



## STRUCTURAL ANALYSIS OF FE-AL COATINGS APPLIED BY GAS DETONATION SPRAYING

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### Abstract

The article analyzes the formation of oxide phases in the structure of intermetallic FeAl coatings applied by gas detonation spraying (GDS). The structural properties of powder charge particles and FeAl coating formed during GDS were determined. The effect of the GDS process on phase changes in FeAl coating applied under controlled conditions was examined. The results indicate that at specific process parameters, FeAl powder particles are strongly oxidized in a hot stream of gases produced during supersonic combustion. Powder particles undergo very strong plastic deformation during the process, and the resulting multiphase coating contains oxide phases that form thin membranes along grain boundaries.

The results of structural analyses and microanalyses of chemical composition (SEM/EDS) and phase composition (XRD) indicate that strongly heated FeAl particles undergo surface oxidation during GDS and are transformed into grains (splats) when they collide with a steel substrate. The produced FeAl coating has a multi-layered and multi-phase structure characteristic of the sprayed material, and it contains thin oxide layers, mainly  $Al_2O_3$ .

## Introduction

Intermetallic materials have numerous practical applications due to their unique properties (NIEWIELSKI, JABŁOŃSKA 2007). FeAl alloys can be applied by the gas detonation spraying (GDS) method to form protective coatings (HEJWOWSKI 2013). The GDS method is characterized by supersonic flow of the two-phase (gas-powder) metallizing stream. Strongly heated powder particles have very high kinetic energy when they collide with the substrate (ASSADI et al. 2016, FIKUS et al. 2019, LIU et al. 2007). FeAl coatings produced in the GDS process have many advantages, including considerable resistance to high temperature in chemically aggressive environments and very high resistance to tribological wear (BOJAR et al. 2002).

The thermal energy of gaseous detonation products directly influences the metallurgical quality of sprayed FeAl coatings (CHROSTEK et al. 2019). Research has demonstrated that even minor changes in a single parameter of the GDS process, including the fuel-oxidizer ratio, the amount of gas transporting powder particles, spraying frequency, spraying distance, and powder position inside the barrel at the time of detonation, significantly affect the kinetic and thermal energy of the stream of gaseous detonation products, which influences the quality of the sprayed coatings (NIKOLAEV et al. 2003, SADEGHIMERESHT et al. 2017).

The rate of chemical reactions in strong shockwaves is extremely high during thermal spraying. These reactions produce free radicals which significantly affect the oxidation of strongly heated powder particles. Powder particles undergo partial surface melting, and their oxidation is further exacerbated during transport by gaseous detonation products (SENDEROWSKI et al. 2016).

The aim of this study was to compare the structural parameters of FeAl powder and FeAl protective coating applied by the GDS method. The results of the comparison were used to evaluate the degree of oxidation and phase stability of intermetallic coating sprayed with a detonation gun.

## Materials and Methods

The analyzed intermetallic protective coating was produced by GDS of powder composed of a mixture of Fe and Al elemental powders with a composition of Fe<sub>40</sub>Al<sub>0.05</sub>Zr-50 ppm B, at%. The powder was manufactured by LERMPS-UTBM with the use of the Vacuum Inert Gas Atomization (VIGA) method. The substrate was a sample of 15HM (13CrMo4-5) boiler steel measuring 50×50×5 mm which was blasted with alumina directly before spraying. Surface roughness after sandblasting the substrate was Ra = 18.98 μm. The coating in the form of circular deposit was sprayed by placing the substrate material

in a fixed position relative to the barrel of the detonation gun operating at a frequency of 6.66 Hz (Fig. 1). The barrel had a length of 1,090 mm, and it was positioned at a distance of  $L = 110$  mm from the sprayed substrate. The powder with  $5 \div 40 \mu\text{m}$  particle size was loaded into the gun, and it was located at a distance of 412.5 mm from the barrel outlet at the time of detonation (powder injection position – PIP). Spraying parameters, the composition of the explosive detonation mix, and the flow rate of powder-transporting air are presented in Table 1. The FeAl coating was sprayed with the use of the Perun-S detonation gun at the Department of Protective Coatings, E.O. Paton Electric Welding Institute of the Ukrainian National Academy of Sciences. The variations in the geometric dimensions of the sprayed FeAl coating after 100 gun shots were determined with a PG10 profilometer (Fig. 1b).

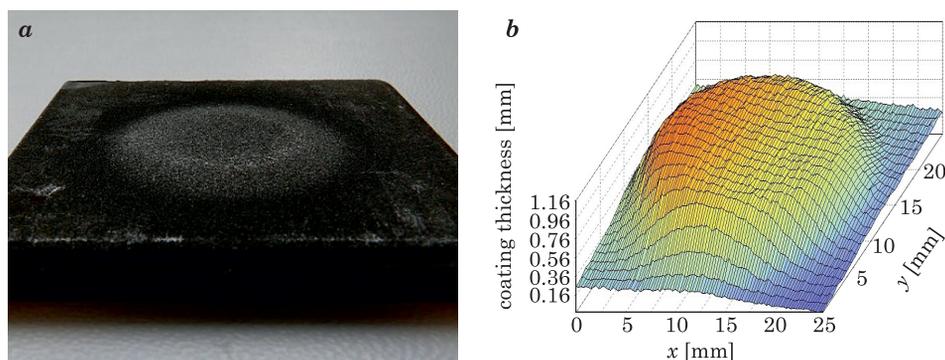


Fig. 1. FeAl coating sprayed onto 15HM (13CrMo4-5) boiler steel under GDS conditions specified in Table 1: *a* – macro image, *b* – 3D geometric dimensions of the FeAl coating after 100 gun shots

Table 1

GDS spraying parameters			
Fe40Al0,05Zr at%+50 ppm B powder Particle size distribution (granulation) 5-40 $\mu\text{m}$			
Spraying frequency $f$ [Hz]	6.66	powder transporting gas – air	0.4 $\text{m}^3/\text{h}$
		oxygen-fuel mixture	$\text{C}_3\text{H}_8$ – 0.45 $\text{m}^3/\text{h}$ $\text{O}_2$ – 1.52 $\text{m}^3/\text{h}$ air (as diluter gas)– 0.65 $\text{m}^3/\text{h}$
Spraying distance $L$ [mm]	barrel length $l$ [mm]	powder injection position* PIP [mm]	thickness of the FeAl coating after 100 gun shots $H$ [mm]
110	1,090	412.5	0.68 – 0.75

\* Powder injection position – powder position inside the barrel at the time of detonation

Structural analyses, including analyses of the morphology, chemical composition and phase composition of the original powder particles (as supplied by the manufacturer) and the produced FeAl coating, were performed under a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD).

A point analysis and an analysis of the surface distribution of elemental powder components and the sprayed FeAl coating were conducted under the Quanta 3D FEG Dual Beam scanning electron microscope with a secondary electron (SE) detector which supports the acquisition of high-quality topographic images, and a backscattered electron (BSE) detector which supports the acquisition of topographic images and analyses of differences in chemical composition. Chemical composition was analyzed by SEM/EDS in microregions with the use of the EDAX Genesis Spectrum v.6.29 analyzer. The Quanta 3D FEG Dual Beam microscope relies on a focused coherent electron beam for analyzing the chemical composition of microregions with a diameter of 0.5  $\mu\text{m}$  (for point analysis) and an area of 10  $\text{mm}^2$  (for mapping).

X-ray diffraction analysis was conducted with the Rigaku Ultima IV diffractometer with focused monochromatic  $\text{CoK}_\alpha$  radiation and a spectral wavelength of  $\lambda = 0.178897$  nm.  $\text{CoK}_\alpha$  filtering was applied, and the operating parameters of the radiation lamp were set at 40 kV/40 mA. Data were collected within the angular range of  $20^\circ$  to  $120^\circ$  at a scanning speed of 1 mm/min.

## Results and Discussion

The size, morphology and phase composition of powder particles significantly influence the metallurgical quality of coatings produced by thermal spraying, including GDS. These parameters considerably affect the thermophysical properties of powders and, consequently, the performance of the produced protective coatings.

A structural analysis (VIGA) of the original FeAl powder (as supplied by the manufacturer) revealed considerable differences in particle size. Powder particles were spherical in shape regardless of their size (Fig. 2a). The observations of metallographic specimens of FeAl powder produced with the VIGA method revealed variously shaped and sized pores in differently sized powder particles (Fig. 2). Powders are produced in the liquid phase of FeAl alloy melting in a vacuum induction furnace, and they are sprayed with high-purity argon to prevent oxidation. Pores are probably formed under the influence of the argon stream and during the shrinkage of a solidifying alloy when gas bubbles inside powder particles create empty spaces.

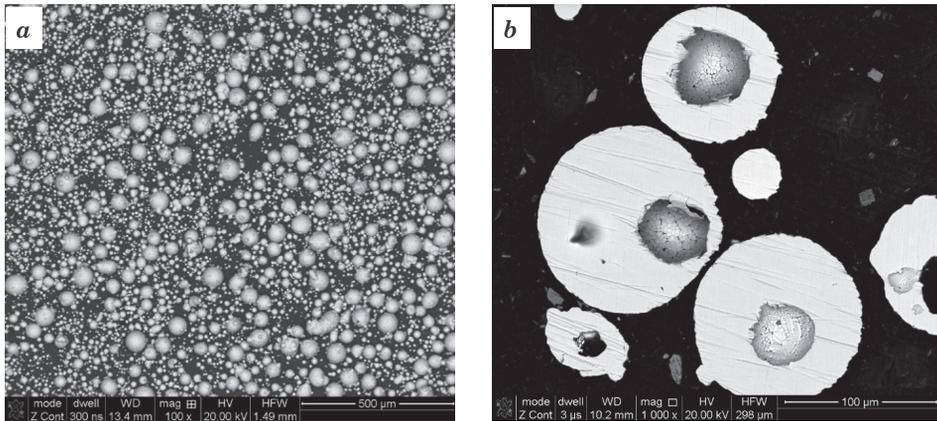


Fig. 2. Original FeAl powder (as supplied by the manufacturer) (VIGA) in the SEM/EDS analysis: *a* – differences in particle size, *b* – porous FeAl powder particles at the cross-section of the prepared metallographic specimen

The SEM/EDS surface microanalysis conducted at the cross-section of the original FeAl powder particles (as supplied by the manufacturer) demonstrated that their chemical composition corresponds to the FeAl phase with estimated 44% Al content and no oxygen (Fig. 3). This result indicates that argon effectively prevents the oxidation of sprayed FeAl particles made of inductively melted FeAl alloy in the VIGA process.

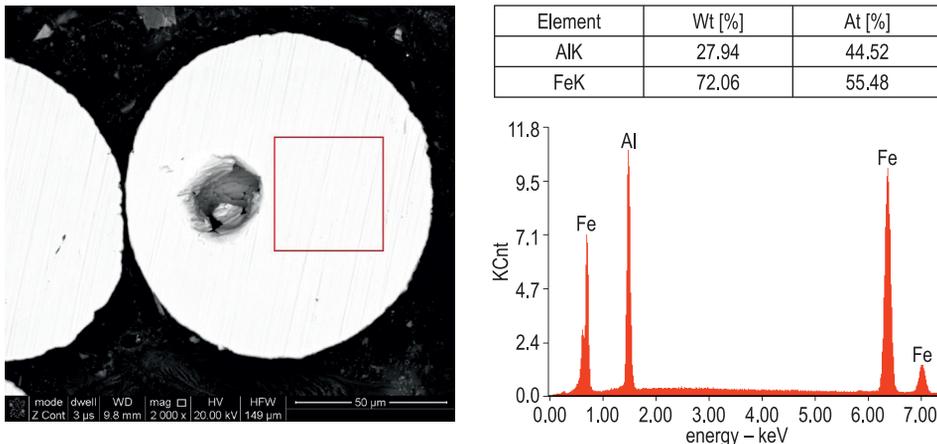


Fig. 3. Surface microanalysis of the chemical composition of original FeAl powder particles (as supplied by the manufacturer) with a marked region of SEM/EDS analysis

The XRD analysis of phase composition revealed the single-phase structure of FeAl powder particles with a characteristic reflection {100} of the B2 superstructure, which confirms that the original FeAl powder particles (as supplied by the manufacturer) were not oxidized (Fig. 4). A very small half-width of X-ray reflections with highly intense peaks, which is characteristic of a given family of FeAl phase lattice planes within a specified range of Bragg angles, can be attributed to the homogeneous chemical composition of individual powder particles and very low residual stress values. The above preserves the structural integrity of the crystal structure of the FeAl phase, which is a secondary solid solution of Al in Fe(*a*) and constitutes the basis of the single-phase powder without oxide phases.

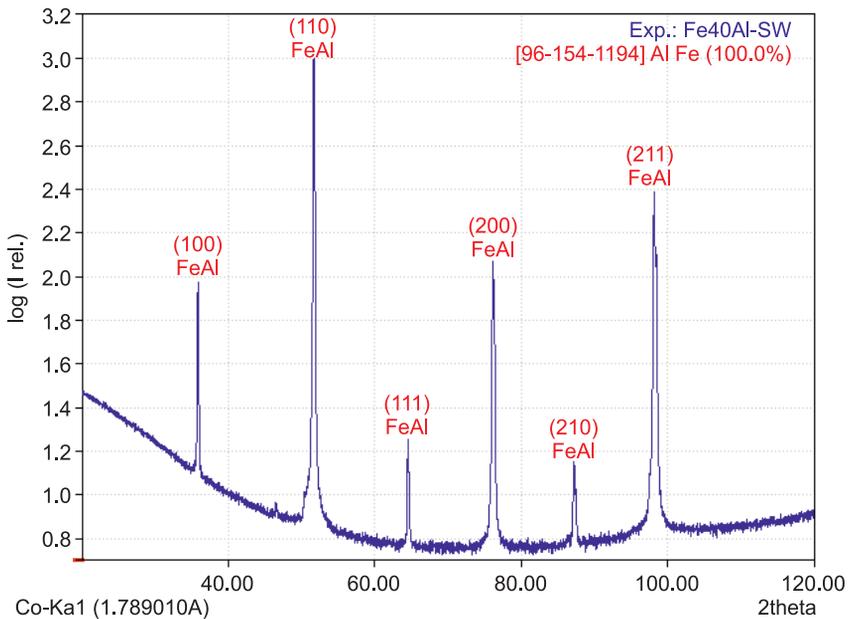


Fig. 4. XRD phase composition analysis of the original FeAl powder (as supplied by the manufacturer) produced in the VIGA process

Gaseous detonation products which create a two-phase metallizing stream with the FeAl powder are characterized by high kinetic energy and very high thermal energy during detonation spraying of FeAl coatings. These gases lead to the volumetric deformation of powder particles which are heated to near-melting temperature, and the formation of protective coatings when powder particles collide with the steel substrate material.

A review of the literature indicates that thermal and kinetic phenomena during detonation can be controlled by modifying heating and spraying parameters,

including fuel type, the fuel-oxidizer ratio, PIP in the barrel at the time of detonation, spraying frequency and distance (SENDEROWSKI 2015). The heating of powder particles can be controlled by adapting GDS conditions to the type of coating material, including its melting temperature, thermal and physical parameters, and the size and morphology of powder particles (ULIANITSKY et al. 2011).

The structural analysis of FeAl coating revealed significant changes in the physicochemical and mechanical properties of FeAl powder particles sprayed with a frequency of 6.66 Hz (Fig. 5). The observed changes resulted from particle heating and their plastic deformation.

The particle deformation analysis and the SEM/EDS microanalysis of the surface of FeAl coating revealed partial melting of powder particles in selected regions (Fig. 5). Particle melting leads to very strong oxidation of diffused aluminum and the formation of oxide phases on the surface of partially melted FeAl particles that form dark grains with a varied morphology in SEM/BSE images (Fig. 5). The SEM/EDS point microanalysis confirmed considerable variations in the chemical composition of grains in the FeAl coating, where aluminum content was estimated at 4-45 at% and oxygen content was determined

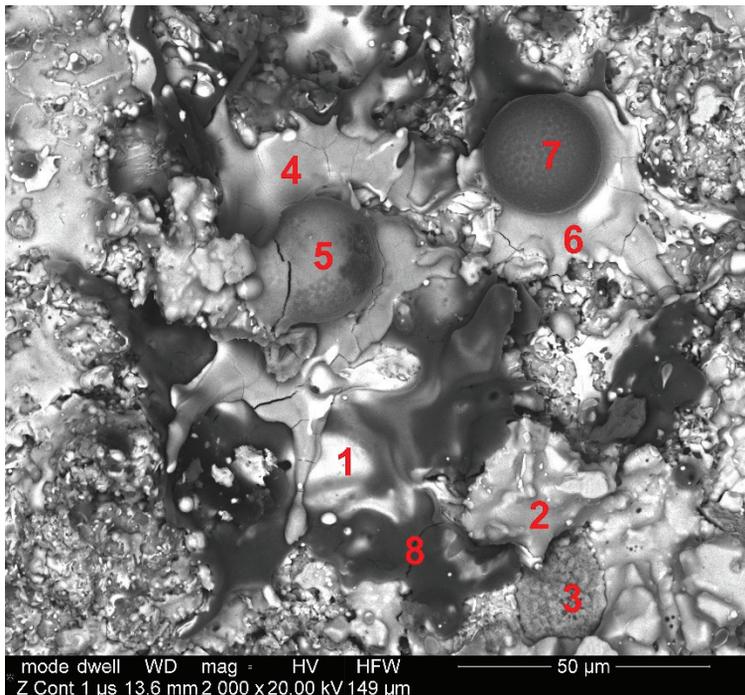


Fig. 5. SEM/EDS microanalysis of the chemical composition of FeAl coating sprayed with a detonation gun

at up to 52 at% in the region of dark grains (Fig. 5, Table 2). These results clearly indicate that the intermetallic phases of FeAl alloys differ considerably in aluminum content and are characterized by a high content of oxygen which forms complex aluminum oxides  $\text{Al}_2\text{O}_3$  and oxide spinels.

Table 2

Results of the SEM/EDS point microanalysis of the chemical composition of grain microregions on the surface of FeAl coating (GDS) presented in the SEM/BSE image in Figure 5

Phase	Element	Wt%	At%	Phase	Element	Wt%	At%
1	Al	4.78	8.84	5	Al	18.79	20.24
	Fe	92.51	82.69		Fe	52.29	27.22
	O	2.71	8.47		O	28.92	52.55
2	Al	27.65	42.47	6	Al	3.83	4.88
	Fe	70.27	52.14		Fe	72.56	44.55
	O	2.08	5.39		O	23.61	50.57
3	Al	19.47	22.32	7	Al	32.23	32.04
	Fe	56.57	31.34		Fe	38.19	18.35
	O	23.96	46.34		O	29.59	49.61
4	Al	8.06	10.93	8	Al	52.86	45.04
	Fe	74.35	48.77		Fe	12.47	5.14
	O	17.60	40.29		O	34.67	49.82

The SEM/EDS structural analysis of FeAl coating (GDS) performed at the cross-section of the metallographic specimen revealed lamellar grains with a multi-phase structure and varied chemical composition. In the images acquired with the use of the BSE detector, differences in the chemical composition of different regions on the surface of FeAl coating were presented in shades of gray (Fig. 6a).

The observed variations in the chemical composition of plastically deformed FeAl powder particles (with a single-phase structure in the original state) can be attributed to chemical reactions that take place in the stream of gaseous detonation products and the *in situ* formation of oxide phases in the form of oxide membranes in the GDS process (dark layers in Fig. 6a). When analyzing the oxidation of the FeAl coating produced by the GDS method, special attention should be paid to the preferential sites for the formation of oxide phases. These sites represent partially melted FeAl powder particles where thin oxide layers are formed, undergoing strong non-dilatational strain when the particles collide with the substrate material in a supersonic detonation wave. The produced coating has a mosaic structure (Fig. 6). Aluminum is depleted, and the intermetallic

$\text{Fe}_3\text{Al}$  phase and the secondary Al solution in  $\text{Fe}_\alpha$  are formed in regions adjacent to strongly oxidized phases with a chemical composition of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}(\text{Al}_2\text{O}_4)$  and  $\text{Fe}_3\text{O}_4$ .

The content of alloy elements and oxygen mapped in the SEM/EDS microanalysis of chemical composition at the cross-section of FeAl coating (GDS) is presented in Table 3.

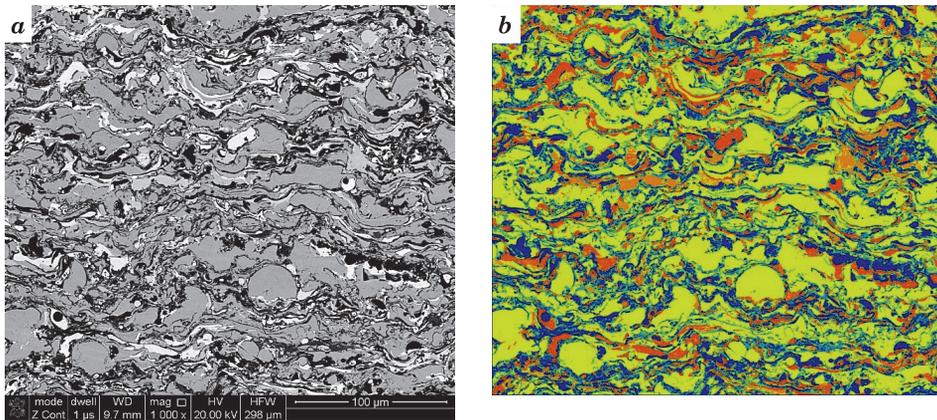


Fig. 6. SEM/BSE image of the multi-phase structure of FeAl coating produced in the GDS process (a); SEM/EDS surface microanalysis of the chemical composition of alloy elements with oxygen (b)

Table 3

Content of alloy elements and oxygen mapped in the SEM/EDS microanalysis of chemical composition at the cross-section of FeAl coating (GDS) (Fig. 6b)

Analyzed region on coating surface		Content of alloy elements [% at]			Probable phase
Color	content [% vol.]	Fe	Al	O	
Blue	13	0.91	47.66	51.43	$\text{Al}_2\text{O}_3$ phase
Light blue	8.58	22.00	34.33	43.66	$\text{Fe}(\text{Al}_2\text{O}_4)$ phase
Green	14.62	49.05	11.36	39.59	$\text{FeO}$ , $\text{Fe}_2\text{O}_3$ , $\text{Fe}_3\text{O}_4$ oxide phases
Yellow	47.46	55.72	40.61	3.68	weakly oxidized FeAl phase
Orange	9.41	76.44	18.88	4.68	weakly oxidized $\text{Fe}_3\text{Al}$ phase
Red	6.92	92.53	1.01	6.37	oxidized ferrite

The SEM/EDS surface microanalysis of the chemical composition of the FeAl coating revealed a high degree of oxidation (Fig. 6 and Tab. 3). The FeAl phase (marked in yellow) of the FeAl coating (GDS) was predominant (approx. 48% vol.), and it was composed of strongly plastically deformed splats (Fig. 6b). The proportion of oxide phases (blue, light blue and green in Fig. 6b) on the

surface of strongly deformed powder particles was also high and significant, and it was estimated at 36% vol. of the FeAl coating (GDS).

Thin oxide phase membranes along grain boundaries in the intermetallic FeAl coating did not cause granular delamination in the form of microcracks, which was potentially possible due to differences in the values of the linear coefficients of thermal expansion for the FeAl phase and ceramic oxides. The SEM/EDS analysis revealed that the  $\text{Fe}_3\text{Al}$  phase (orange), which was depleted of aluminum due to the formation of oxide phases, accounted for around 10% vol. of the FeAl coating and was created directly in the region of oxide phase formation (Fig. 6 and Tab. 3).

The X-ray diffraction analysis of FeAl coating (GDS) confirmed that the FeAl phase is the main structural component that is inherited from FeAl powder (VIGA). The analysis also confirmed the presence of the  $\text{Fe}_3\text{Al}$  phase and the following oxide phases: aluminum oxide –  $\text{Al}_2\text{O}_3$ , spinel –  $\text{Fe}(\text{Al}_2\text{O}_4)$ , magnetite –  $\text{Fe}_2\text{O}_3$  and ferrous oxide –  $\text{FeO}$  (Fig. 7).

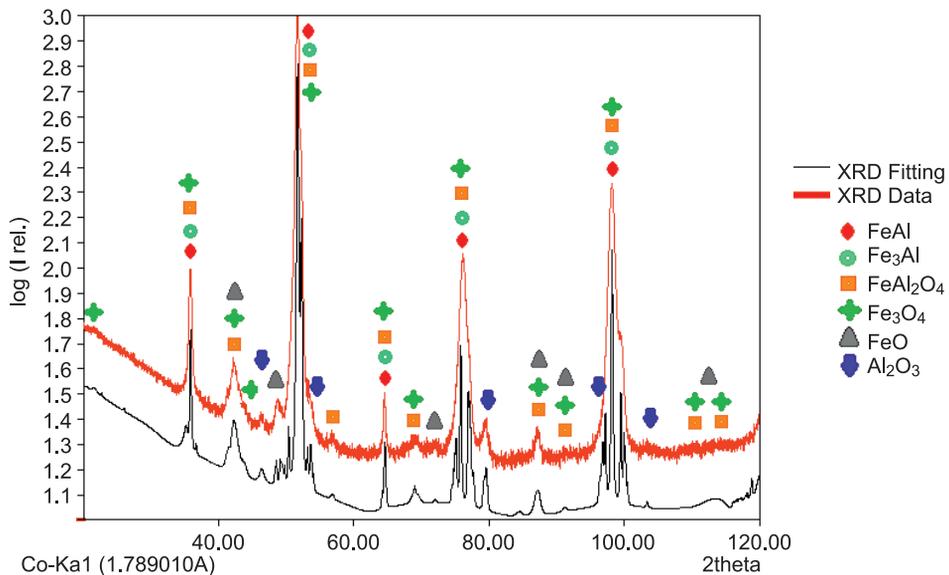


Fig. 7. XRD analysis of the phase composition of FeAl coating sprayed with a detonation gun

A comparison of the XRD image of the FeAl coating (GDS) (Fig. 7) with the XRD image of the original FeAl powder (Fig. 4) indicates that an increase in the half-width of FeAl coating reflections and a decrease in reflection intensity probably resulted from the high dispersivity of  $\text{Al}_2\text{O}_3$  phases and oxide spinels identified as  $\text{Fe}(\text{Al}_2\text{O}_4)$ . The oxide phases identified in XRD analysis contribute

to the formation of pseudo-composite coating and increase residual stress in the structure of the intermetallic FeAl coating, which also widens the reflections of diffraction peaks.

The behavior of the superstructure peak {100} indicates that the sprayed coating is based on the FeAl (B2) phase which has a less ordered structure and contains the aluminum-deficient Fe<sub>3</sub>Al phase without superstructure reflection (Fig. 7).

## Conclusions

During the GDS of intermetallic FeAl coating with the use of single-phase FeAl alloy powder produced by the VIGA method, the detonation wave and gaseous detonation products lead to the oxidation of particle surfaces and the formation of oxide membranes which are an integral part of coatings with a layered structure. The supersonic metallizing stream causes strong volumetric deformation of powder particles when they collide with the substrate material. Thin oxide membranes are formed along the boundary of strongly flattened grains without impairing their cohesiveness. Aluminum is depleted in the region where oxide phases are formed, and a solid solution of the secondary Fe<sub>3</sub>Al phase is formed in microregions.

The pseudo-composite structure of intermetallic FeAl coating with oxide phases is characterized by a less ordered structure and higher residual stress which is exacerbated by dispersive oxide phases. Residual stress generated during GDS does not cause microcracks in the multi-phase structure of FeAl coatings containing ceramic oxides which stabilize the structure during high-temperature heating, including in aggressive corrosive environments.

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