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DETONATION DEPOSITED Fe-Al COATINGS
PART I: MORPHOLOGY OF Ni(Al) AND Cr(Ni) TRANSITION LAYERS AND
COATINGS OF Fe-Al TYPE SPRAYED ONTO CARBON STEEL SUBSTRATE

POWŁOKI Fe-Al OSADZANE DETONACYJNIE
CZĘŚĆ I: WARSTWY POŚREDNIE Ni(Al) I Cr(Ni) ORAZ POWŁOKI Fe-Al
OSADZANE DETONACYJNIE NA PODŁOŻU ZE STALI 045

The microstructure of transition layers of Ni(Al)– pure Ni with Al and NiAl particles as well as Cr(Ni) – pure Cr in the Ni matrix, occurred between the coating of Fe-Al type intermetallic phases and the 045 carbon steel substrate was analysed in the present work. The investigations were aimed at the adherence of transition layers and the outer coating deposited with the detonation-gas spraying. The structure was examined using the methods of scanning (SEM) and transmission electron (TEM) microscopies as well as the analysis of chemical composition in microareas (EDS). Silica grains at the boundary of the substrate and the layer of Ni(Al), aluminium oxide at the boundary and inside the Ni(Al) layers, an Al based $AlNiO_x$ phase, columnar crystals at the boundary of the coating of Fe-Al type phases and an adjacent Cr(Ni) layer were observed. The results were discussed in reference to earlier examinations of bending strength considering cracking and delamination of the coating off the substrate. They were then compared with the state of the boundary between the coating and the steel substrate analysed in former works. It seems, that the substrate boundary free from silica inclusions and the prevention of the formation of aluminium oxides at the boundary of transition layers and the substrate should improve the adherence of the whole multi layer and the coating.

Keywords: intermetallics of Fe-Al type, coatings, D-gun spraying

W pracy poddano analizie mikrostrukturę warstw pośrednich: Ni(Al)– czystego niklu z cząstkami Al i faz NiAl oraz warstwy Cr(Ni)– chromu w osnowie Ni, występujących pomiędzy powłoką faz międzymetalicznych typu Fe-Al i podłożem ze stali węglowej 045. Badania wykonano z punktu widzenia przyczyn przyczepności warstw pośrednich i powłoki zewnętrznej, naniesionych przez natryskiwanie detonacyjno-gazowe DGS. Analizę struktury przeprowadzono na podstawie badań metodą skaningowej (SEM) i transmisyjnej mikroskopii (TEM) elektronowej oraz analizy składu chemicznego w mikroobszarach (EDS). Stwierdzono wystąpienie ziaren krzemionki na granicy podłoża z warstwą Ni(Al), obecności ziaren tlenku glinu na granicy i wewnątrz warstw Ni(Al) oraz fazy na bazie glinu $AlNiO_x$ i kryształów kolumnowych na granicy powłoki faz typu Fe-Al oraz warstwy Cr(Ni) chromu do niej przylegającej. Wyniki badań mikrostruktury dyskutowano w odniesieniu do rezultatów wcześniejszych pomiarów wytrzymałości na zginanie w aspekcie pęknięcia powłoki oraz delaminacji podwarstwy od podłoża. Porównano je także do stanu granicy powłoki z podłożem stalowym dokonanych w poprzednich pracach. Jest prawdopodobne, iż granice podłoża pozbawione wtrąceń krzemionki oraz zapobieżenie tworzeniu tlenków glinu na granicy warstw pośrednich i podłoża powinno poprawić przyczepność całej multiwarstwy i powłoki.

1. Introduction

The coatings of Fe-Al type together with a contribution of transition layers of Ni(Al) – pure Ni and NiAl particles as well as transition layers of Cr(Ni) – Cr in the Ni matrix deposited with detonation gas spraying technique (DGS) belong to the system of multi layer composite coatings. Their good adherence to the sub-

strate is one of the basic properties of a coating [1-3]. They reveal high resistance to abrasive wear and high temperature oxidation and are used in turbines and jet engines.

The investigations of adherence of DGS coatings were performed with the technique of tri-support bending correlated with the results of acoustic emission [4]. The analysis allowed the establishing the value of limit

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bending load, which cannot be exceeded because of danger of cracking or delamination. The investigations of adherence of multi layer coatings and the results of acoustic emission showed that the highest bending strength of the hybrid coating system was revealed by the joint of substrate with the Ni-5 wt.% Al transition layer, compared with the Ni-20Al and Ni-20Cr transition layers with the Fe-Al coatings [4]. However, the highest delamination was observed in the joint of steel with Ni(Al) transition layer, while the Cr(Ni) transition layer revealed a higher bending strength.

A higher content of oxygen in the DGS process or the addition of Al_2O_3 phase to the powders in the coating built of Fe-Al type phases brings about the occurrence of microcracks. The worst strength properties and bad adherence of the coating was observed in the case of Fe-Al coatings sprayed with the DGS technique directly onto the steel substrate. Good adherence was observed in FeAl/Cr(Ni), FeAl/ Ni(Al) and Ni(Al) / Cr(Ni) connections [4].

The objective of the work was to describe the morphology of a multilayer coatings of Fe-Al type produced with the DGS technique in order to deduce structure reasons for as well as to find how to elevate the adherence of the coating to the substrate of 045 steel with Ni(Al) and Cr(Ni) transition layers.

2. Experimental

The Ni(Al) transition layer with inclusions of Al particles or NiAl phases and another transition layer of Cr in the Ni matrix, Cr(Ni), at the boundary with Fe-Al coating at the 045 steel substrate were subjected to examinations. Additionally, the microstructure of coating produced of powders of intermetallic phases of Fe-Al type was analysed. Both, the transition layers and the coating were detonation sprayed (DGS). Materials for the experiments were delivered from the Military University of Technology, Warszawa. The parameters of deposition process (DGS) are given in work [5]. The steel for the substrate was stress relieved and mechanically cleaned.

The obtained coatings were examined by scanning (SEM) and transmission (TEM) electron microscopy techniques. Cross-sections of the coatings for SEM studies were inspected using back-scattered electrons. The measurement of the chemical composition in the interaction zone were carried out using a Link ISIS energy dispersive X-ray (EDX) spectrometer attached to a Philips XL 30 scanning electron microscope operating at 20kV voltage. The chemical composition was calculated applying the ZAF (Z-atomic number, A-absorption, F-fluorescence) correction procedure and using stan-

dards of relevant elements and the resulting relative error (look table Fig.2a,2b).

Thin foils for the TEM were prepared using a focused Ga^+ ion beam (FIB- Focus Ion Beam technique), in a Quanta 200 3D, FEI instrument) and then examined in a Philips CM 20 Twin microscope equipped with an EDAX Phoenix EDX spectrometer. The microscope operated at accelerating voltage 200 kV in the nanoprobe mode with a LaB_6 cathode. 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 energy dispersive spectroscopy system.

3. Results and discussion

3.1. SEM microstructure and EDX analysis

The investigations were performed on samples with coatings of Fe-Al type obtained with the DGS technique. The surface of the 045 steel was DGS sprayed with Ni(Al) transition layer of pure Ni with inclusions of Ni15 at.% Al and pure Al followed by the Cr(Ni) layer of Cr and Ni. Next, a coating consisting of phases: FeAl, FeAl_2 , Fe_2Al_4 and Fe_3Al was deposited on the above mentioned transition layers. The coating was 50-100 μm thick, while the Cr(Ni) transition layer was 20 μm and Cr layer 1-2 μm wide.

The SEM microstructure in the coating cross section shown in Fig. 1 derives the substrate of 045 steel at its left side adjoining the boundary with the Ni(Al) inter-layer, which is built of characteristic wavy boundaries of the transition layers resulting from inhomogeneity of the detonation wave in the DGS process and partial melting of powders. Next layer was identified as Cr(Ni) followed by Fe-Al coating.

The EDX local analysis revealed black inclusions of SiO_2 phase located in hollows of the steel surface (Fig. 1 a). It might have come from sand-blast cleaning before the DGS treatment. Narrow, bowed particle in the bottom part of the image and black particles in the background of the Ni(Al) transition layer was identified as Al_2O_3 (Fig. 1b). It appeared as a result of oxidation of partially melted particle of pure Al during the DGS process.

A distinct boundary of the Ni(Al) transition layer and Cr(Ni) layer with the Fe-Al coating is very fuzzy and wavy, which indicates partial melting of the sprayed grains of Fe-Al (1200°C) and Cr (1800°C).

Fig. 1a shows an analysis of the SiO_2 inclusion, while Fig. 1b presents the analysis of NiAl and Al_2O_3

inclusions in Ni(Al) layer of 70 μm width and good quality followed by smooth cross section of Cr(Ni) tran-

sition layer and the Fe-Al coating (on the right) of larger porosity than the Ni(Al) transition layer.

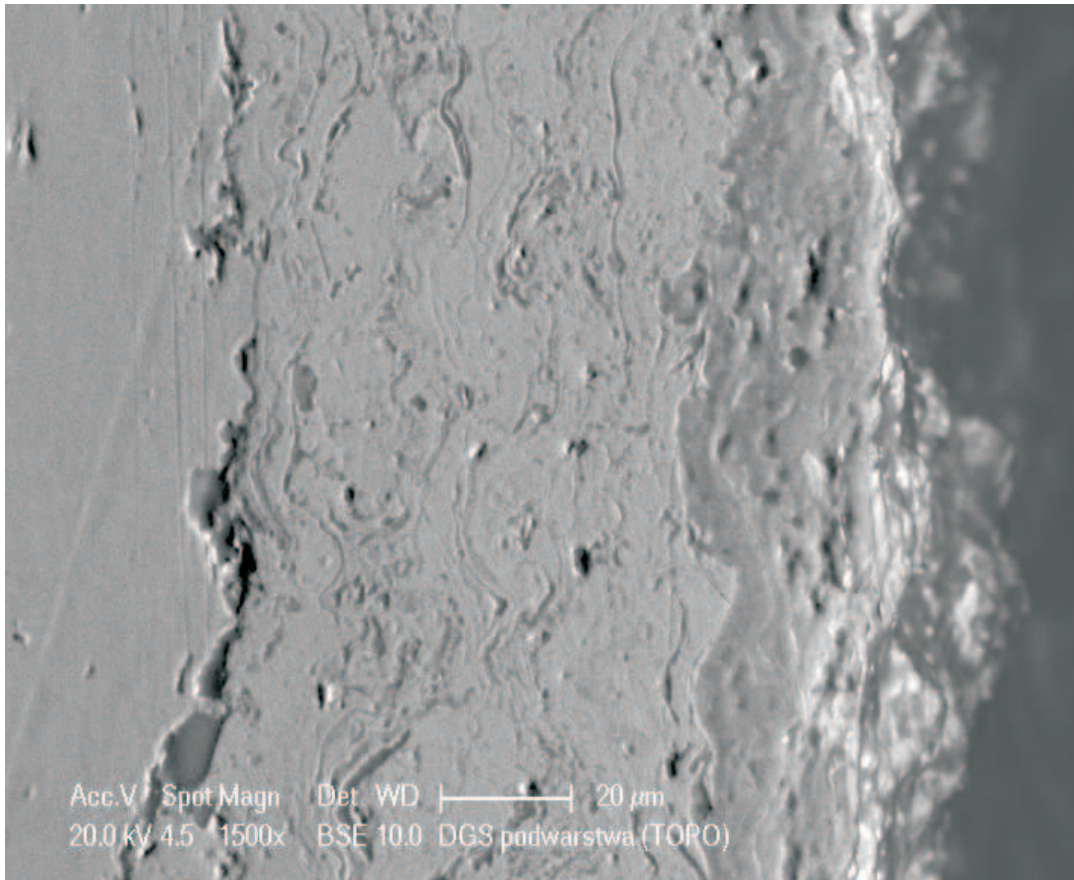


Fig. 1. SEM microstructure of Fe-Al coating (right side) DGS sprayed onto the 045 steel substrate (on the left) with transition layers of Ni(Al) and Cr(Ni)

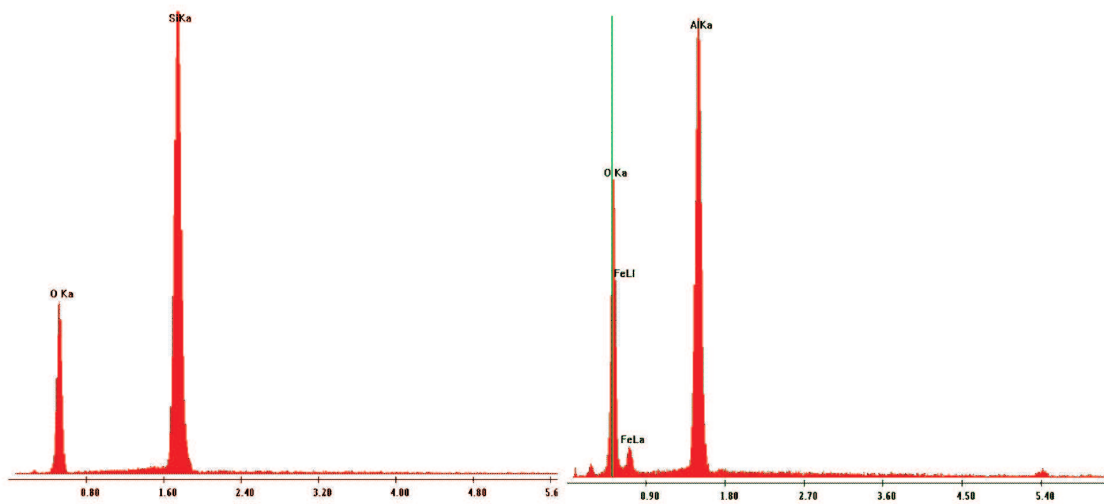


Fig.1a.

Fig.1b.

Fig. 1 a. (SEM/EDX) point analysis of composition of silica grain at the boundary of 045 steel substrate and the Ni(Al) transition layer.
 Fig. 1.b. (SEM/EDX) point analysis of composition of corundum grain at the boundary of Ni(Al) and Cr(Ni) transition layers and inside the Ni(Al) transition layer

The Al oxides appear in the transition layer during the DGS process most often because of the oxidation of partially melted Al or Ni(Al) particles. It seems that the SiO₂ and Al₂O₃ inclusions are responsible for the delamination of the coating and transition layers.

Fig. 2 presents a SEM microstructure of the coating with linear changes of composition (EDX). Starting from the top, they refer to oxygen, aluminium, chromium, iron, and nickel present within the layers of the coating.

The point analysis of composition (EDX) in individual grains of Ni(Al) (Fig. 2a-c) revealed the content of Al from 4 to 46 wt.%. However, it should be taken into consideration that such measurements are semi qualitative because of quite high depth of the electron beam penetration.

The Al low phase Ni-4 wt.% Al +5 wt.% Fe was observed in the direct vicinity of the substrate due to the Fe diffusion to the Ni phase. The number of particles with increasing Al content in Ni-Al phase grew together with the distance from the substrate. A grain of Ni and 22 wt.% Al was observed at the distance 52

μm from the substrate and corresponded to the solid solution based on βgNiAl phase. The phases containing 11 and 13 wt.% Al were the Ni₃Al phase, which were frequently accompanied with corundum (Al₂O₃). About 60 μm away from the substrate, the Cr(Ni) phase began at the line of content measurement, also accompanied with corundum.

The boundary of transition layers Ni(Al) and Cr(Ni) was determined by the appearance of Cr peak (Fig. 2). In the area of Ni(Al) at some distance from the boundary of Cr(Ni) layer and Fe-Al coating, a particle of pure Cr was identified. Fig. 2a presents the measurement of composition of the Fe+36Al+20wt%Cr phase at the boundary Cr(Ni)/FeAl. Within the coating at the boundary with the Cr(Ni) transition layer, the Al low Fe₃Al phase containing 19 wt.% Al, ε phase with 44 wt.% Al and 43wt%Al as well as the FeAl₂O₄ phase were identified. All the above contents were established in the EDX point analysis. As an example, the composition of the FeCr10Al21 (wt.%) measured at the Fe-Al / Cr(Ni) boundary is shown in Fig. 2 c.

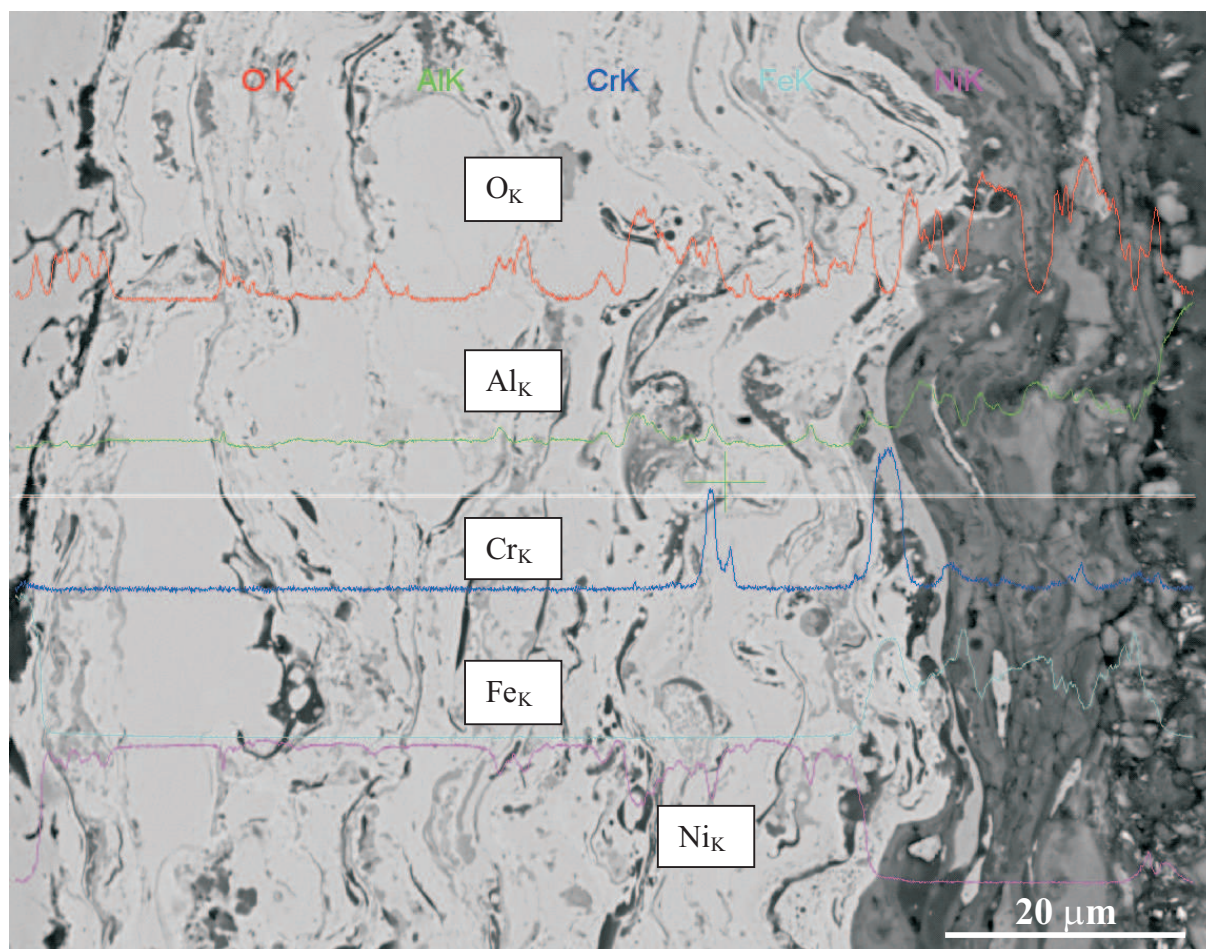


Fig. 2. SEM-EDX image of the DGS coating (starting from the left side): steel/ Ni(Al)/Cr(Ni)/Fe-Al (cross section)

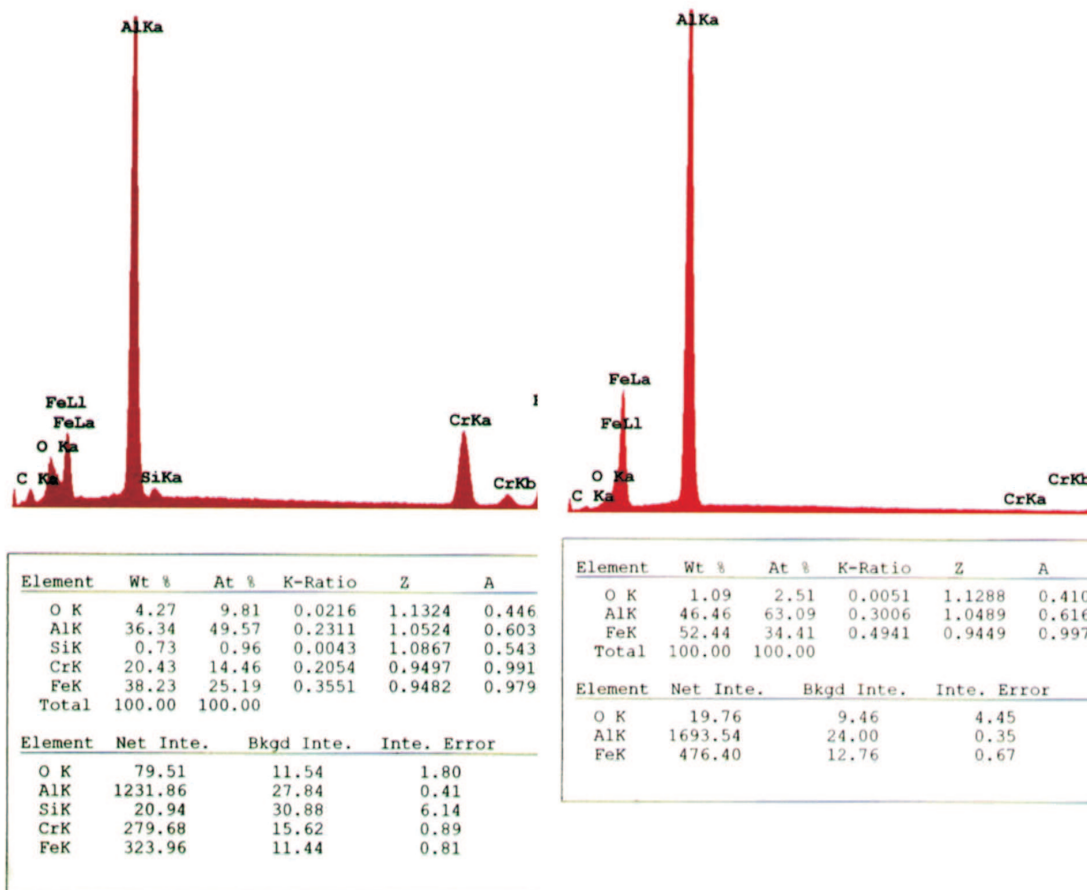


Fig.2a.

Fig.2b.

Fig. 2 a. Composition of FeAlCr phase measured using EDX analysis close to the coating boundary. Fig. 2 b. Composition of FeAl phase inside the coating

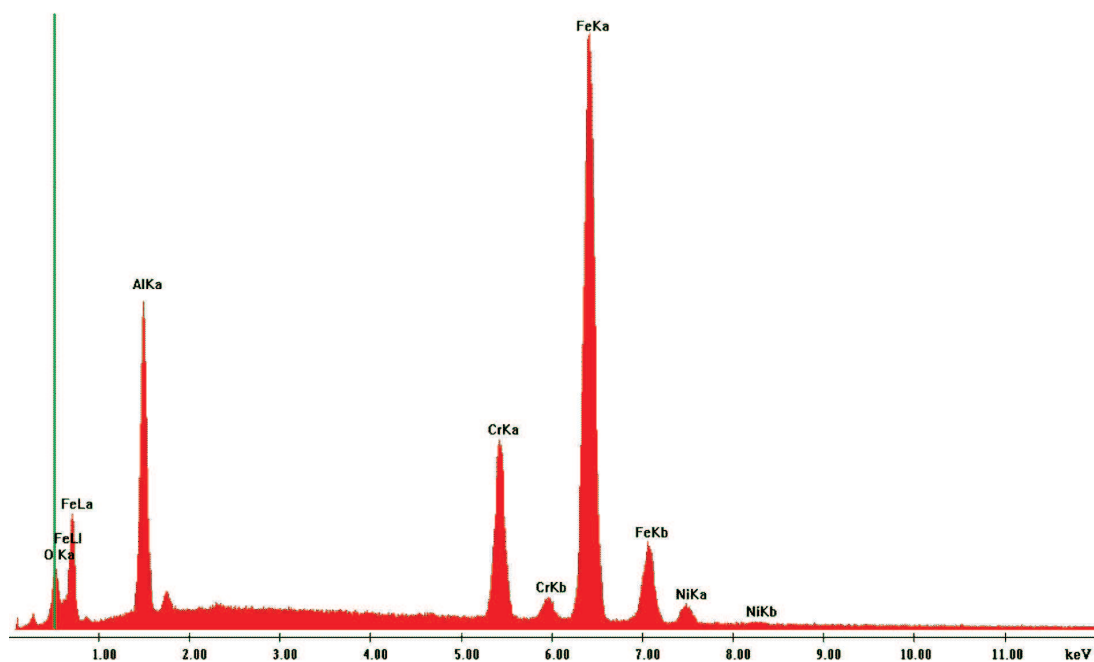


Fig. 2 c. Example of EDS point analysis at the boundary of FeAl coating and the transition layer Cr(Ni)

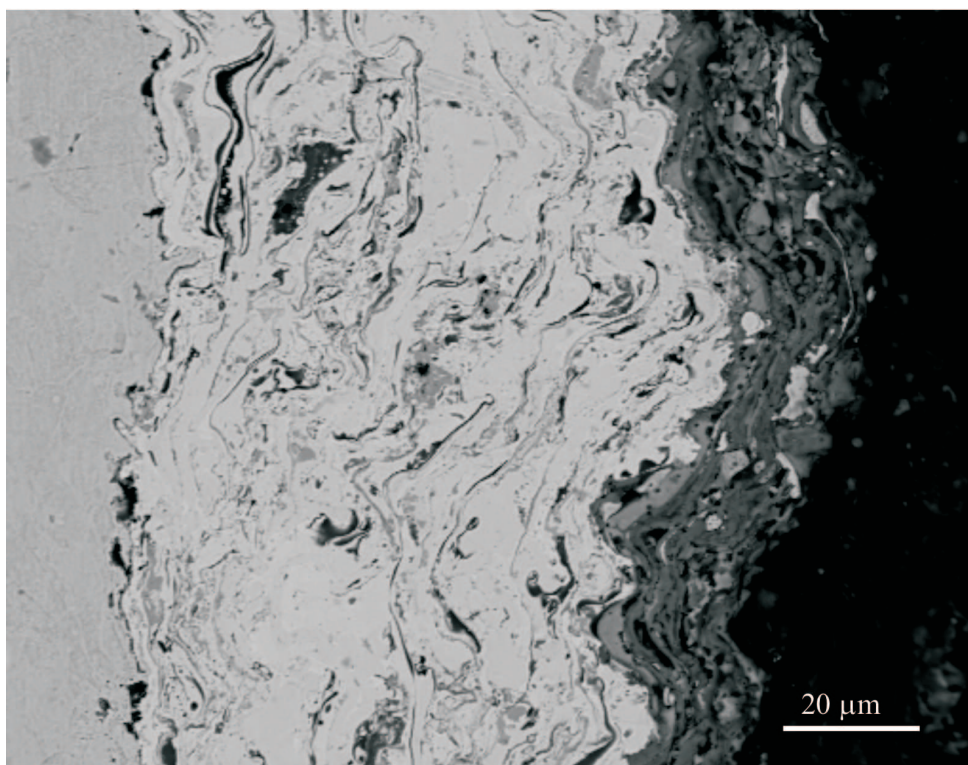


Fig. 3 a. SEM microstructure of transition layers Ni(Al) and Cr(Ni) (upper image)

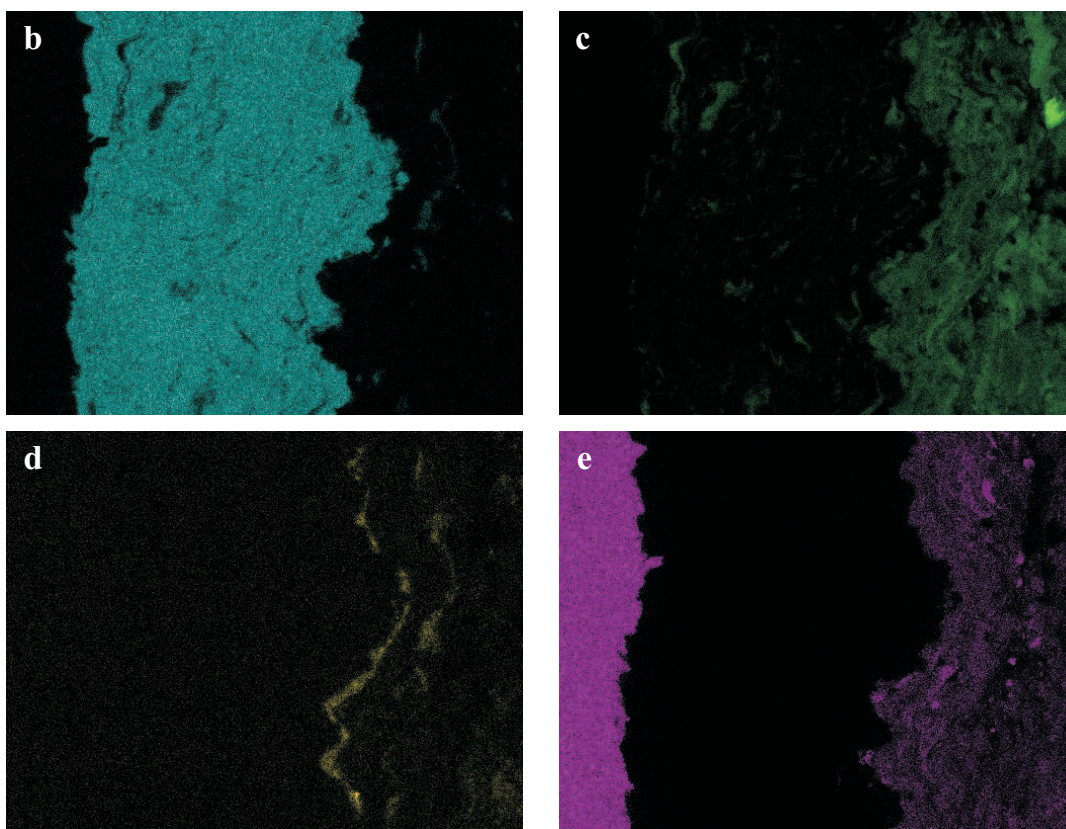


Fig. 3 b. Map of Ni distribution in the area of Ni(Al) and Cr(Ni) transition layers (lower photo). Fig. 3 c. Ni(Al) and Cr(Ni) transition layers, map of Al distribution. (light regions). Fig. 3 d. Cr(Ni) transition layer, map of Cr distribution (light regions). Fig. 3 e. Substrate on the left side and coating (on the right side), map of Fe distribution (light regions)

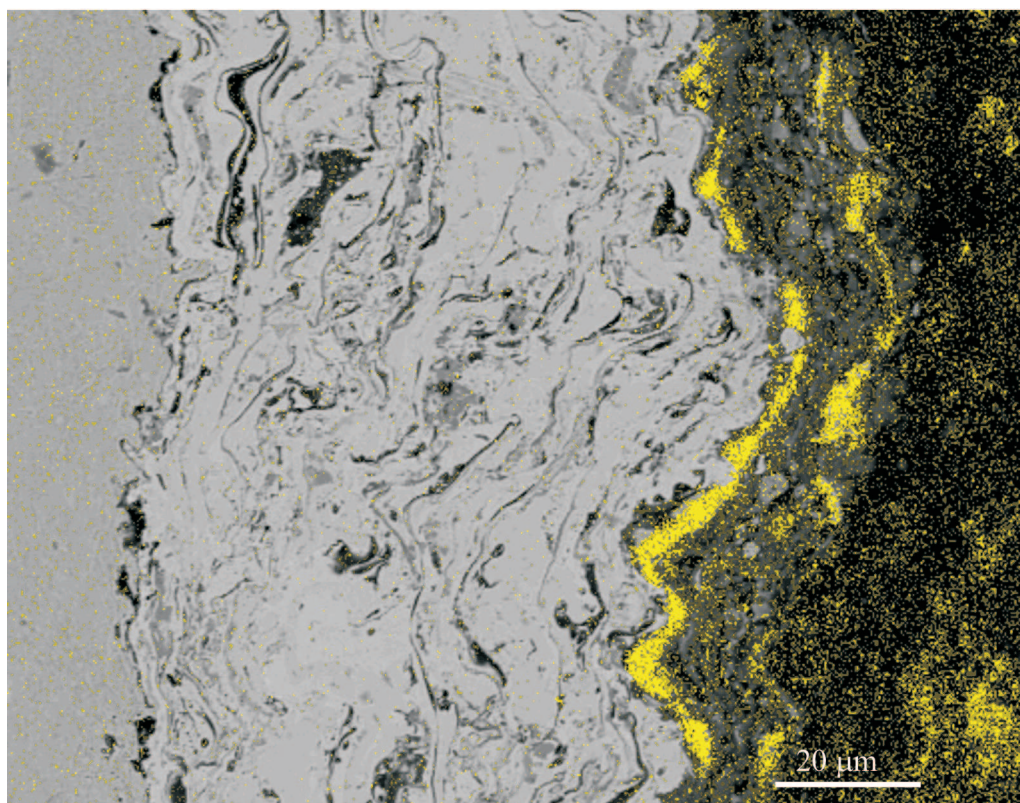


Fig. 3 f. SEM microstructure of Ni(Al) and Cr(Ni) transition layers and the coating, map of Fe, Al and Cr distributions (light regions)

Analysing the SEM image in Fig. 3 a along a selected section of the Fe-Al coating and its transition layers Ni(Al) and Cr(Ni), it can be concluded, that Ni dominated in the first layer of width about 70 μm deposited on the steel substrate. The map presented in Fig. 3 c reveals also regions of elevated content of Al. Fine cracks and sticking out irregularities were observed at the surface of steel. Apart from NiAl phases, quite numerous Al₂O₃ oxides were seen within the Ni(Al) layer (Fig. 3 e).

A 20 μm Cr(Ni) layer with a thin film of pure chromium of 1-2 μm width was observed at the boundary between the Ni(Al) layer and the Fe-Al coating (Fig. 3 d). In the region containing Fe (Fig. 3 e) and Al (Fig. 3 f), 8 μm farther from the boundary, another Cr film consisting of a series of Cr particles was identified.

SEM microstructure of the substrate surface with SiO₂ inclusions is shown in Fig. 4 a, where instead of

Cr(Ni) layer, an area of elevated Cr content, 10-12 μm wide, followed by its individual particles was registered at the boundary of region containing Fe and Al (Fig. 4 b). High amount of aluminium oxides were observed in the area of Ni(Al) layer (Fig. 4. c).

Fig. 5 contains the topography of the coating surface consisted of intermetallic phases of the Fe-Al type after polishing off about 5wgμm. It revealed inhomogeneity of surface in the aspect of grain sizes, differing from about 20 μm (FeAl₂O₄ containing 36 at.% Al and 60 at.% O down to sizes of about 2 μm (Fe₂Al₅ with 69 at.% Al), which prevailed (Fig. 5 b.) The small ones surrounded the larger grains, which formed in the detonation beam at the end of the process. An average composition of the surface about 100x100 μm revealed 44 at.% Fe, 27 at.% Al and 26 at.% O (Fig. 5 a), which indicated that only small volume of grains was oxidized.

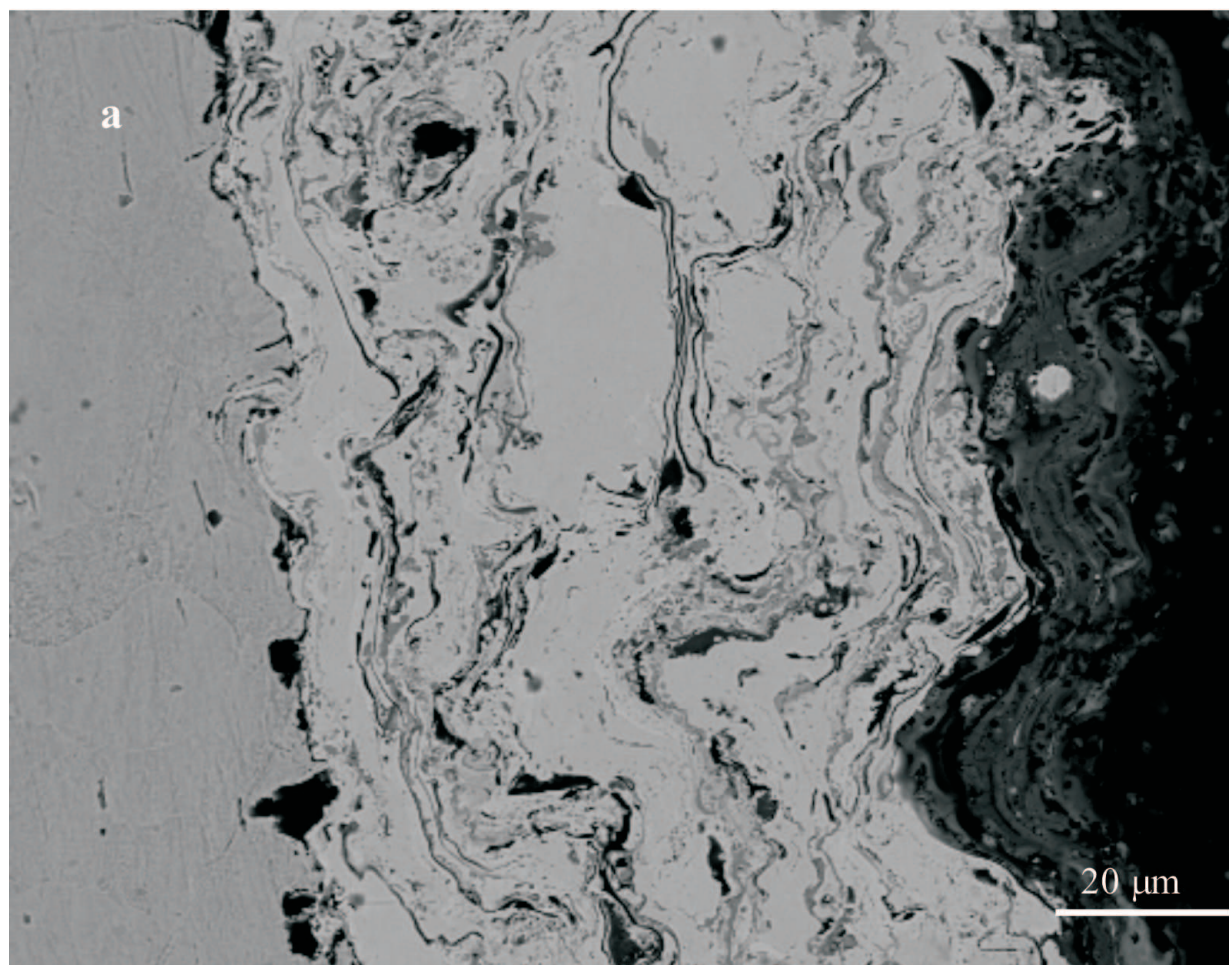


Fig. 4 a. SEM image of transition layers and the Fe-Al coating

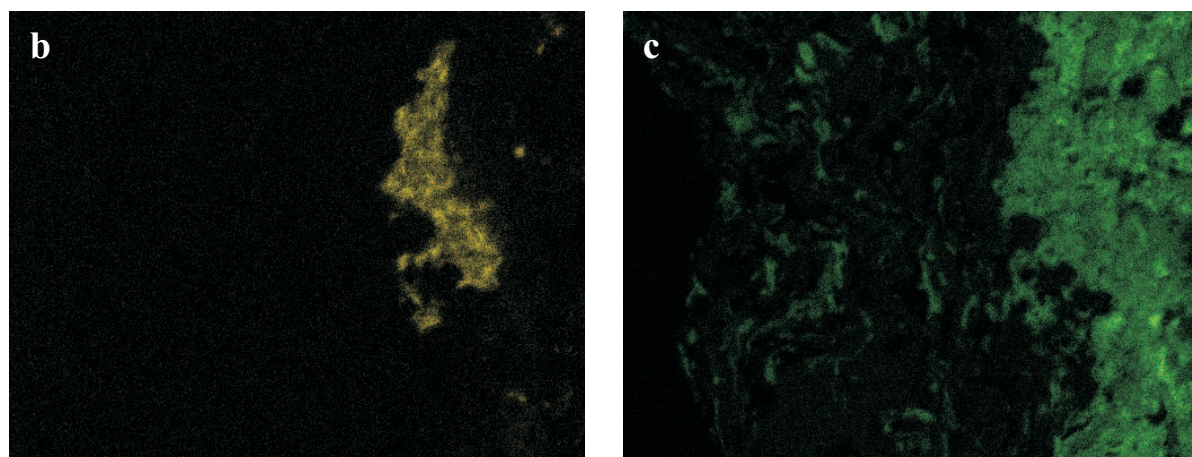


Fig.4 b. Cr(Ni) layer, map of Cr distribution (light regions). Fig. 4 c. Ni(Al) and Cr(Ni) transition layers and Fe-Al coating, map of Al distribution (light regions)

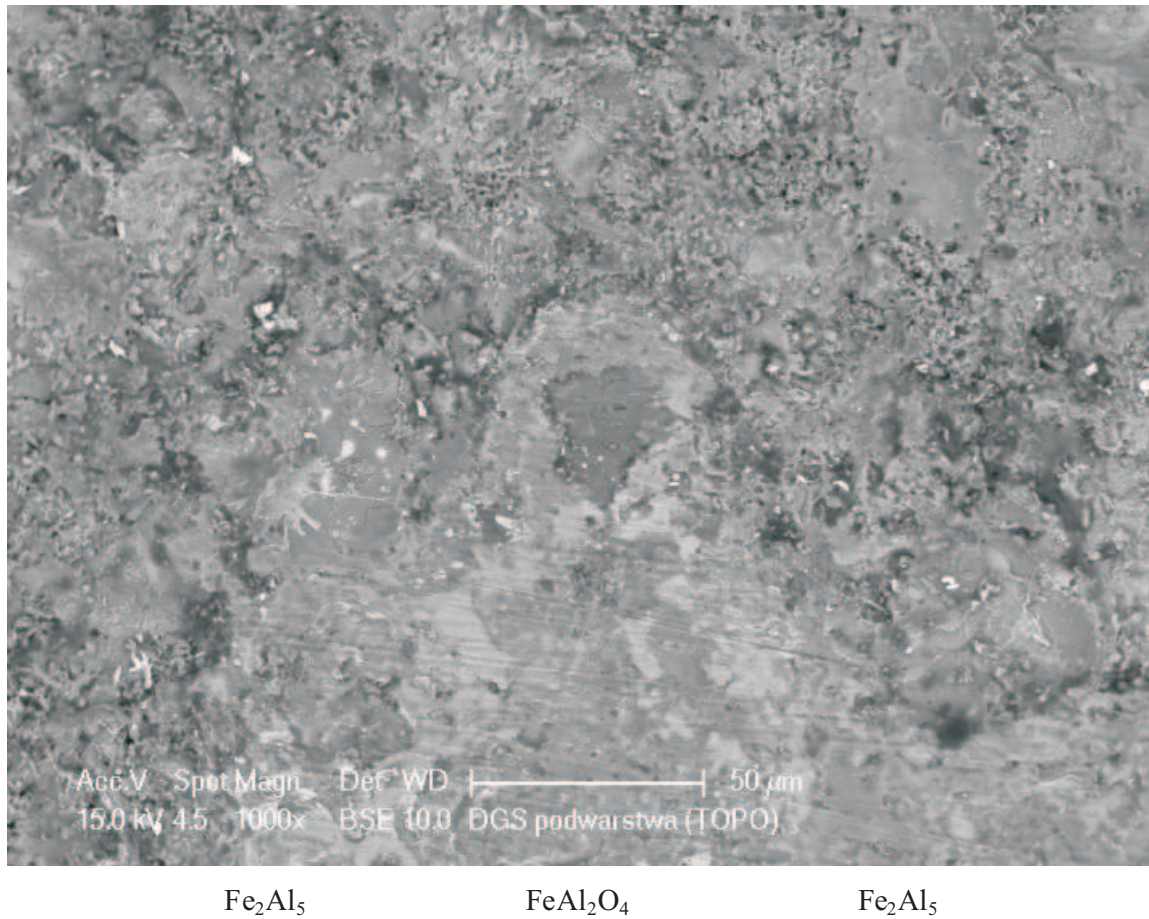


Fig. 5. Surface topography of DGS FeAl coating after grinding by 50 μ m

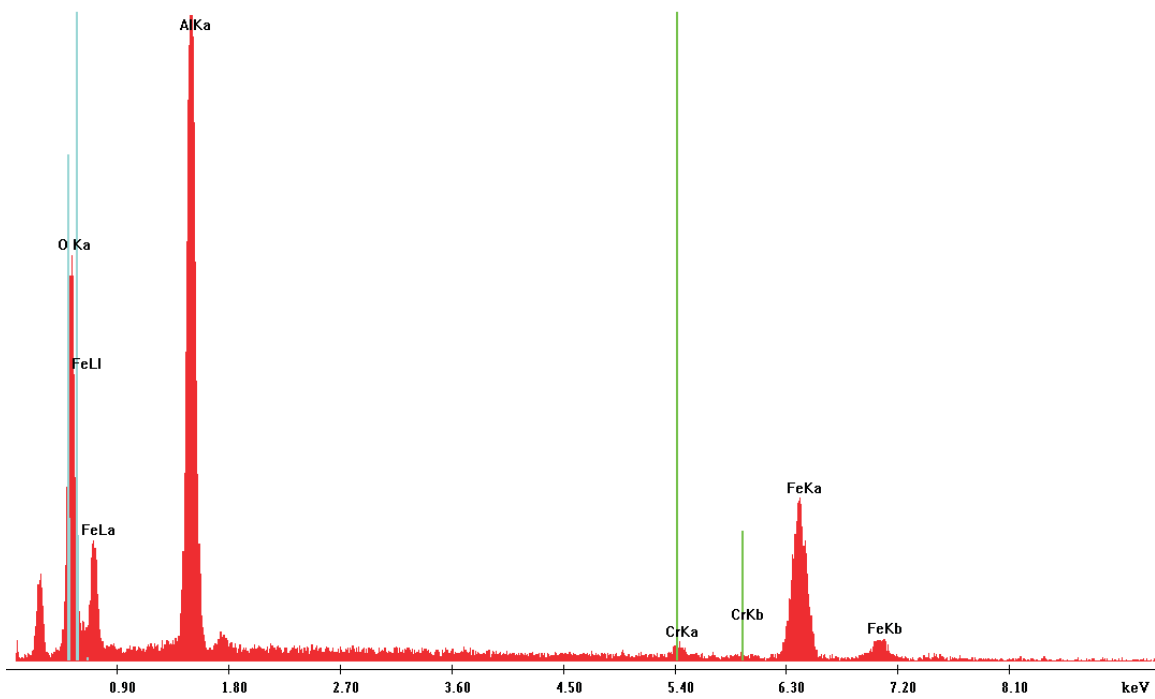


Fig. 5 a. Average composition of area 100x 100 μ m shown in Fig. 5

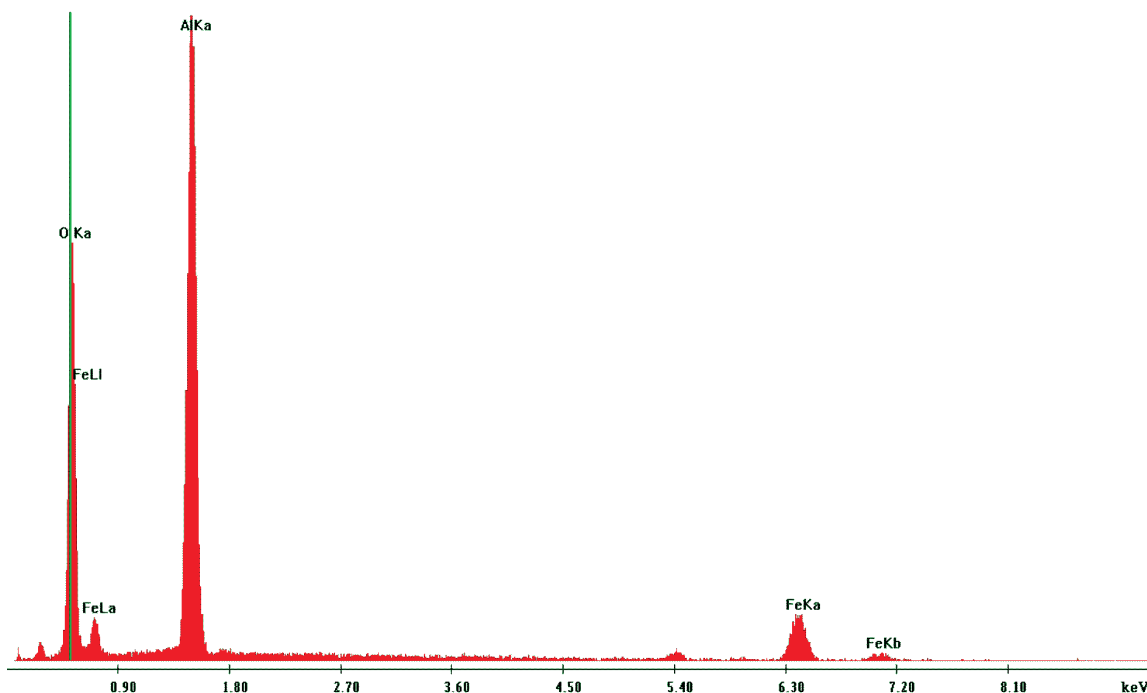


Fig. 5 b. SEM/EDX point analysis of the area in the centre of the image of Fig. 5. FeAl_2O_4 phase

4. Summary

It results from the performed examinations using the SEM-EDX technique, that the lower adherence at boundary steel/ Ni(Al) transition layer established in strengths tests [2] may have been brought about by the presence of SiO_2 particles stuck into the surface before the spraying. The boundary free from the SiO_2 particles should reveal better properties. Thin bands of pure Cr in the Ni matrix was observed in the Cr(Ni) layer at the boundary with the Fe-Al coating. The boundary between Ni(Al) and Cr(Ni) layers was free from inclusions apart from the individual films of Al oxide of less than $1 \mu\text{m}$ width, which was of wavy shape as a result of partial melting of primary grains.

The occurrence of Al_2O_3 indicated, that too high amount of oxygen was used in the DGS process. The grains of Al oxide were found in small amount also at the boundary of Cr(Ni) transition layer and Fe-Al coating.

The examinations of surface microstructure of Fe-Al coating showed inhomogeneity of grain size (from 5 to $10 \mu\text{m}$) and composition of phases. Within the coating the grain size differed from $5 \mu\text{m}$ to more than $50 \mu\text{m}$ (Fig. 5).

5. Conclusions

1. First transition layer Ni(Al) detonation sprayed (DGS) at the substrate was about $70 \mu\text{m}$ and consist-

ed of nickel with inclusions of AlNiO_x . The oxidation occurred during partial melting of an Al particle in the DGS process. The inspection of the substrate revealed also SiO_2 particles stuck into the substrate coming from the sand-blast cleaning of steel. They can be the reason for the deterioration of Ni(Al) layer adherence to the substrate. The layer revealed low porosity, in spite of a high spread of chemical composition of individual grains, which contained from 4 to 46 wt.% Al.

2. The second transition layer Cr(Ni) was about $20 \mu\text{m}$ wide and revealed the occurrence of pure Cr layers of $1\text{-}2 \mu\text{m}$ width in the Ni matrix, particularly at the boundary with the Fe-Al coating. Inclusions of Al oxides and micropores were also observed. The Fe Cr10Al21 (wt.%) phase was identified at the boundary of Cr(Ni) transition layer and the coating Fe-Al.

3. The wavy boundary of Cr(Ni) transition layer and the Fe-Al coating resulted from the inhomogeneous flux of partially melted Fe-Al grains during the DGS process. The Fe_3Al , ϵ (Fe-44 wt.% Al) and FeAl_2O_4 phases were identified in the area of the coating at the boundary with the Cr(Ni) transition layer, apart from large porosity.

4. The established occurrence of Al oxides at the boundaries of transition layers and the substrate could be the reason for the delamination. That is why, the use of aluminium should be limited. The idea of deposition of transition layer is by all means justified, but it follows from the performed study, that the application of one layer would be sufficient. It could be Cr(Ni) transition

layer, which would increase the strength of the joint and adherence of the coating.

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