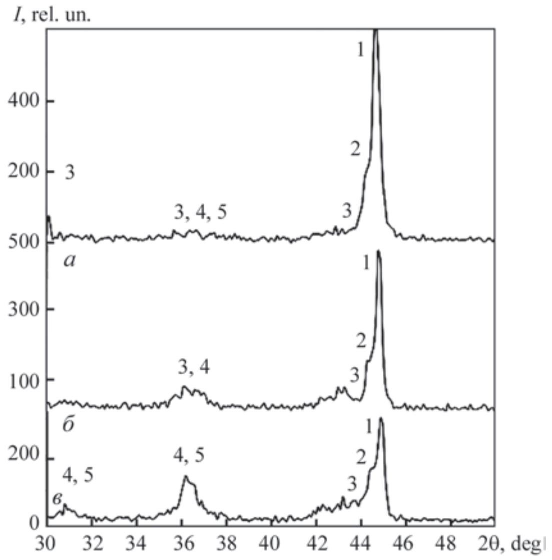

Figure 2. Fragments of X-ray image of detonation coatings, received at different relationship of oxygen and propane-butane in detonation mixture β: *a* — 2.1; *b* — 2.6; *c* — 3.1 (descriptions 1–5 see in the text)

This phenomenon was found in study of dependence of splat shape (deformed particles of sprayed powder) on spraying conditions, in particular, relationship of oxygen and combustion gas consumption. Figure 3 represents the splats, received at β = 2.2; 4.1 and 4.6. In the second and third cases the splats were formed from the particles of overheated melt, having low ductility and including oxide phase.

A mode for spraying of detonation coatings of mechanical mixtures and MA powders of Fe–Al system was selected based on the results of carried experiments on index of oxidation level of the sprayed material particles. This was used for producing coating samples and further examination of their structure, phase composition and microhardness:

Mixture consumption 60 % C_3H_8 + 40 % C_4H_{10}, m^3/h	0.5
Oxygen consumption, m^3/h	1.3
Dilution air consumption, m^3/h	0.6
Spraying distance, mm	110

The following was determined as a result of examination of structure of the detonation coatings of

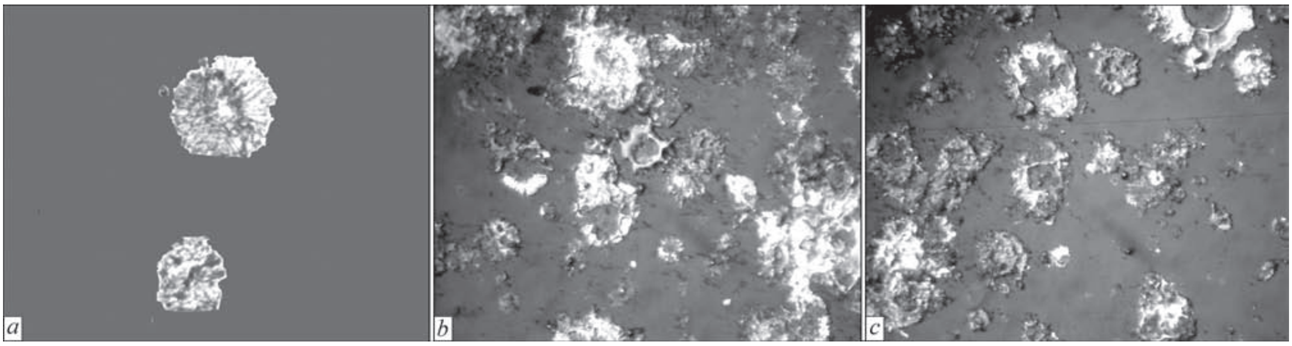

Figure 3. Splats of detonation coatings of Fe_3Al at different relationship of «oxygen–propane–butane» consumption (×500):β = 2.2 (*a*), 4.1 *(b)*, 4.6 (*c*)

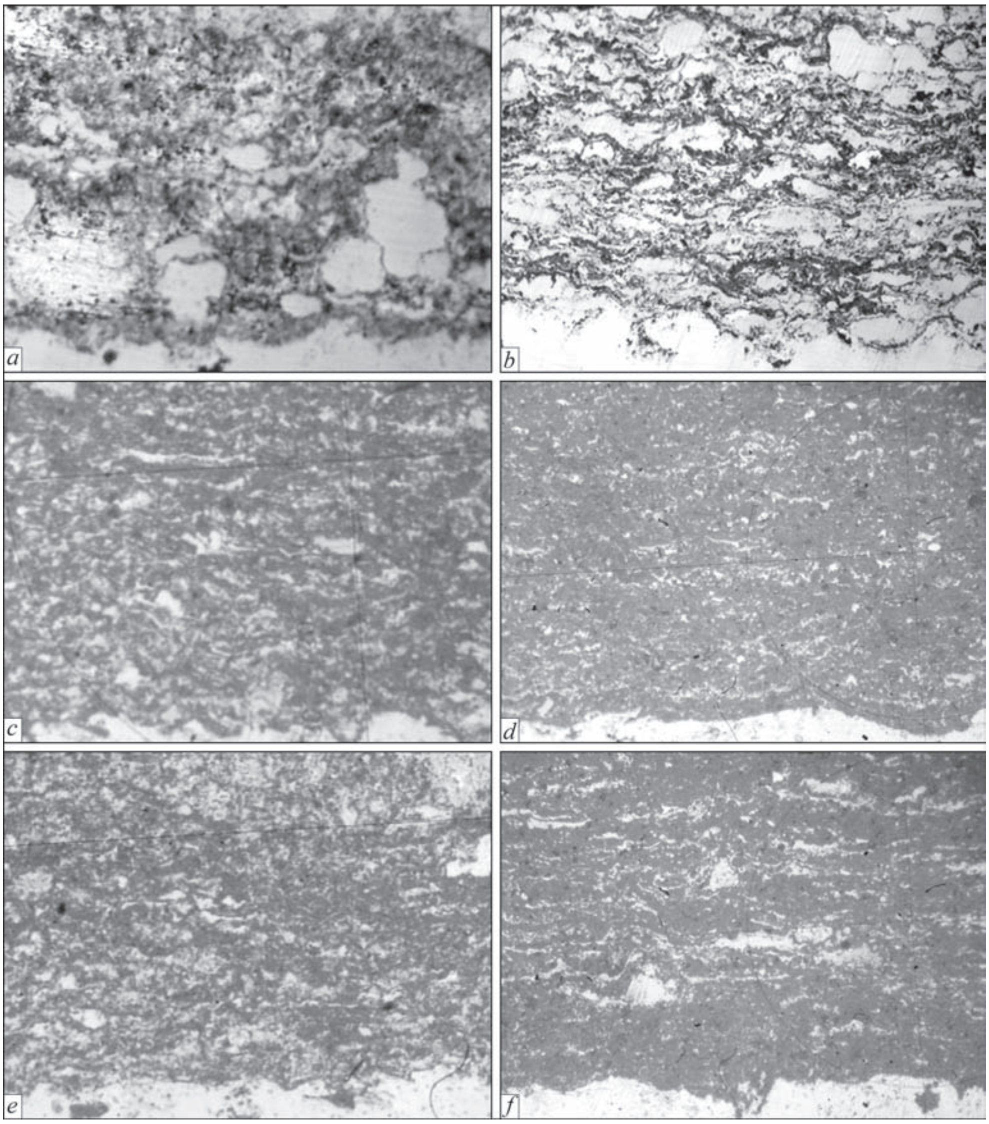

Figure 4. Microstructure (×400) of detonation coatings: of mechanical mixture, wt.%: *a* — 86Fe + 14Al; *c* — 67Fe + 33Al; *e* — 45Fe + 55Al; of intermetallic powder: *b* — Fe_3Al; *d* — FeAl; *f* — Fe_2Al_5

Fe–Al system intermetallic powders of three compositions as well as Fe + Al powder mixtures, meant for obtaining the same compositions in spraying.

Coarse grain dense structure is formed in process of spraying of mechanical mixtures, at that defects and delaminations at the boundary with basis are absent (Figure 4, *a*, *c*, *e*). Structure of coatings from MA-powders is fine, lamellar with alteration of light (metallic) and dark (oxide) lamellas (Figure 4, *b*, *d*, *f*).

According to XSPA data it was determined, that a level of interfacial interaction of the components does not provide realization of synthesis process of corre-

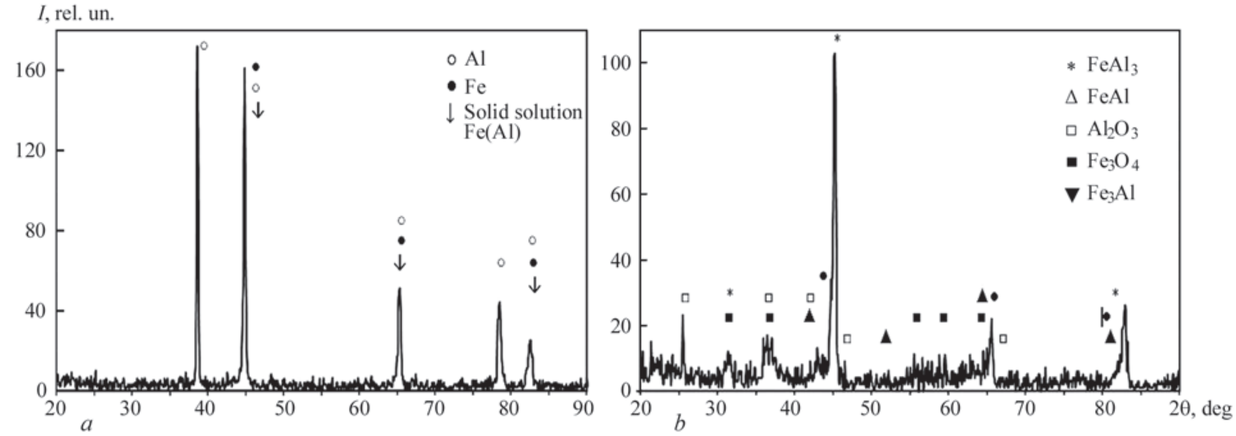

Figure 5. X-ray images of detonation coatings: *a* — of mechanical mixture 86Fe + 14 Al (wt.%); *b* — of MA-powder Fe_3Al

Table 3. Characteristics of detonation coatings of Fe–Al powders, produced by mechanical mixing and MA method

Powder		Coating		
Composition	Method for production	H_μ, MPa	XSPA	Microstructure characteristics
86Fe + 14Al (wt.%)	Mechanical mixture	1490±240 (650, 1250)	Solid solution Fe(Al), Al, Fe	Coating is dense, coarse grain, formed of a bit fused undeformed particles of initial powders and solid solution
Fe_3Al	MA	4580±860 (4500)	Fe_3Al, FeAl, $FeAl_3$, Al_2O_3, Fe_3O_4, $FeAl_2O_4$	Structure is lamellar with alternating interlayers of intermetallic and oxide lamellas
67Fe + 33Al (wt.%)	Mechanical mixture	3640±1210 (2350, 5050)	Fe, Al, FeAl, Fe_3O_4, $FeAl_2O_4$	Coating is dense, structure is lamellar, with alternation of oxide metallic lamellas, unmelted metallic particles are found
FeAl	MA	5575±1020 (4750)	Fe, Fe(Al), FeAl, Fe_3O_4, $FeAl_2O_4$	Structure of coating is fine lamellar, without cracks and delaminations from basis
45Fe + 55Al (wt.%)	Mechanical mixture	2000±700 (1100, 2300)	Al, Fe, FeAl, Fe(Al), Al_2O_3, Fe_3O_4	Structure of coating is coarse grain with iron particle inclusions
Fe_2Al_5	MA	5710±1070 (6150)	Fe, FeAl, Fe_2Al_5, Al_2O_3, Fe_3O_4, $FeAl_2O_4$	Coating is dense with fine lamellar structure, without cracks and delaminations from basis

*Given are average and in the brackets the most possible values of coating microhardness.

sponding to calculated intermetallic phases under conditions of detonation spraying of mechanical mixtures of Fe and Al powders, initial Fe and Al components are preserved in the coatings. Intermetallic phases are found in small quantity together with aluminum and iron oxides (Figure 5, *a*, 6, *a*, 7, *a*, Table 3).

Phase composition of coatings of MA powders also does not have complete correspondence with composition of the initial powders. Intermetallic powders are found in the coatings of Fe_3Al(Fe_3Al, FeAl, $FeAl_3$), FeAl (FeAl), Fe_2Al_5(FeAl, Fe_2Al_5) powders. In the case of FeAl and Fe_2Al_5 powders these are mainly solid solutions of aluminum in iron. Iron, aluminum oxides and complex oxides (Figure 5, *b*, 6, *b*, 7, *b*, Table 3) were formed as a result of interaction with environment.

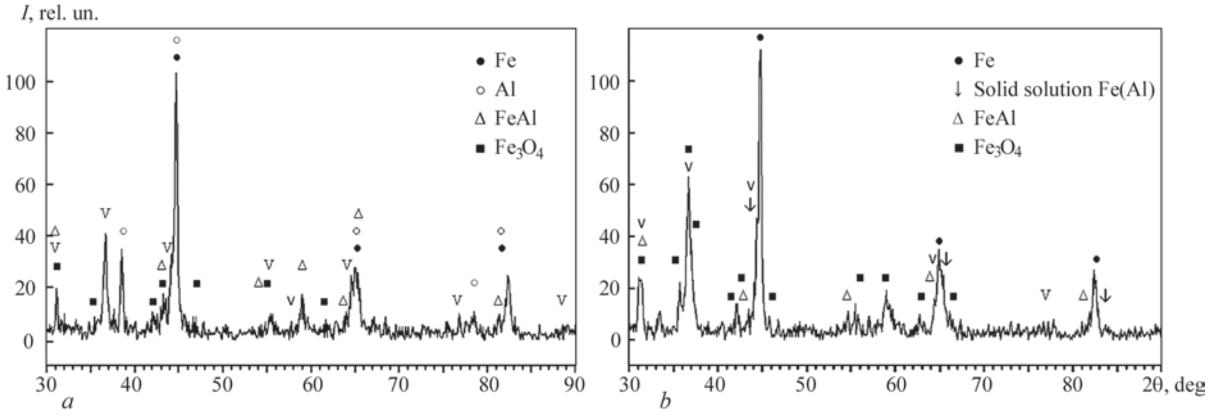

Figure 6. X-ray images of detonation coatings: *a* — of mechanical mixture 67Fe + 33Al (wt.%); *b* — of MA-powder FeAl

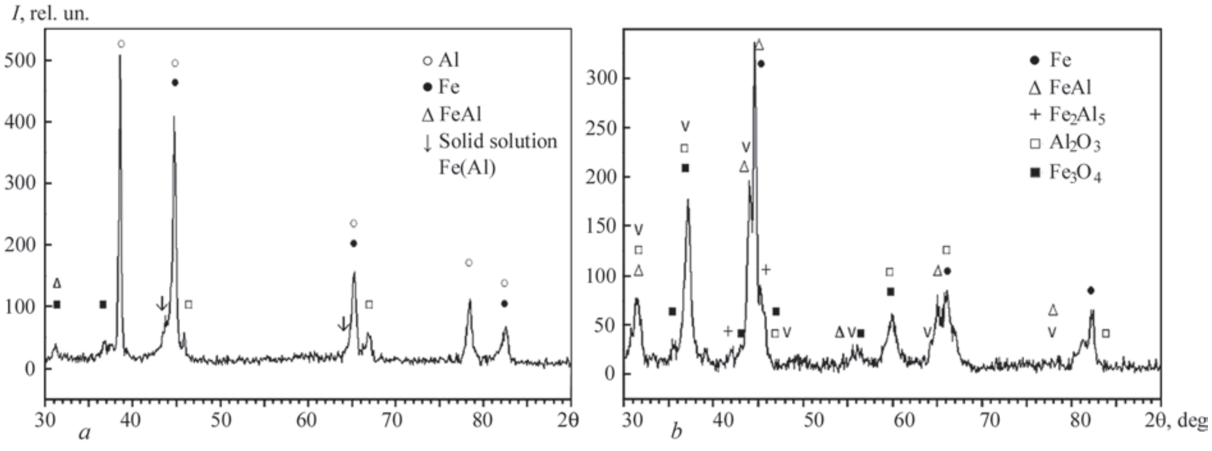

Figure 7. X-ray images of detonation coatings: *a* — of mechanical mixture 45Fe + 55Al (wt.%); *b* — of MA-powder Fe_2Al_5

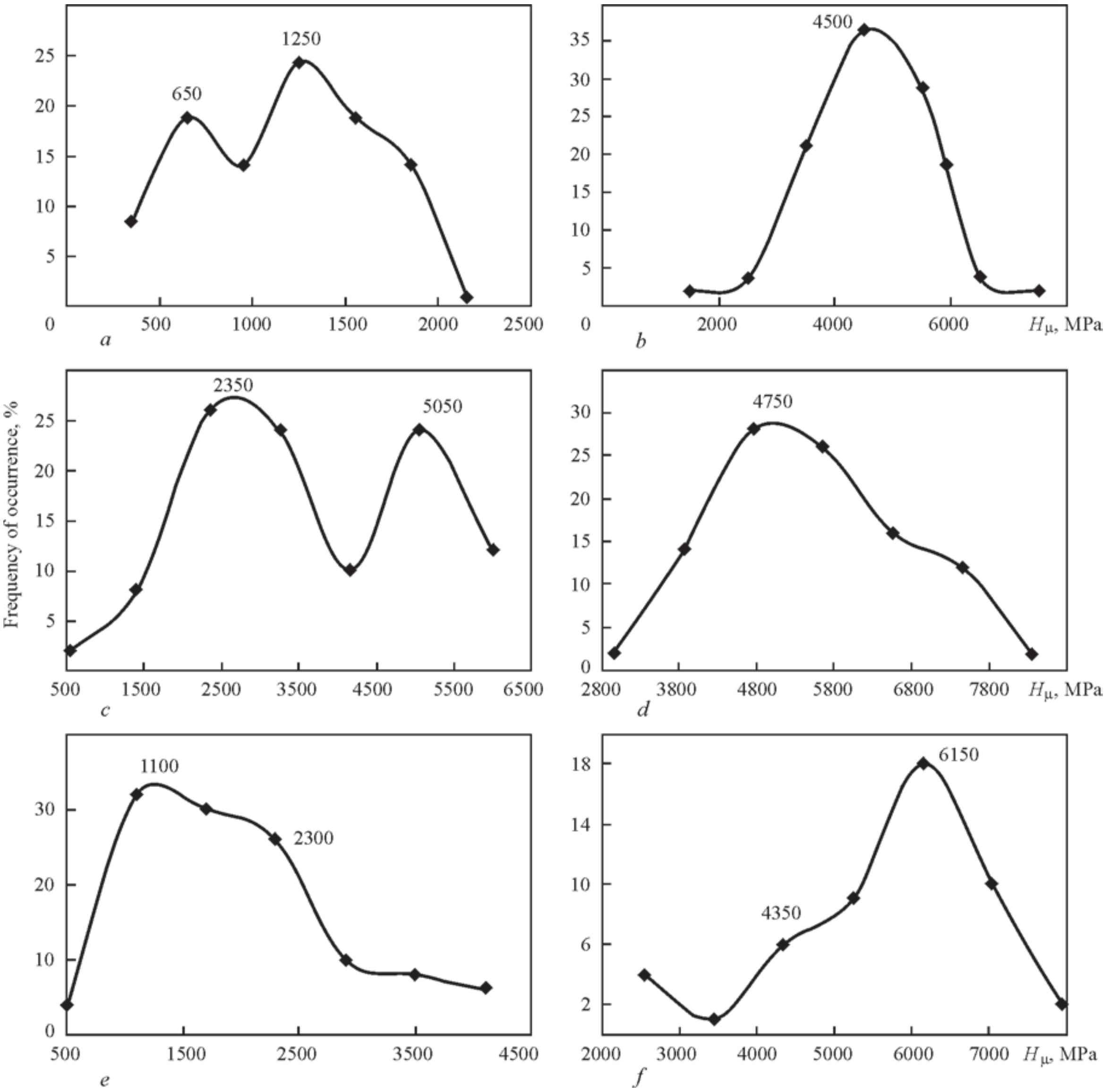

Figure 8. Variation curves of microhardness of detonation coatings, produced from mechanical mixtures Fe + Al (*a*, *c*, *e*) and MA (*b*, *d*, *f*) powders: *a*, *b* — Fe_3Al; *c*, *d* — FeAl; *e*, *f* — Fe_2Al_5

The microhardness variation curves were plotted (Figure 8) based on the results of microhardness measurement in detonation coatings of Fe + Al mechanical mixtures and Fe_3Al, FeAl, Fe_2Al_5 MA powders. Nature of the variation curves indicates homogeneous distribution of microhardness for coatings of powder with Fe_3Al initial composition (Figure 8, *b*). At that, average (4580±860) as well as the most probable (4500 MPa) values of microhardness exceed the results for initial powder (4060±1010 MPa, Table 1). More significant increase of coating microhardness in comparison with initial powder is observed for two other compositions (FeAl and Fe_2Al_5 intermetallics). It is obviously related with presence of large amount of oxides in sprayed coatings.

Conclusions

1. Detonation Fe–Al coatings are formed using intermetallic Fe_3Al, FeAl and Fe_2Al_5 powders obtained using MA method and mixture of Fe and Al powders with composition corresponding to these intermetallics.

2. It is determined that process of detonation spraying provokes variation of initial grain-size composition of Fe–Al powder with 40–80 μm conglomerated structure resulting in appearance of 40–55 wt.% fraction of 10–40 μm size.

3. Analysis of development of oxidation process in sprayed material of Fe–Al coating, carried with the help of XSPA and splat-test, showed dependence of content of oxide phase on relationship of oxygen to propane-butane amount in detonation mixture β. Rapid increase of oxide content from approximately 5 to 30–40 wt.% takes place at rise of β more than 3.5.

4. It is determined that conditions of detonation spraying using mechanical mixtures of Fe + Al powders do not allow ensuring active interfacial interaction between the components and forming intermetallic phases. Structure of such coatings mainly consists

of separate particles of components. When using MA Fe–Al powders, dense detonation coatings with cermet structure, consisting of metallic phases mixture (intermetallics, solid solutions, metals) and oxidation products, are formed.

5. Structure and phase composition of the detonation coatings of MA Fe–Al intermetallics powders indicate significant development of process of their oxidation, that results in partial loss of the intermetallic structure with formation of Fe_3O_4, Al_2O_4 and $FeAl_2O_4$ phases. Coatings' microhardness depends on composition of initial powder and rises at transfer from Fe_3Al to Fe_2Al_5, from 4580 to 5710 MPa.

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