A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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TEM MICROSTRUCTURE OF Fe-Al COATINGS DETONATION SPRAYED ONTO STEEL SUBSTRATE

MIKROSTRUKTURA TEM POWŁOKI Fe-Al NATRYSKIWANEJ DETONACYJNIE NA PODŁOŻE ZE STALI

The microstructure analysis of Fe-Al intermetallic coating deposited by detonation-gaseous spraying (DGS) on the 045 carbon steel substrate was presented in the paper. The microstructure was investigated using scanning (SEM) and transmission (TEM) electron microscopy, as well as selected area electron diffraction (SAED) techniques. The chemical concentration in microareas was revealed using the energy dispersive X-ray (EDS) spectroscopy technique. The TEM technique was applied to the analysis across the coating as well as close to the coating/substrate interface. The vicinity of the substrate was composed of an amorphous phase and columnar crystals as a result of rapid solidification of the partially melted FeAl powder. The Fe_3Al phase was identified inside the coating, while at its surface Fe_2Al_5, Fe_3Al and FeCrAl phases were found. Their occurrence and also the $FeAl_2O_4$ phase and aluminium oxide were confirmed by the X-ray diffraction method.

W pracy przedstawiono analizę mikrostruktury powłoki międzymetalicznej faz typu Fe-Al naniesionej przez natryskiwanie detonacyjno-gazowe (DGS) na podłoże ze stali węglowej 045. Analizę tą przeprowadzono na podstawie badań metodą skaningowej (SEM) i transmisyjnej mikroskopii elektronowej(TEM). Metodą TEM analizowano budowę powłoki zarówno w głębi jak i w pobliżu granicy z podłożem. W sąsiedztwie podłoża stwierdzono fazę amorficzną oraz kryształy kolumnowe jako rezultat szybkiego krzepnięcia nadtopionej części proszku FeAl. W głębi powłoki zidentyfikowano fazy Fe_3Al, zaś na jej powierzchni fazy Fe_2Al_5 i Fe_3Al oraz FeCrAl. Występowanie tych faz oraz $FeAl_2O_4$ i tlenku glinu potwierdzono metodą dyfrakcji rentgenowskiej.

1. Introduction

The TEM microstructure investigations of the coating deposited with the detonation -gas spraying (DGS) process have been aimed at revealing to which extent the formation of the coating takes place simultaneously with its transition into liquid state [1], which kind of the ordering in the intermetallic FeAl phase, as well as what the mechanism of coating formation in the DGS process is. Such problems have occasionally been reported [2,3,4], and their explanation may contribute to the description of microstructure effects of the spraying method. The DGS technique enables obtaining a coating characterized by the high wear and corrosion resistant and hardness. The properties of the coating obtained with the DGS method are significantly higher than these attained with the plasma spraying [5, 6]. Such coatings find their application in the aircraft and space industry for turbines and turboprop engines. The intermetallic protective coatings of the Fe-Al type detonation gas spraed on the substrate of typical constructional materials such as 045 carbon steel or Ni based NiCrAl superalloys reveal high exploitation properties. They are resistant to the high temperature corrosion and thermal shocks. They have good mechanical and lubricating properties, high adhesion, low porosity and first of all excellent resistance to abrasive wear [4, 5]. The high energy transferred to the Fe-Al particles of the coating material during the DGS results in the formation of layer morphology of flattened grains [7] as well as partial melting of the Fe_3Al, $FeAl_2$ and FeAl phases, which freeze as amorphous phases at rapid cooling.

The aim of the present work has been the description of the detonation sprayed coating morphology and the explanation of the mechanism of its formation with the contribution of partial melting of powders of the Fe-Al type on the carbon steel substrate. A possible modifications of the coating formation has also been studied.

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1.1. Experimental

The coating obtained by detonation-gaseous spraying with powders Fe_2Al_5, Fe_3Al and FeAl of 40-60 μm grain size on the 045 carbon steel substrate was produced in the Military University of Technology, Warsaw. The details of the spraying process has been given elsewhere [7]. The process of the coating deposition of circa 50 μm was preceded by heating the powder up to 100 °C. The steel of the substrate after rolling was annealed and then cleaned. The obtained coatings were examined by scanning (SEM) and transmission (TEM) electron microscopy techniques. Cross-section of the coatings for SEM studies were inspected without etching using back-scattered electrons. The measurement of the chemical composition in the interaction zone were carred out using a Link ISIS energy dispersive X-ray(EDX) spectrometer attached to a Philips XL30 scanning electron microscope operating at 20 kV voltage. The chemical decomposition was calculated applying the ZAF (Z-atomic number, A-adsorption, F-fluorescence and using standards of relevant elements and resulting relative error was about 4%. The X-ray phase analysis was conducted on Philips PW 1710 diffractometer at CuK radiation.

Thin foils for the TEM were prepared using Focus Ion Beam techniquw (Quanta 3D, FEI) and then examined in a Philips CM20 Twin instrument equipped with an EDAX Phoenix EDX spectrometer. The microscope operated voltage 200 kV in the nanoprobe mode with a LaB_6 catode. A high resolution X-ray mapping was applied in order to determine partitioning of the elements across the coating. It was accomplished using the TEM TECNAI G^2FEG super TWIN(200kV) microscope equipped with High Angle Angular Dark Field(HAADF) detector and integrated EDAX energy dispersive spectroscopy system.

1.2. Results

1.2.1. Preliminary examinations: SEM, EDX, phase analysis XRD

The SEM microstructure in Figure 1 shows a cross-section of the coating deposited with the DGS method. The coating had band-like morphology. The super-cooled FeAl phase at the substrate, then Fe_3Al crystalline phases were observed along the scan line. The areas where point EDX analysis was performed are indicated by the numbers. The corresponding results are shown in Table1. The large amount of oxygen was detected in the $FeAl_2$ phase. Those grains were ten times smaller at the substrate tan at the surface. large amount of oxygen was detected in the Fe_2Al phase. They were ten times smaller at the substrate than at the surface.

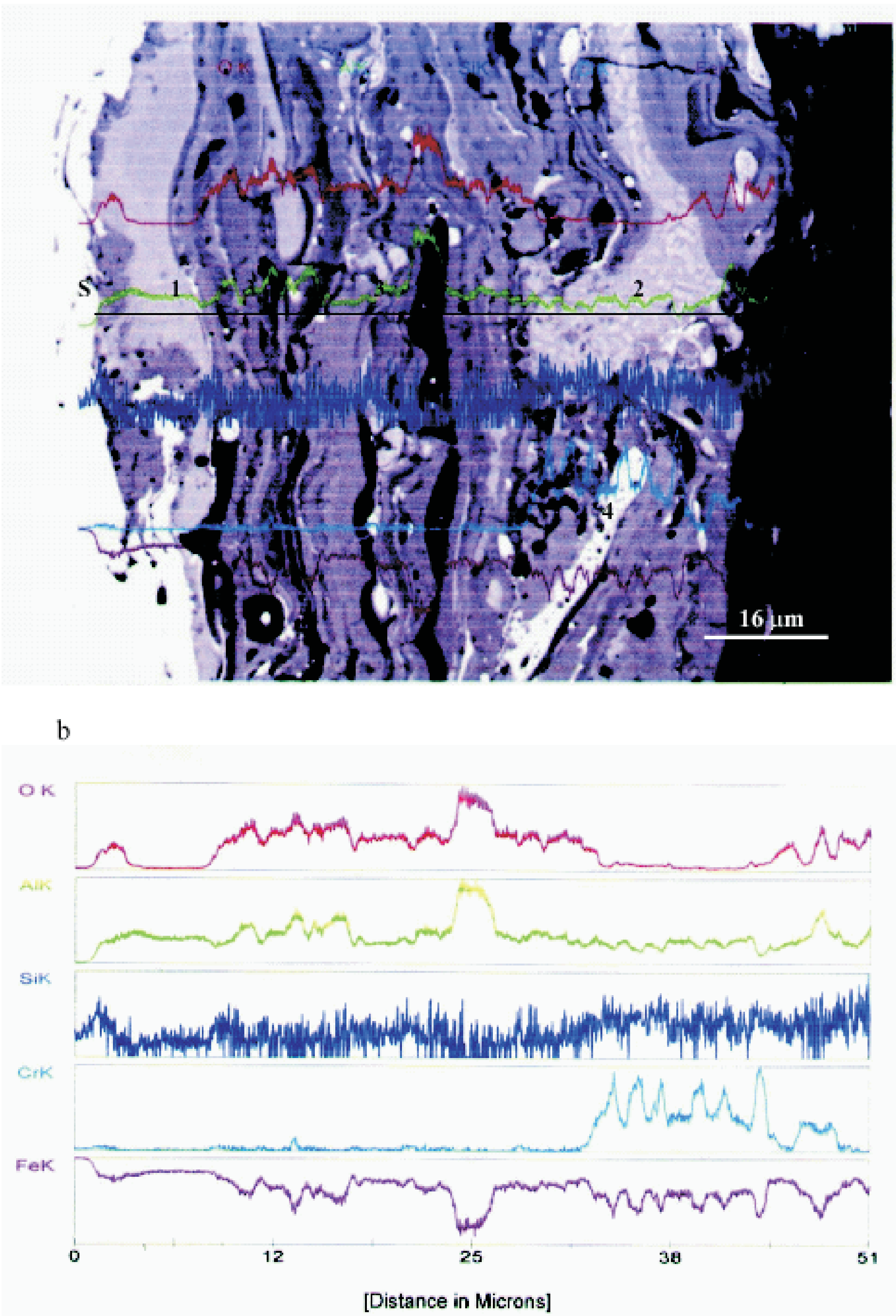


Fig. 1. SEM image of the coating a) with analysis of composition, b). Substrate on the left side of the image

TABLE

Chemical composition of phases in the coating

Area	[at%]	Fe	Al	Cr	O_2
No. 1	Faza FeAl	35	50	–	15
No. 2	Faza $(Fe,Cr)Al_2$	25	49	14	12
No.3	Faza $FeAl_2$	34	63	–	3
No. 4	Faza Al_2O_3	3	36	–	61

The results of the X-ray phase analysis of the Fe-Al type coating detonation sprayed on the substrate of carbon steel 045 is shown in Figure 2, in which the presence of the following phases can be seen: 1 – $FeAl_2O_4$ (311), (400), (442), (622); 2 – FeAl (111), (220) and inclusions 3 – $Al_2O_{3-\gamma}$.

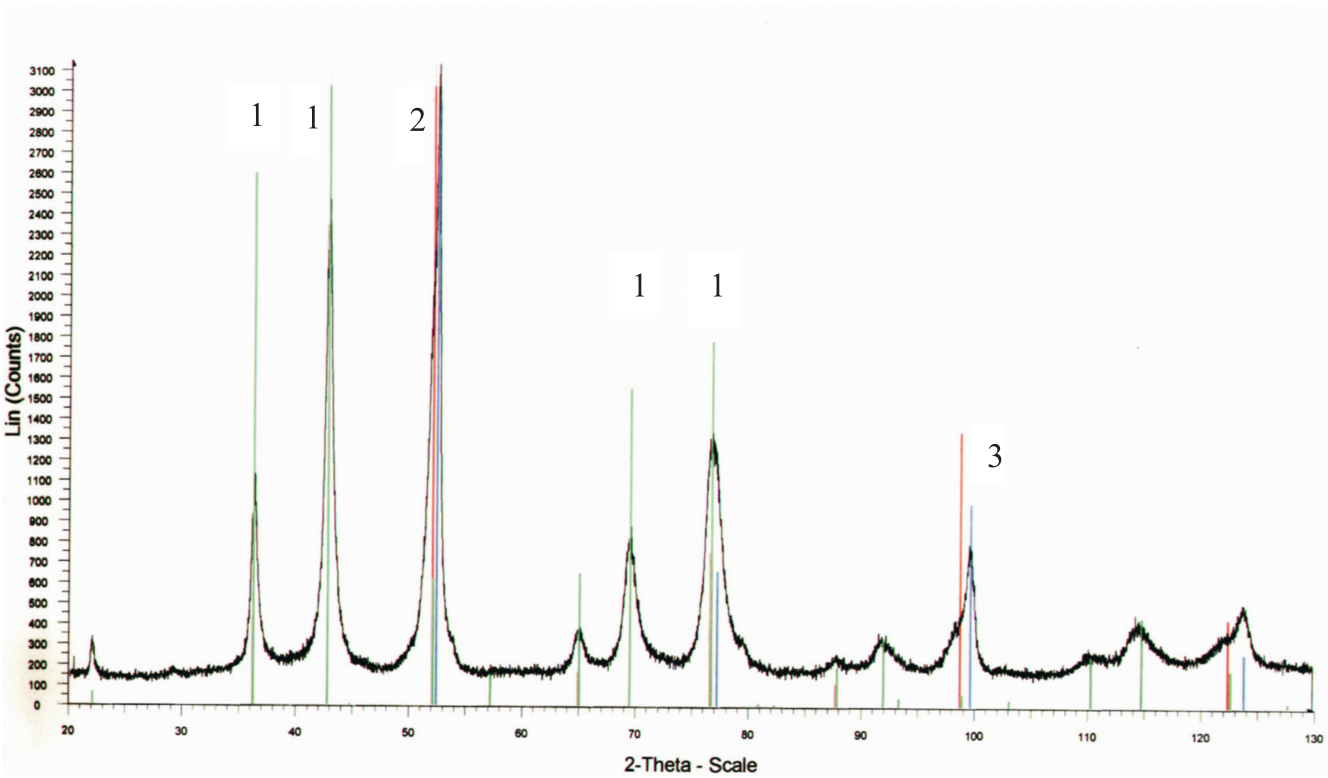


Fig. 2. X-ray phase analysis of Fe-Al type coating detonation sprayed on the substrate of carbon steel 045: phase 1 – $FeAl_2O_4$, phase 2 – FeAl, phase 3 – $Al_2O_{3-\gamma}$

This method was particularly suitable for the identification of the FeAl phase containing less than 50 at.% Al, which were not detected with the SEM/EDX technique. These both methods helped to identify the existing phases containing chromium and oxygen. The Al oxide was found in the form of sublayers (white areas in Fig.1 and 3)

1.2.2. Results and disccussion of TEM, SAED and EDX examinations

A detailed TEM, SAED and EDX investigations were performed on cross-sections of the coating in order to elucidate the formation mechanism of multi-layer coating structure containing the Fe-Al intermetallic phases obtained in the DGS process.

A layer about 10 μm thick consisting of an amorphous phase (A) was observed in the nearest vicinity of the substrate. Next, colonies of columnar crystals (CC) and amorphous phase appeared in sequence as a result of high rate solidification of a Fe-Al powder particles partially melted on the substrate (Fig. 3). Approaching the central zone of the coating, spheroidal grains of original powders (OG) were present, although strongly plasticized due to flattening when flung at very high kinetic energy during the DGS process.

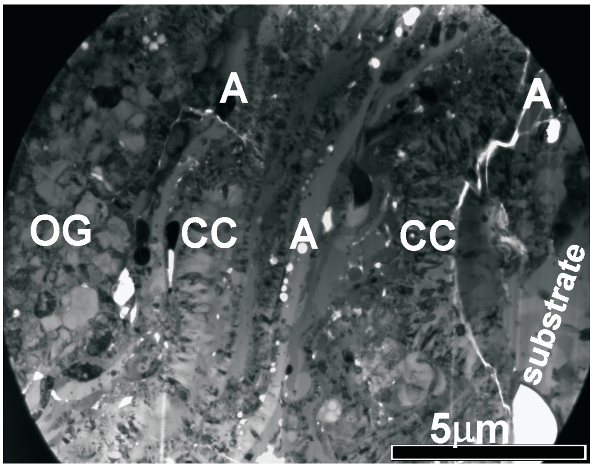


Fig. 3. TEM image of the Fe-Al coating deposited in the DGS process close to the surface of the substrate visible at right side

Such an amorphous phase and columnar crystals, in similar to the DGS process, were also observed by Mayers[8] in the explosive cladding process.

The partial melting of Fe-Al particles in the DGS process resulted from the collisions of powder particles ejected at rate 1500 m/s, heated up to 2500 K and at pressure 25 MPa.

Also Jain and Chistman [9] found dislocations and 15 vol.% partially melted Fe_3Al phase as well as a superstructure manifested in the form of rings in electron diffraction patterns in the detonation sprayed Fe-28Al-2Cr at.% phase obtained at rate 1250 m/s, pressure 10 GPa and at temperature 550 °C.

In the presented DGS technology of protective coating formation based on intermetallic Fe-Al phases, the area of the amorphous phase in the zone of coating and substrate junction had the form of single sublayers about 1-2 μ m wide and 10-50 μm long (Fig. 4).

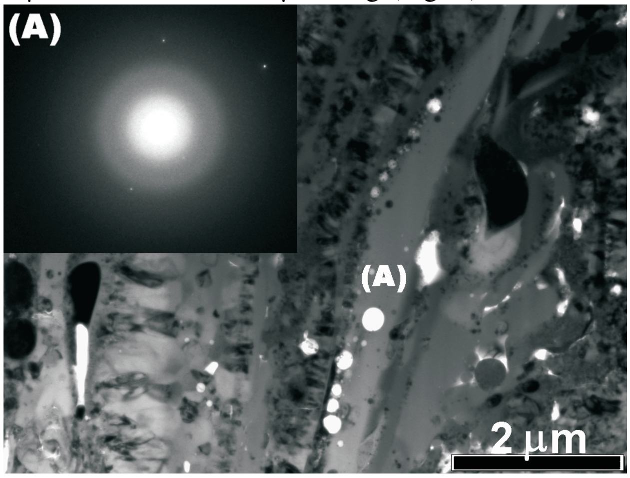


Fig. 4. TEM microstructure with amorphous phase (A) and corresponding selected area electron diffraction pattern

The SAED technique showed that the TEM identified columnar crystals presented in Fig.5a crystallized in the form of grain Fe_2Al_5 grains of (130), (222), (402), (530), (532) orientations and FeAl grains of (100), (110), (200), (222) orientations (Fig. 5b). They were arranged in sublayers. The distance between the columnar grains was about 200 nm.

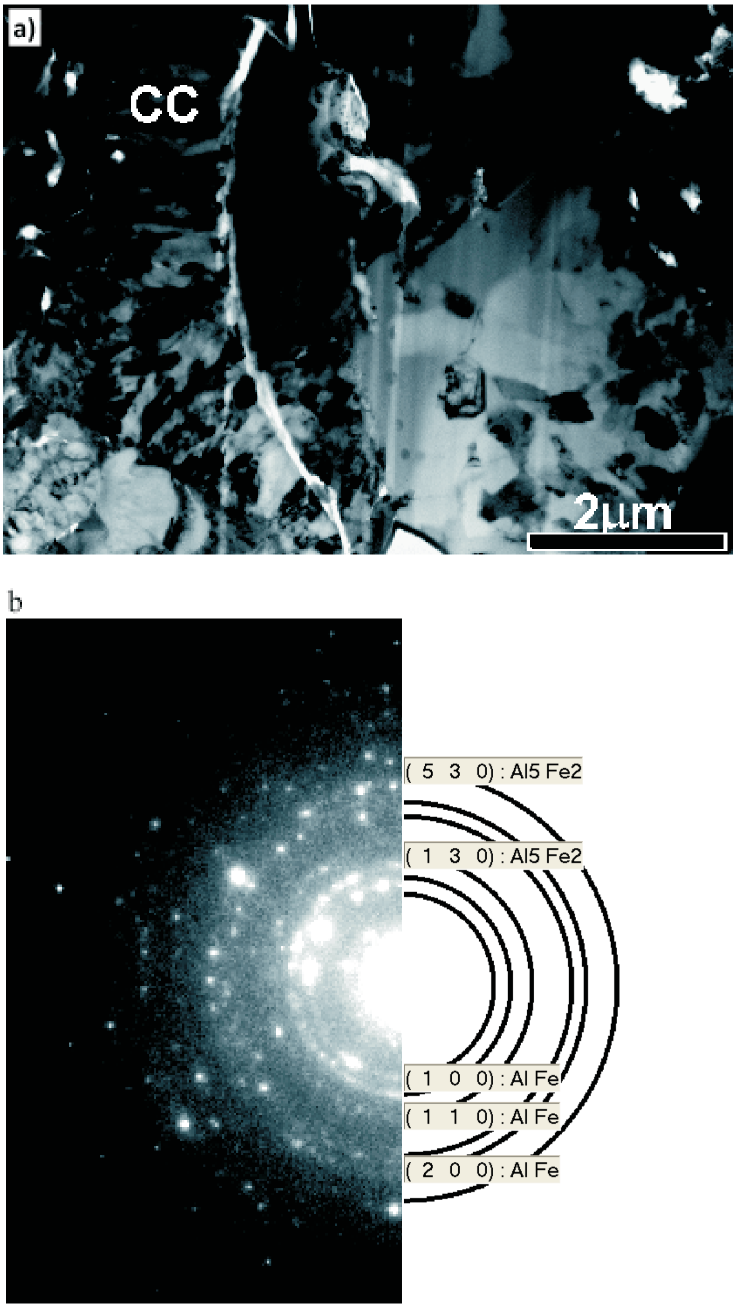


Fig. 5. TEM microstructure with columnar crystals of Fe_2Al_5 and FeAl phase, b) phase identification based on corresponding electron diffraction

The subgrains of spheroidal morphology and size about 300 nm shown in Fig. 6 andobserved in not melted grains (OG) near the central part of the coating (visible in Fig. 3) were identified using SAED technique as the FeAl phase of (110) and (200) orientations. They formed a polycrystalline sublayer about 2.6 μm wide and 10 μm long (Fig. 6).

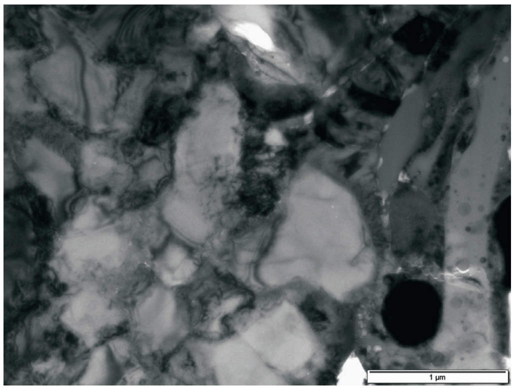
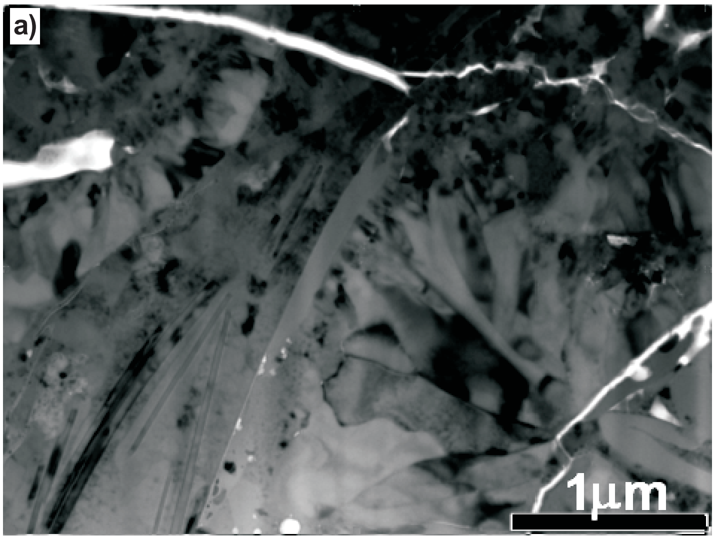


Fig. 6. TEM microstructure of not melted subgrains in original grains

The spherical particles as well as the complex oxide films or particles were observed in the area of subgrains of dispersive structure formed from the FeAl. The oxides were identified as $Al_2O_{3-\gamma}$ (dark contours in Fig. 6) They are responsible for the depletion of FeAl phase in Al (Fig. 7a). The FeAl phase was found to have B2 structure and (222), (200) and Fe_2Al_5 phase (310) orientations and revealed strong ordering manifested by the character of the identified rings in SAED visible in Fig. 7b.

However, directly in the vicinity of the oxides, apart from the FeAl phase, sublayers identified as Fe_3Al phase formed, induced probably by the compressive strains in the coating due to the really high kinetic energy of powder particles, sprayed in the DGS process.



b

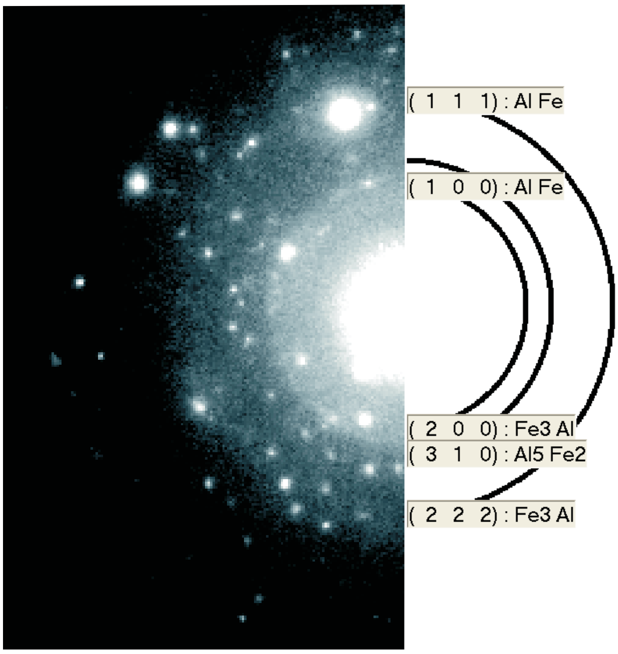


Fig. 7. TEM microstructure showing the morphology of the Fe_3Al phase, a); and corresponding SAED together with its solution, b)

That was why, the EDX method of element distribution detection was the following stage towards better understanding and the identification of phase structure of the Fe-Al coating. It was performed at the interface between area the coating and the 045 steel substrate (Fig. 8). The microstructure of the coating consisted of grains of different degree of greyness in the TEM image (HAADF Detector). The qualitative analysis based on the set of element distribution maps allowed stating that heavy element contents like iron rich particles (Fe_Kα) corresponded to very bright areas, while FeAl particles were visible as light grey (Al_Kα). Aluminium rich particles ($Al_2O_{3-\gamma}$ were visible as very dark areas and the Fe-Al type spherical particles as dark-grey. The grey areas were confirmed as the FeAl phase of elevated Al content. The oxygen, in turn, gave dark images, similarly to Al. The FeAl grain registered close to the surface contained considerable amount of Cr observed across the whole coating (Fig1 and 8).

The same referred to the direct neighborhood of sublayers of the Fe_3Al phase. Equlibrium content of intermetalline phases : Fe_3Al- 25at%Al, FeAl-47at%Al, $FeAl_2$-65at%Al, Fe_2Al_5- 70at%Al, [11].

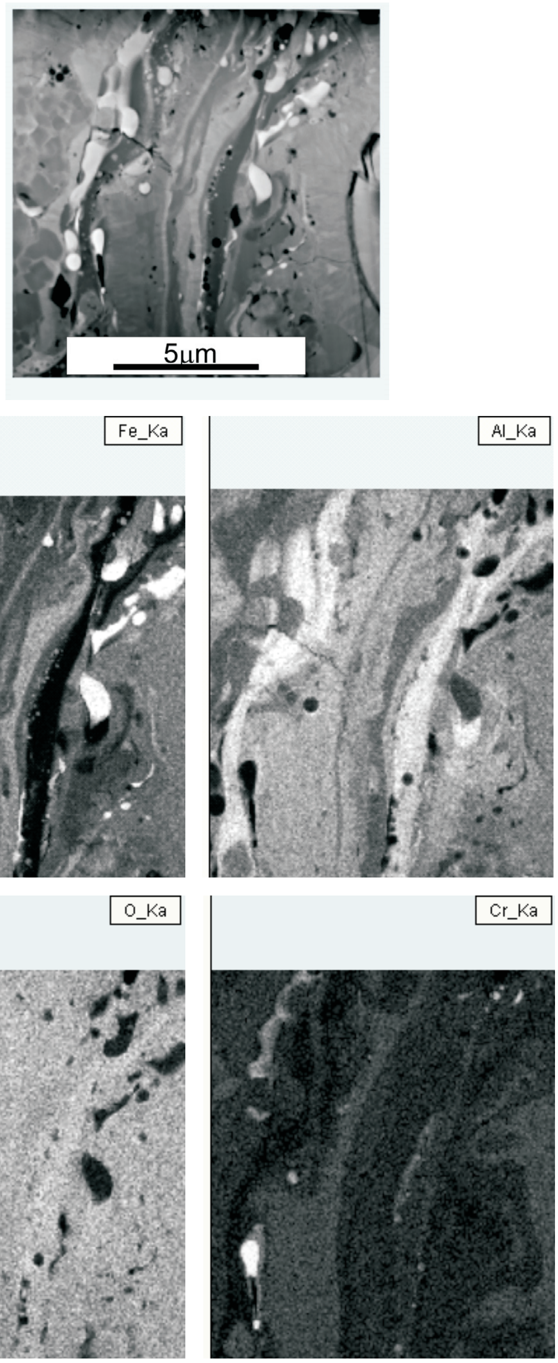


Fig. 8. TEM structure and corresponding element distribution maps with characteristic EDX spectrum from the selected area of coating-substrate containg-substrate contact

It can be concluded, that the mechanism of detonation sprayed coating formation consisted is the deposition of partially melted particles of FeAl phase on the substrate. They solidified in the form of amorphous phases of high content of Al and columnar crystals. Not melted part of the particle got strongly flattened during hitting the substrate and its composition was close to the starting composition of the sprayed particles. However, it was reported by Pawłowski et al.[10] based on microcalorimetric examination, that they underwent phase transformations such as transition of γFe into αFe (Fe-2at.% Al) as well as an ordering procesess in the Fe- 42at.% Al. Apart from them, the Fe-Al type phases containing oxygen were observed contaminated by chromium, which might have originated from the process of the gun tube abrasion during the DGS.

In dependence on the kind of the coating applied, its properties may be controlled through the modification of detonation spraying process. Partial melting of the starting particles and the resulting fractions of the amorphous phase and columnar crystals can be limited to some extent by controlling the rate, temperature and pressure of the gases in the gun tube.

Summing up the obtained results of the qualitative assessment of the alloying element distribution supplemented with the analysis of electron diffraction paterns and local X-ray micro analysis, it was found, that dark areas corresponded to Al oxides $Al_2O_{3-\gamma}$, dark-grey were the Al rich Fe_2Al_5 and $FeAl_2$ phases [11], while the grey areas, prevailing in the structure, corresponded to a second FeAl based phase of various degree of oxidation. On the other hand, light and light-grey particles were in fact the Fe3Al phase already earlier identified –HAADF technique. The presence of relatively large contribution of chromium could be explained with the abrasion of the detonation gun tube, apart from a some amount contained as an alloying addition in the powders used for the DGS process.

2. Conclusions

1. The detonation sprayed coating of the Fe-Al type revealed a sublayer, pseudo-composite morphology of partially melted, flattened grains of the following sequence: amorphous phase – columnar crystals – not melted part of grains.
2. The amorphous phase of high Al -amount, columnar crystals consisted of alternate FeAl and $FeAl_2$ phases appeared in partially melted and quickly solidified particles close to the substrate. The equiaxial grains of Fe_3Al and Fe_2Al_5 phases were observed in the central part of the layer.
3. Grains with chromium content were observed across the whole coating. They were ten times smaller at the substrate than at the surface.
4. Such a morphology can be responsible for high properties of the coatings obtained with the DGS method, reported in literature. Possibilities of controlling the structure refer to the size of meltings and kind of appearing phases.

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