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DETONATION DEPOSITED Fe-Al COATINGS PART III: MORPHOLOGY OF THE Ni(Cr) AND Ni(Al) INTERLAYERS AND Fe-Al COATING SPRAYED ONTO THE 045 STEEL SUBSTRATE

POWŁOKI Fe-Al OSADZANE DETONACYJNIE. CZĘŚĆ III: BUDOWA WARSTW POŚREDNICH Ni(Cr) I Ni(Al) ORAZ POWŁOKI Fe-Al NA PODŁOŻU STALI WĘGLOWEJ OSADZANYCH DETONACYJNIE

The morphology of interlayars and the coating of Fe-Al phase detonation sprayed (DGS) on the substrate of 045 steel was analysed in the work. The Ni(Al) layer, first from the substrate side consisted of Ni with inclusions of Al oxide. The second deposited layer was Ni(Cr), which contained lamellas of Cr in the Ni matrix. The phases present in the transition layers and in the coating were identified with SEM, and EDX methods (linear and point changes of chemical composition). The identification was confirmed with the X-ray technique and TEM microstructure analysis.

It was established that Al oxides and AlNiO phases appeared in the DGS process after partial melting and oxidation of Al particles, while in the not melted part of grains small grain morphology was observed.

Using the X-ray method, the $FeAl_2O_4$, Fe_3Al and FeAl phases were identified in the coating, the Cr and Cr_2Ni_3 phase in the Ni(Cr) interlayer as well as pure nickel and the NiAl phase in the Ni(Al) interlayer.

The occurrence of brittle phases of Al oxide and AlNiO phases near the boundaries of layers might result in the increase of tendency to delamination. Hence the reduction of the Al content seems advantageous from the point of view of mechanical properties of the joint.

Keywords: G-dun spraying, Fe-Al intermetallic coatings, Ni(Al) and Ni(Cr) interlayers

W pracy poddano analizie metodą skaningowej - SEM i transmisyjnej- TEM mikroskopii elektronowej, budowę warstw pośrednich i powłokę faz typu Fe-Al natryskiwanych detonacyjnie (DGS) na podłoże stali 045. Warstwa Ni(Al) pierwsza od podłoża składa się z niklu z wtrąceniami Al i tlenku glinu. Na niej osadzona jest warstwa druga Ni(Cr) składającą się z warstewek chromu w osnowie niklu. Metodami EDX, liniowej zmiany składu oraz punktowej analizy zidentyfikowano fazy w warstwach pośrednich i powłoce. Tą identyfikację potwierdzono techniką X-ray oraz analizą mikrostruktury TEM. Ustalono, że tlenki oraz AlNiO fazy powstały w procesie DGS po nadtopieniu i utlenieniu cząstek Al, zaś w nie nadtopionej części ziaren zaobserwowano drobnoziarnistą budowę. W powłoce zidentyfikowano metodą X-ray fazy: $FeAl_2O_4$, Fe_3Al oraz FeAl, w warstwie pośredniej Ni(Cr) – chrom i fazę Cr_2Ni_3 w osnowie niklu, zaś w warstwie Ni(Al) czysty nikiel i fazę NiAl. Występowanie faz tlenku glinu i faz AlNiO w pobliżu granic warstw pośrednich powodować może zwiększenie tendencji do delaminacji. Korzystnym byłoby zatem obniżenie ilości aluminium.

1. Introduction

The coatings of Fe-Al type together with a contribution of transition layers of pure Ni and NiAl particles and pure Al as well as layers of Ni(Cr)-Cr in the Ni matrix deposited with detonation gas spraying (DGS) belong to the system of multilayer composite coatings. Their adherence to the substrate together with protective functions is one of main features [1-3]. They reveal high resistance to abrasive wear and high temperature oxidation and find application in jet turbines.

Because of essential effect of adhesion force of multilayer coating on the substrate, the examinations of adherence were carried out using the three-support bending correlated with the results of acoustic emission examinations [4]. The analysis helped to determine the value of limit bending load, which could not be exceeded in danger of cracking or delamination.

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The investigations of adherence of multilayer coatings and 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 interlayer, compared with the Ni-20 wt.% Al and Ni-20 wt.% Cr interlayers with the Fe-Al coating. However, the highest delamination was observed in the joint of steel with Ni(Al) layer, while the Ni(Cr) layer containing chromium in the matrix of nickel revealed a higher bending strength.

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

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

2. Experimental

The Ni(Al) interlayer with inclusions of Al particles or NiAl phases and another interlayer of Cr in the Ni matrix, Ni(Cr), 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 interlayers and the coating were detonation gas sprayed (DGS). Materials for the experiments were delivered from the Military University of Technology in Warszawa. The parameters of deposition process (DGS) were given in work [5]. The steel for substrate was stress relieved and mechanically cleaned.

The obtained coatings were examined by scanning (SEM) and transmission electron microscope (TEM) techniques. Cross-section of the coatings were inspected using back-scattered electrons in SEM studies. The measurements of the chemical composition in the interaction zone were carried out using a Link ISIS energy X-ray (EDX) spectrometer attached to a Philips XL 30 scanning electron operating at 20kV voltage.

Thin foils the TEM prepared using a focused Ga^+ ion beam (FIB-Focus Ion Beam) technique in a Quanta 200 3D, FEI and then examined in a Philips CM 20 Twin instrument equipped with an EDAX Phoenix EDX spectrometer. The microscope operated at accelerating voltage 20 kV in the nano probe mode with a LaB_6 cathode. A high resolution X-ray mapping was applied in order to determine partitioning of the across to coating. It was accomplished using the TEM TECNAI G^2FEG super TIN(20 kV) microscope equipped with High Angle Angular Dark Fild (HAADF) detector and integrated energy dispersive spectrometry system.

The X-ray phase analysis of the coating at the of which layers 50 μm thick were removed subsequently (mechanical polishing) was performed using Philips PW1710 diffractometer with the radiation Co Kα.

3. Results and discussion

3.1. SEM analysis of microstructure

The investigations were performer on samples with intermetallic coatings of Fe-Al type obtained with the DGS technique. The surface of the 045 steel was DGS deposited with Ni(Al) transition layer of pure Ni with inclusions of Ni 15at%Al and pure Al following by the Ni(Cr) layer of Cr and Ni. Next, a coating consisting of intermetallic phases of Fe-Al type: FeAl, $FeAl_2$, Fe_2Al_4 and Fe_3Al phases was deposited on the above mentioned interlayers. The coating was 50-μm thick, while the Ni(Cr) interalayer was 20 μm and pure Cr layer 1-μm.

The SEM microstructure in the coating cross section in Fig. 1 produces the substrate of 045 steel, at its left side, adjoining the boundary with the Ni(Al) interlayer of pure Ni with NiAl inclusions, which has a characteristic wavy of the small layers resulting from the inhomogeneity of the detonation flux in the DGS process and partial melting of powders. Next transition layer as identified as Ni(Cr) – pure chromium in Ni matrix followed by the Fe-Al coating. Inclusions of NiAl and Al_2O_3 phases were observed in the Ni layer : Ni(Al)+Ni(Cr) which was 70 μm wide and good quality, next a smooth cross section of the Ni(Cr) layer followed by the Fe-Al coating (on the right side of the image) of increased porosity compared with the Ni(Al) interlayer.

The local EDX analysis revealed, that black inclusions at the substrate and –Ni(Al) layer boundary are SiO_2 phase localized in hollows of the steel (Fig. 1a). It might have originated from the sand-blast clearing of steel prior to the DGS treatment. The narrow bent particle in the lower part of the image as ell as black particles inside the Ni(Al) layer were identified as Al_2O_3 phases (Fig. 1b) and it could appear as a result of oxidation Al particle partially melted during the detonation.

The distinct boundary of the inter layers with the Fe-Al coating was observed to be uneven and wavy, which might indicate the partial melting of sprayed grains of Fe-Al (1200°C) and Cr (1800°C).

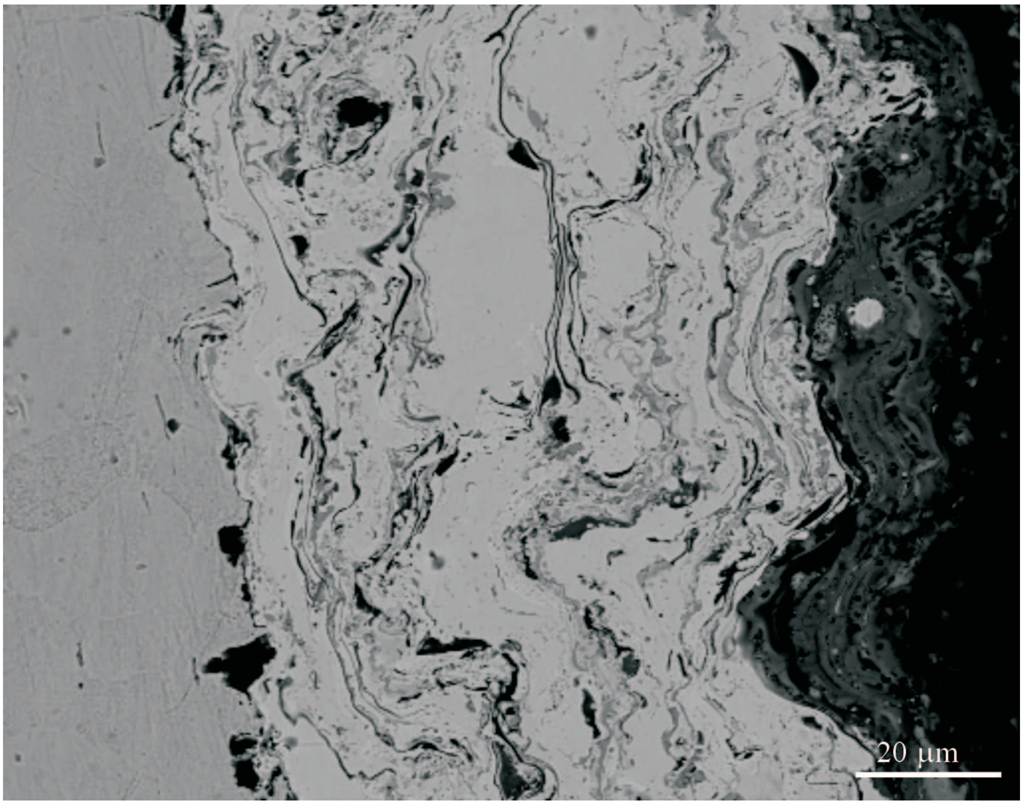

Fig. 1. SEM image of Fe-Al coating (on the right) with transition layers Ni(Al) and Ni(Cr) sprayed with the DGS technique

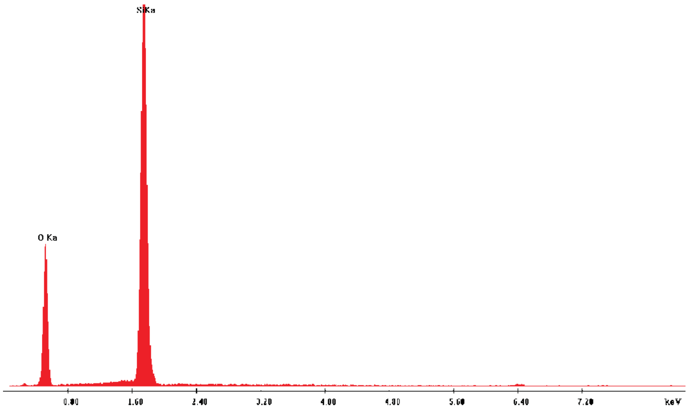

Fig.1a. Point analysis of chemical composition SEM/EDX of silica grain at the boundary of substrate and Ni(Al) layer.

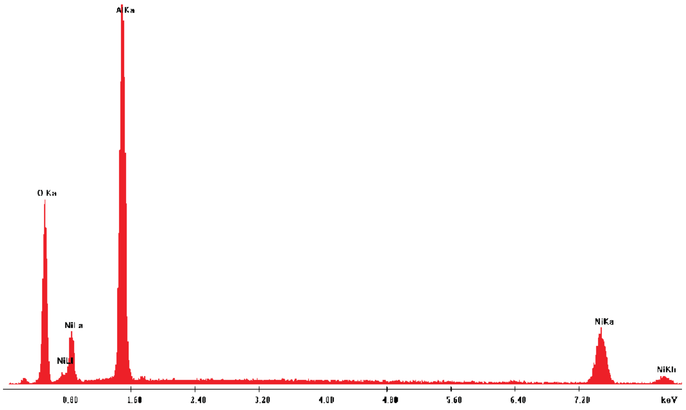

Fig.1b. Point analysis of chemical composition SEM/EDX of Al_2O_3 phase at the boundary of Ni(Al) and Ni(Cr) and within the Ni(Al)layer

The Al oxides appeared in the transition layer during the DGS process most in the case of presence of Al particles or as the effect of oxidation of partially melted NiAl phase. It seemed that SiO_2 and Al_2O_3 inclusions were responsible for the delamination of the coating and transition layers.

3.2. X-Ray analysis

The examination with the X-ray diffraction technique were carried out in the transition layer of pure chromium in the Ni matrix-Ni(Cr) and in the Fe-Al coating after grinding of 50 μm of the coating. Fig. 2 presents the obtained image of Cr layer deposited on the Ni(Cr) layer and the steel substrate as well as the remaining coating.

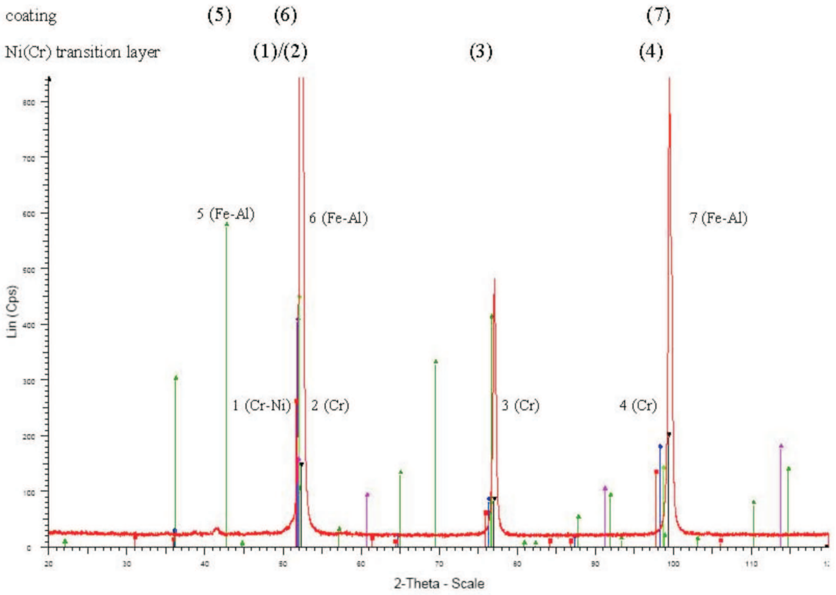

Fig. 2. X-ray diffraction of Fe-Al coating and phases with Ni(Cr) interlayer, after polishing off part of (50 μm) coating

The following phases of the Cr containing interlayer were identified:

(1) Cr_2Ni_3 at plane (111) (55 wt%.Ni) angle 2th – 51.7

(2) Cr at plane (110) angle 2th – 52

(3) Cr at plane (200) angle 2th – 77

(4) Cr at plane (211) angle 2th – 99.3

The identified phases of Fe-Al. coating:

(5) $FeAl_2O_4$ at plane (400) angle 2th – 43

(6) Fe_3Al at plane (311) angle 2th – 52

(7) FeAl at plane (220) angle 2th – 99.4

The results confirmed the presence of the phases, identified with the SEM-EDX method, in the coating Fe-Al and Ni(Al), interlayer according to the data establishment in work [6]. The lack of data from the Ni(Cr) layer shows that the X-ray penetrated only the coating and the Ni(Cr) layer.

In order to identify the phases in the Ni layer, the X-ray analysis was performer after removal of subsequent 50 μm of the layer (Fig. 3).

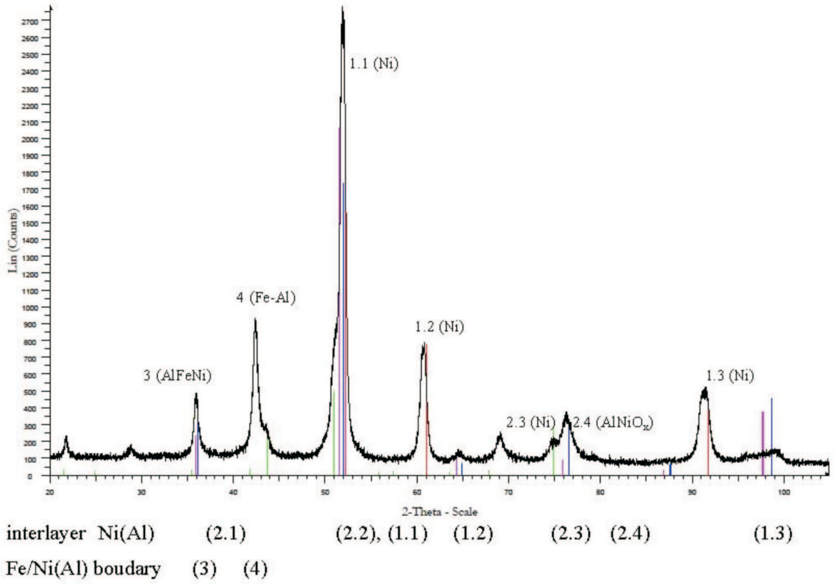

Fig. 3. X-ray diffraction of the Ni(Al) layer at the 045 steel substrate

Two phases Ni-γ and Ni-Al 62wt.% as well as traces of AlFeNi were recorded in the first layers:

(1.1) Ni-γ at plane (111) angle 2 theta – 52.1 interlayer
(1.2) Ni-γ at plane (200) angle 2 theta – 61.0 „
(1.3) Ni-γ at plane (220) angle 2 theta – 91.8 „
(2.1) NiAl at plane (100) angle 2 theta – 36.1 „
(2.2) NiAl at plane (110) angle 2 theta – 52.0 „
(2.3) NiAl at plane (200) angle 2 theta – 76.5 „
(2.4) $AlNiO_x$ at plane (200) angle 2 theta – 76.5 „
(3) AlFeNi at plane (100) angle 2 theta – 35.8 boundary of substrate
(4) $FeAl_2O_4$ at plane (400) angle 2 theta – 44.4

Based the analysis of X-ray diffraction it was established that in the first sprayed interlayer – Ni(Al), on the substrate side pure nickel and inclusions of NiAl were present as well as traces of the AlFeNi phase, which originated from the diffusion of nickel and aluminium from the layer to the substrate. The results confirmed the SEM/EDX observations.

3.3. TEM analysis of Ni(Cr) and Ni(Al) interlayers

At first the Fe-Al coating and the Ni(Cr) interlayer were examined in the aspect of microstructure (Fig. 4).

The TEM image Fig. 4 illustrates and area of the Ni(Cr) interlayer lying directly under the Fe-Al coating. The observed amorphous region in the form of slanted band was identified as AlNiO based on Al oxide. Columnar crystals can be seen in the left, upper side of the image. These structural elements occurred in the result of partial melting of coating in the process of detonation and rapid solidification of the Ni(Cr) layer with inclusions of Al particles. The Ni matrix can be observed as a back ground. A small of pure Cr is also to be observed in this part of the image.

Fig. 5 presents the microstructure of Ni small grains in the Ni(Cr) transition layer, which appeared during the detonation spraying. Distinctly deformed grains of elongated forms are to be observed in the part of the transition layer Ni(Cr) away from the coating.

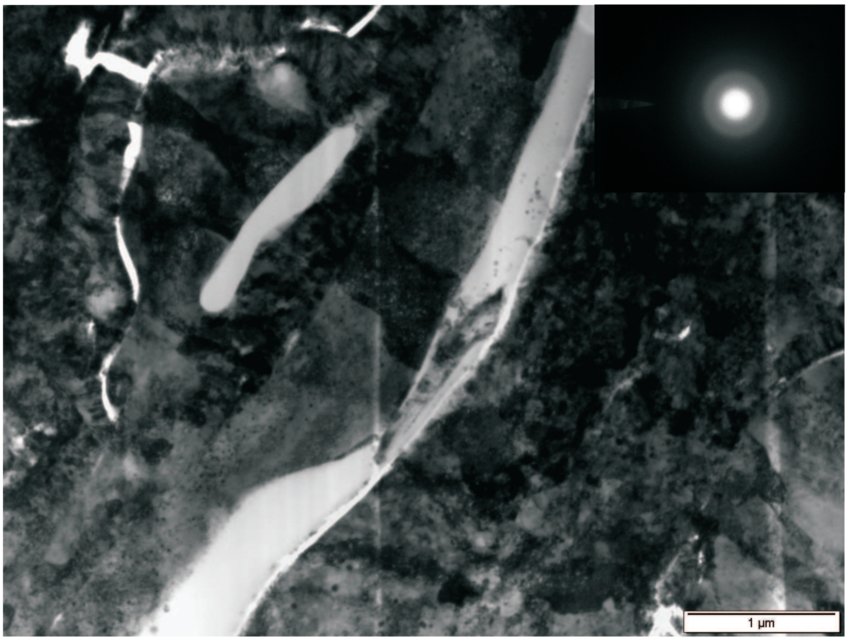

Fig. 4. The Ni(Cr) interlayer with amorphous phase and columnar crystals, electron diffraction with slanted bands

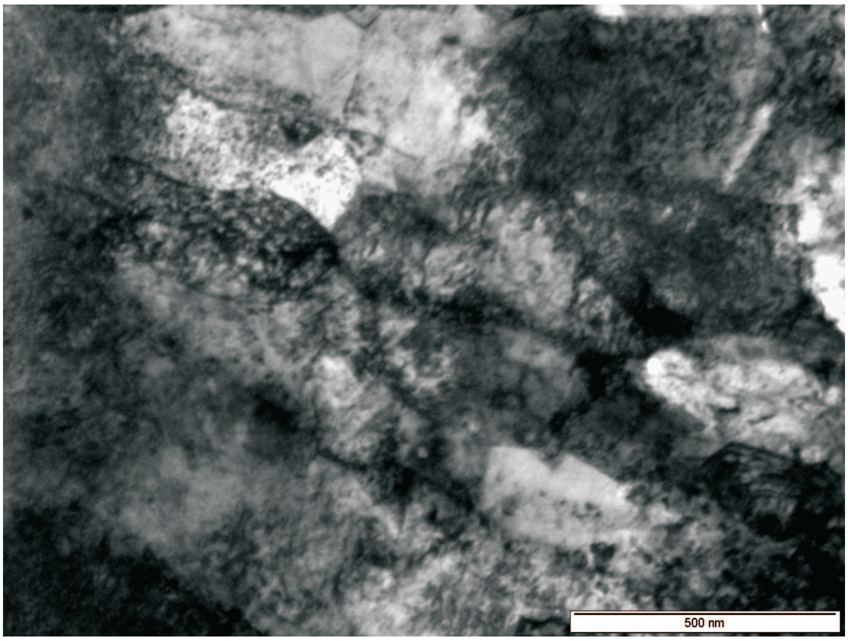

Fig. 5. Small grains of Ni(Cr) transition layer away the boundary with Fe-Al coating

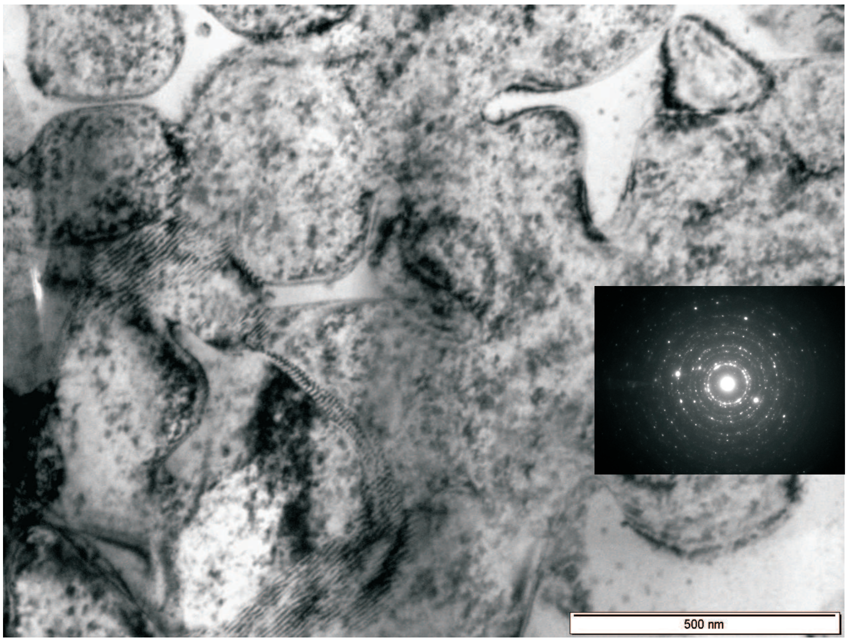

Fig. 6. Ni(Al) transition layer on the steel substrate-AlNiO phase (SAED-[6]) away from the substrate

The of AlNiO oxide composition, which appearyed as the area not too away from the substrate (Fig. 6). It solidified at lower rate the phase at boundary with the substrate. Grain boundaries of high density dislocations were recorded.

Summing up the TEM microstructure observations, it can be stated that tree elements play an import role resulting from partial melting of sprayed grains and their quick crystallization.

These are amorphous phases based on the aluminium oxide, quickly solidifying near the boundaries of layers and AlNiO phase (second element) which crystallize at a lower than the amorphous phases.

Columnar crystals are third element, which effect from the solidification of partially melted regions of the transition layer. Parts of not melted grains undergo a heavy deformation in the Process of detonation which results in the formation of small grains. Since the amorphous phase and the AlNiO oxide constitute brittle elements of layers localized at their boundaries, they affect in a disadvantageous way the properties of the coating. So, the limitation of amount of Al particles in the structure of transition layers and particularly in the Ni(Al) seems the way to improve their quality.

4. Conclusions

1.The Ni(Al) transition layer sprayed at the 045 steel substrate by the detonation method consisted of: Ni matrix and the AlNiO amorphous phase based phase appearing in the process of oxidation of Al particles during the detonation spraying of partially melted grains. Columnar crystals and small grains were observed in the not melted parts of grain, which formed also in the DGS process.

2.The Ni(Cr) transition layer was built of Cr particles in the matrix, which underwent partial melting and deposited at the Ni(Al) layer. The phased on the Al oxide formed in the process of solidification were accompanied by Al-oxides of composition AlNiO which crystallized at lower rate than amorphous phases and were located farther away from the Fe-Al coating, as well as small grains formed in the not melted part of the matrix. Small layers of pure Cr in the Ni matrix were observed in the vicinity of the coating.

3.X-ray diffraction investigation revealed the presence of $FeAl_2O_4$, Fe_3Al, and FeAl phases in the coating, as well as and Cr_2Ni_3 phase were indentified in the Ni(Al) transition layer close to the substrate .

4. The TEM investigations confirmed the presence of Cr lamellas of 1-2 μm width in the Ni matrix and the Ni(Cr) transition layer, as well as particles of a Al_2O_3 phase based.

5.The occurrence of boundaries phases and brittle amorphous phases and AlNiO phases in the neighbourhood of interlayer boundaries brought about the increase of tendency to the delamination of the coating. The decrease of Al amount and better distribution of primary particles in the detonation spraying process can strongly limit these disadvantageous defect.

The Al oxides appeared in the transition layer during the DGS process most in the case of presence of Al particles or as the effect of oxidation of partially melted NiAl phase. It seemed that SiO_2 and Al_2O_3 inclusions were responsible for the delamination of the coating and transition layers.

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