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
Volume 56 2011 Issue 1
DOI: 10.2478/v10172-011-0008-x

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DETONATION DEPOSITED Fe-Al COATINGS PART II: TRANSMISSION ELECTRON MICROSCOPY OF INTERLAYERS AND Fe-Al INTERMETALLIC COATING DETONATION SPRAYED ONTO THE 045 STEEL SUBSTRATE

DETONACYJNE OSADZANIE WARSTW Fe-Al CZĘŚĆ II: TRANSMISYJNA MIKROSKOPIA ELEKTRONOWA WARSTW POŚREDNICH ORAZ POWŁOKI FAZ TYPU Fe-Al NATRYSKIWANYCH DETONACYJNIE NA PODŁOŻE STALI 045

The microstructure of detonation gaseous sprayed (DGS) transition layers of Ni(Al), Ni(Cr) and subsequent coating of Fe-Al intermetallic phases deposited on the 045 steel were studied in the paper using transmission electron microscopy. In order to identify phases in the particular interlayers the selected area electron diffraction (SAED) and an energy dispersive X-ray microanalysis (EDX) were applied. It was found that the Ni(Al) interlayer contained basically pure nickel with a small fraction of NiAl phase. The Al based amorphous phase was also observed its area in the form of bands. The Ni(Cr) interlayer basically contained Ni-rich small grains. Pure chromium in the Ni matrix appeared in the vicinity of Fe-Al coating in the shape of bow-like bands, parallel to the coating. The boundary between the Ni(Cr) layer and the Fe-Al coating revealed abrupt decrease of the Ni content in the coating at simultaneous rapid increase of the Fe amount. Improper Al/Cr ratio within the Ni matrix seems to be responsible for the formation of Al-oxides and the bands of almost pure Cr and Ni(Cr) layers and resulting decrease of interlayer adherence.
Keywords: D-gun spraying, Fe-Al intermetallic coatings, Ni(Al) and Cr(Al) interlayers.

W pracy analizowano mikrostrukturę złożonej budowy wielowarstwy składającej się z podłoża ze stali węglowej 045 oraz osadzonych detonacyjnie (DGS) na niej warstw pośrednich Ni(Al) i Ni(Cr) oraz powłoki faz międzymetalicznych typu Fe-Al. W celu identyfikacji faz powłoki i warstw pośrednich zastosowano techniki badawcze: dyfrakcji elektronowej (SAED) oraz analizy składu chemicznego faz (EDX) w transmisyjnym mikroskopie elektronowym. Stwierdzono, że warstwa Ni(Al) zawiera przede wszystkim prawie czysty nikiel z małym udziałem fazy NiAl. Oprócz tego w obszarze ziaren Ni występowała faza amorficzna w postaci pasm oparta na Al i O. Obecność niewielkich rozmiarów ziaren bogatych w nikiel stwierdzono również w warstwie Ni(Cr), wewnątrz których znajdowały się pasma czystego chromu. Granica pomiędzy Ni(Cr) oraz powłoką Fe-Al wykazywała gwałtowny spadek zawartości niklu przy jednoczesnym silnym wzroście żelaza. Obecność tlenków aluminium oraz pasm bogatych w chrom wynikała z niewłaściwych proporcji Al/Cr podczas przygotowania wielowarstw i wpływała negatywnie na ilość mikropęknięć i porów oraz wynikającą z tego adhezję pomiędzy poszczególnymi warstwami.

1. Introduction

The detonation gas spraying (DGS) technique is the promising to obtaine the multilayer and multicomponent advanced materials. The proper characterization of the particular transition layers is focused on the identification of the phases present and their influence on the bond quality between subsequent layers.

These problems have been undertaken quite rarely [1,2] and their explanation may contribute to the development of the technology of detonation deposition of Fe-Al phases onto the substrate of either a steel or Ni-based superalloy with good adherence of the coating. The present paper is a continuation of works [3, 4], which derived the microstructure analysis of Fe-Al coating deposited directly onto the 045 steel substrate. Such a joint was however imperfect, because of frequent delamination from the substrate. The proper selection of interlayers plays an important role in providing good exploatation of properties of joints [5, 6], which find application in the air craft and rocket industry for blades in turbines and turboprop engines.

The present work has been aimed at the description of the morphology of Ni(Al) and Ni(Cr) individual interlayers and their adherence to the substrate of 045 steel

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and the Fe-Al type intermetallic layer obtained due to detonation spraying technique.

The deposition of two intermediate layers: Ni(Al) and Ni(Cr) seems to be more advantageous in comparison with direct deposition of Fe-Al coatings on steel substrate. Especially, Ni(Cr) layer free form Al should not lead to its oxidation and the appearance of brittleness, while the presence of Cr ensures good adherence of coating to the interlayer and subsequently to the substrate.

2. Experimental

The experimental multilayer material was obtained after the detonation-gaseous spraying onto the 045 steel substrate. The first interlayer from the substrate side described as Ni(Al) was deposited using Ni powder with a small fraction of NiAl powder and Al particles. The Ni powder with a contribution of Cr was used to produce another Ni(Cr) layer. The next sublayer was formed with detonation sprayed Fe_2Al_5, Fe_3Al, and FeAl powders of 40-60 μm granulation. The material was supplied by the Military University of Technology in Warsaw. Details of the spraying process have been given in the Ref. [5]. Composition of the interlayers was selected taking into account low stress between Ni and Fe, while lower porosity and diffusion of Al to the substrate should have been ensured by the addition of Al. Chromium was added to increase the strength of layers and their adherence to the substrate.

Preparation of the thin foils for the transmission electron microscopy (TEM) was performed applying of the Ga^+ ion thinning (FIB-Focused Ion Beam) Quanta 3D technique. The TEM examinations - Bright Field (BF) images and Selected Area Electron Diffraction patterns (SAED) – were carried out using TECNAI G^2 FEG super TWIN (200kV) transmission electron microscope equipped with High Angle Angular Dark Field (HAADF) detector and integrated with an energy dispersive X-ray spectroscopy (EDX) system manufactured by EDAX company. Moreover, the observations in scanning-transmission mode (STEM) allowed the visualization of the difference in chemical composition of particular phases.

3. Results and discussion

3.1. TEM analysis of Fe-Al coating

Figure 1 presents the part of obtained Fe-Al coating and Ni(Cr) interlayer. The magnified areas of the Fe-Al denoted by A, B, C are presented in Figs. 2 a-d. The Fe-rich zone is shown in Fig. 2a which was confirmed by the electron diffraction technique (Fig. 2b). Within this zone the precipitates of Fe-Al type intermetallic phases are also visible. Figure 2c presents the microstructure of various detonation sprayed Fe-Al phases. Light areas correspond to phases enriched in Al (e.g. Fe_2Al_5) while the dark ones to these enriched in Fe (e.g. Fe_3Al, FeAl). On the other hand, Al_2O_3 amorphous phase containing single Fe-rich precipitates, which were previously [6] detected and described as $FeAl_2O_4$, is visible in Fig. 2d.

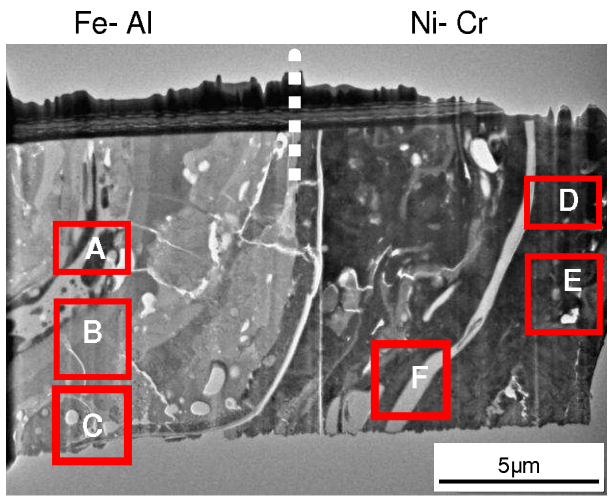


Fig. 1. TEM micrograph of overall view of Fe-Al coating and Ni(Cr) interlayer cross-section

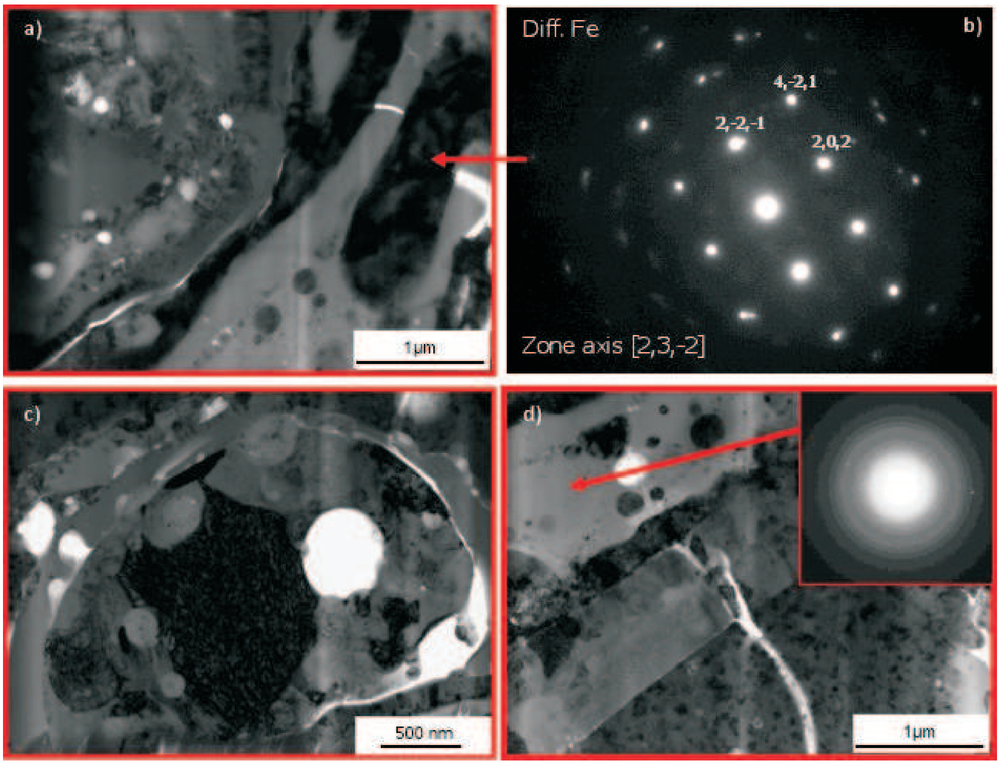


Fig. 2. TEM micrographs of magnified areas of Fe-Al coating show in Fig.1:(a) magnification of area A and SAED pattern taken from precipitate marked by arrow (Fig. 2b), (c) magnification of area B, (d) magnification of area C together whit SAED

3.2. TEM analysis of Cr(Ni) interlayer.

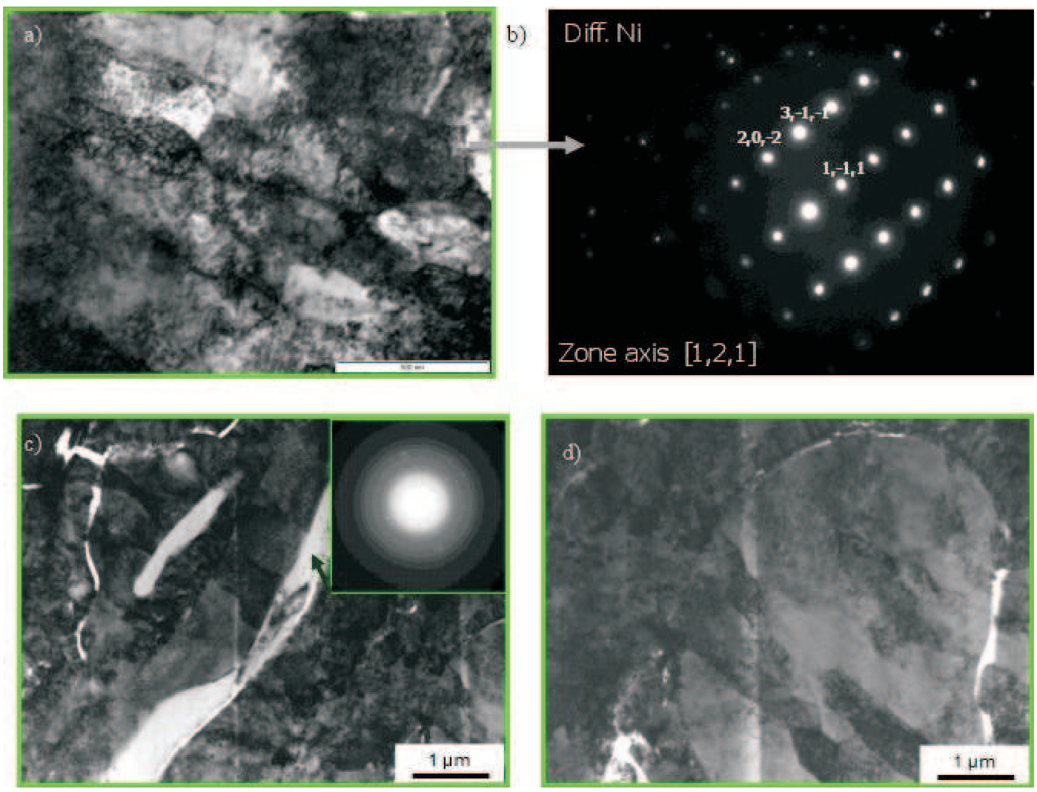


Fig. 3. TEM micrographs of magnified areas of Ni(Cr) interlayer showing in Fig. 1: (a) magnifications of area D and SAED pattern (Fig. 3b), (c) magnification of area E, together with SAED, (d) magnification of area F

The microstructure of Ni(Cr) – based interlayer, containing small grains with high density dislocations is shows in Fig. 3a. The electron diffraction pattern (Fig. 3b) reveals orientation of Ni with the [1,2,1] zone axis. The image taken of the area E (Fig.1) shows the elongated particles identified by the electron diffraction pattern as the amorphous Al_2O_3 phase (Fig. 3c). This rather surprising result can be explained by strong interaction between Fe-Al coating, Ni(Al) and Ni(Cr) interlayers during detonation process. The amorphous phase is surrounded by the Ni subgrains visible in Fig. 3d as while areas and it appears as result of partially melting of the Ni(Cr) interlayer in the detonation process.

3.2.1. STEM microstructure and EDX analysis within of Ni(Cr) interlayer

The EDX analysis was carried out in the relatively large of Ni(Cr) interlayer by element mapping (Fig. 4a). It looks like that most of the analysed area is enriched in Al and O. Nickel appears only in right side of the STEM image while Cr was recorded only in the elongated band of the Ni(Cr) layer. The subsequent microstructure shows (Fig. 4b) the Ni(Cr) layer close to the Fe-Al coating.

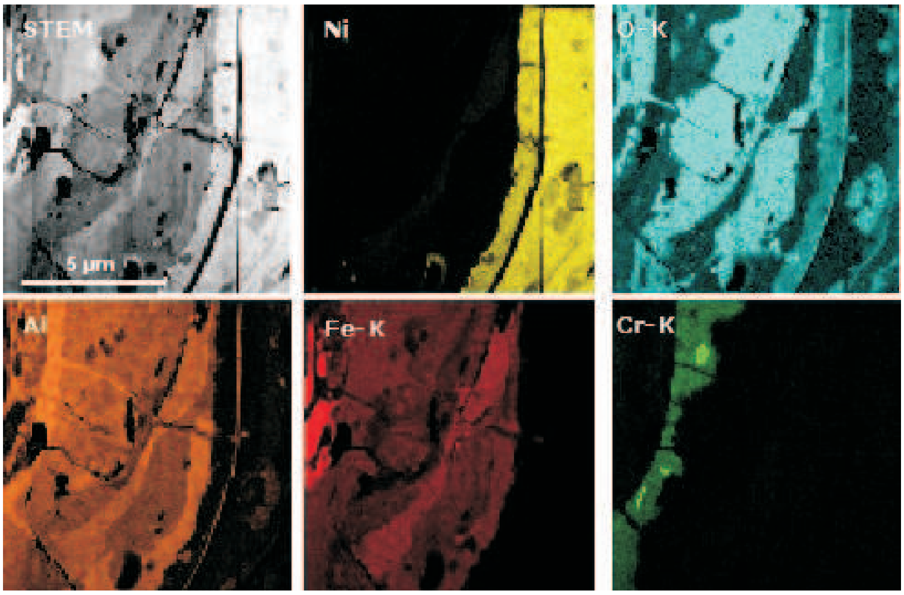


Fig. 4a. STEM micrograph and corresponding EDX maps of elemental distribution of Ni, O, Al, Fe and taken for large area Ni(Cr) interlayer

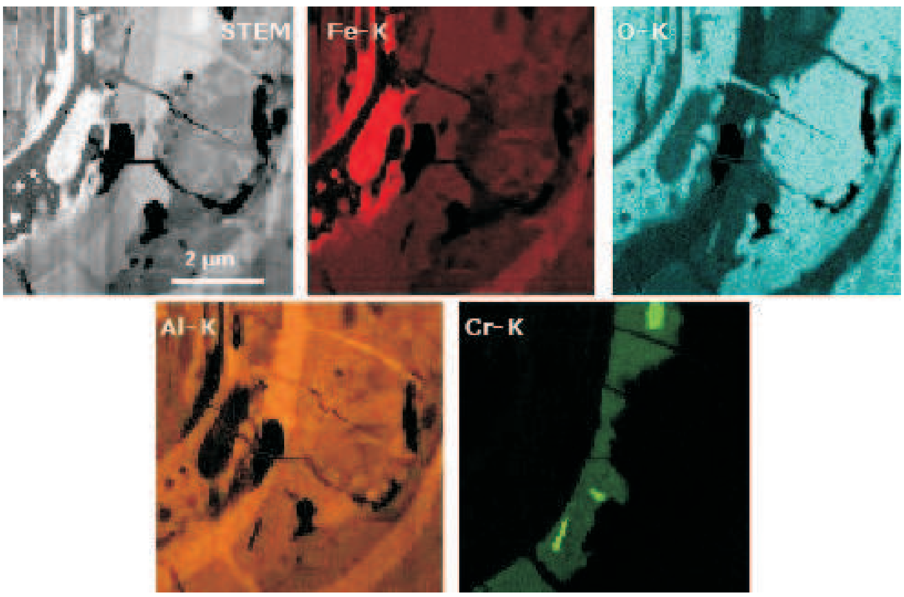


Fig. 4b. STEM micrograph and corresponding EDX elemental distribution o Fe, O, Al, Cr in the Ni(Cr) interlayer close to Fe-Al coating

One can notice that this area is enriched in Fe, Al, O. Chromium is only present in the slab visible in the center of the sample. No Ni was detected which results from the fact that this element appears only in thin slabs (see Fig. 4a) in which the EDX point analysis was not performed. One should note that the microstructure resulting from DGS is not perfect. Some voids an cracks are visible (see STEM micrograph in Fig. 4a,b).

Figure 4c shows the microstructure of the Ni(Cr) layer close to the Ni(Al) interlayer. This region is strongly enriched in Ni. The Al and O in the elongated bands, identified as the amorphous phase was also observed. Chromium was not identified in the area.

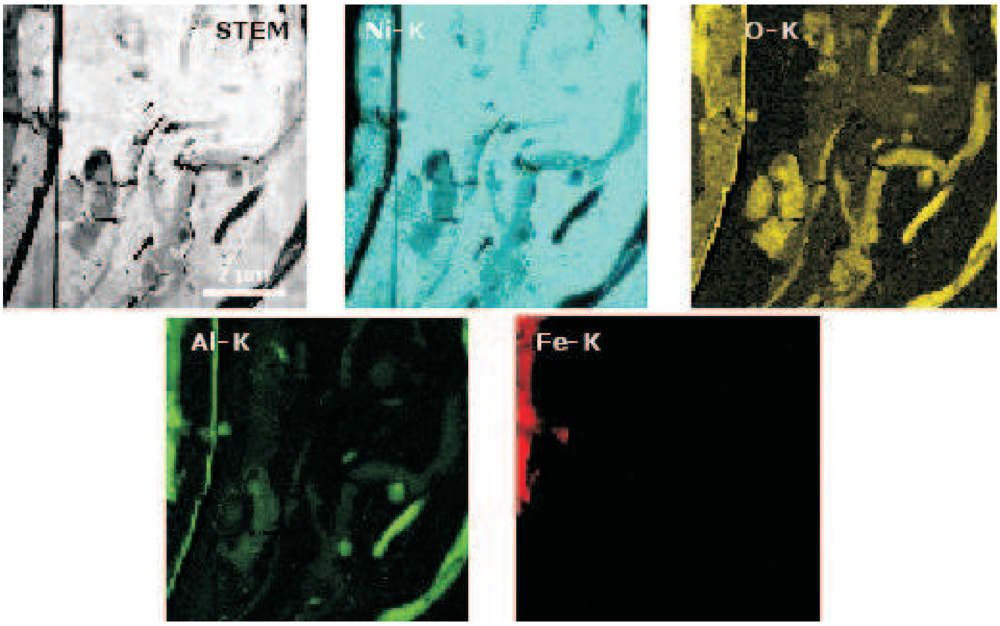
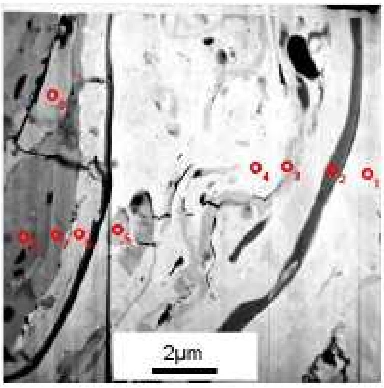


Fig. 4c. STEM micrograph and EDX elemental distribution of Ni, Al, Fe in the Ni(Cr) interlayer dose to Ni(Al) interlayer



	Composition %at			
Point	**O**	**Al**	**Fe**	**Ni**
1	6	0.0	0.4	93.5
2	65.5	29.1	0.0	5.2
3	53	5.9	0.0	40.9
4	18.1	0.0	0.0	81.9
5	55.2	5.9	0.0	38.7
6	41.2	0.7	0.0	57.7
7	5.2	62.9	31.4	0.4
8	63.8	21.5	14.3	0.3
9	5.1	50.9	40.1	3.7

Fig. 5. STEM micrograph and results of EDX point analysis carried out across the Fe-Al/Ni(Cr) interface

The examination of Fe, Al, and O changes carried out across Fe-Al/Ni(Cr) interface presented in Fig. 5 and attached Table. In points 1 to 6 enrichment in Ni and also O is visible. One should be noted that the lack of Cr results from the fact that this element appears only in thin slabs (see Fig. 4a,b) in which the EDX point analysis was performed. One the other hand, the EDX analysis at points 7-9 revealed the enrichment in Al and Fe typical for the Fe-Al coating.

3.3. TEM analysis of Ni(Al) interlayers

The overall view of microstructure of the Ni(Al) interlayer is presented on Fig. 6a. The TEM image (Fig. 6b) taken from area close to the substrate shows the Al_2O_3 phase containing some Ni and traces of Fe.

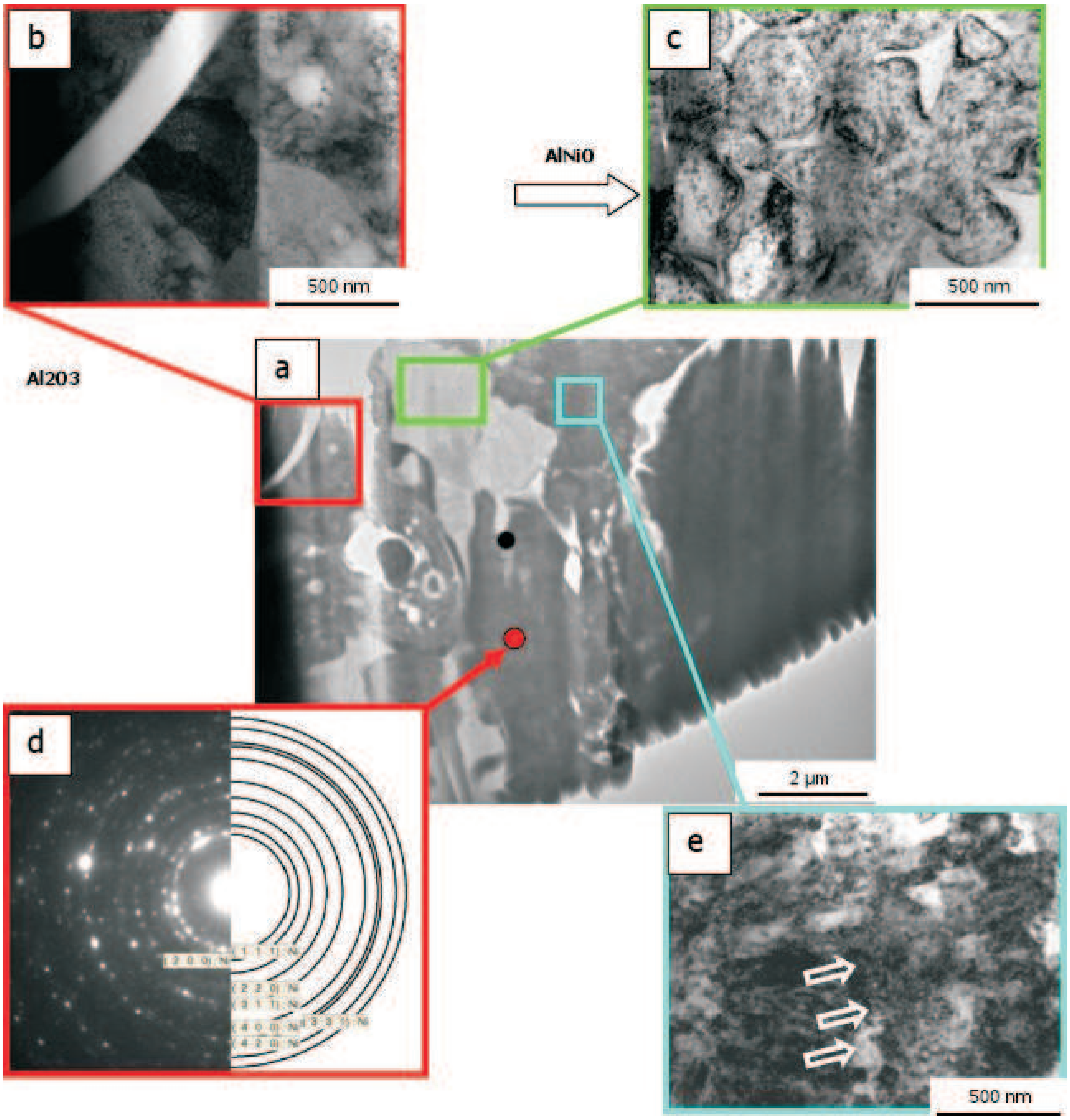


Fig. 6. Microstructure of the Ni(Al) interlayer, (a) TEM micrograph of overall view of Ni(Al) interlayer, - (b, c, d) magnified areas marked by boxes in Fig 6a, (e) SAED pattern taken from area marked by black circle in Fig. 6a

The second detected phase, which crystallized from the liquid (Fig. 6c), contained oxygen, aluminium and nickel. Both phases appeared due to fast cooling of partially melted Al particles enriched in Ni. The second phase reveals the cell morphology, because it solidified at the steel-substrate a lower rate the Al_2O_3 phase. Close to the interface between the Ni(Al) and Ni(Cr) interlayers (the central part of Fig. 6a) two areas of pure Ni were identified by the electron diffraction technique (Fig. 6d). The region in Fig. 6e shows the solidified crystals of almost pure Ni growing in one direction (see arrows).

3.3.1. STEM microstructure and EDX analysis within Ni(Al) interlayer

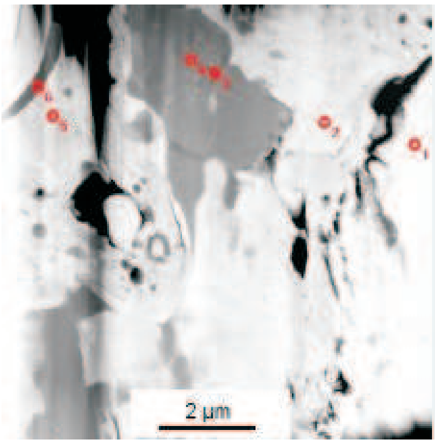


Fig. 7. STEM micrograph of Ni(Al) interlayer. The location of places where EDX analysis was performed is indicated by open circles and numbers

TABLE 1
Results of quantitative point to point EDX analysis

Point No. 1 in substrate

Element	at. %
Al	0.0
Fe	99.8
Ni	0.0

Point No. 2 in the Ni(Al)

Element	at. %
Al	1.2
Fe	0.0
Ni	98.6

Point No. 3 in the region of AlNiO phase

Element	at. %
O	71.1
Al	22.7
Ni	6.2

Point No. 4 in the region of AlNiO

Element	at. %
O	64.2
Al	25.2
Ni	10.6

Point No. 5 in area close to the Ni(Al) interlayer

Element	at. %
Al	8.2
Fe	0.3
Ni	91.5

Point No. 6 in amorphous phase based on Al_2O_3

Element	at. %
O	68.4
Al	24.8
Fe	0.0
Ni	6.6

The quantitative EDX performed in the Ni(Al) interlayer (Fig. 7) showed that majority of Fe is present in the substrate (Table 1-pont 1). The second EDX analysis (Table 1-point 2) performed within Ni(Al) interlayer, revealed the presence of Ni with small amount of Al. On the other hand, the chemical composition of points 3, 4 and 6 (Table 1) suggests the existence of Al_2O_3 phase modified by significant amount of Ni (6.6 – 10.6 at%). The chemical composition of point 5 is typical for the Ni(Cr) interlayer. It is characterized by the high amount of Ni with some Al (8.2 at%) and traces of Fe. The lack of Cr is attributed again to the fact that it appears only in thin slabs, which were located beyond the area of EDX analysis.

4. EDX analysis across interface between the Ni(Cr) interlayer and Fe-Al coating

The results qualitative EDX line-scan across the interface between Ni(Cr) interlayers and Fe-Al coating one presented in Fig. 8. The strong decrease in Fe accompanied by strong increase in Ni is visible at the interface. The changes of oxygen are not sopronounced although the higher content of oxygen is within Fe-Al coating. The most complicated are the change of Al. The average content of Al is rather higher in Ni(Cr) interlayer with tendency to form some inhomogeneneities. The enhancement in Al at the interface suggests the occurrence of the mass transport process at this area.

Summarizing the obtained results one should note that the detected inhomogeneous distribution of both Al and Cr in the interlayers of the joint was due probably to the effect of improper doses of Al, Cr powders in the process of gaseous detonation spraying. The occurrence of pores at the boundary of steel substrate and the Ni(Al)

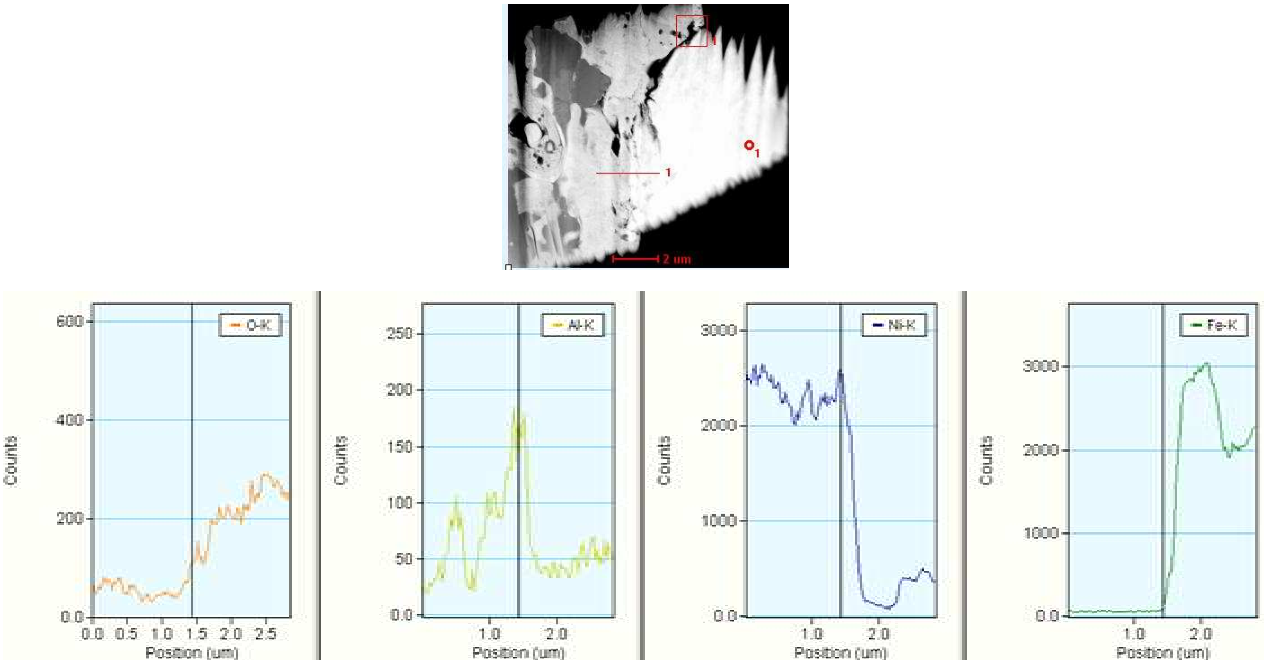


Fig. 8. STEM micrograph and EDX qualitative analysis across interface between the substrate and Ni(Cr) interlayer

interlayer (Fig. 6a and 7) as well as the Ni(Cr) interlayer and Fe-Al intermetallics (Fig. 4c) coating was also its additional result. Another factor, which affected the deterioration of the quality of joint, was too high amount of aluminium. Which brings about the formation of brittle Al oxide- based on amorphous phase. A lower content of Al may have caused the increase of the interlayer adherence.

Comparing the described situation with the case of not using the interlayers in the joint [6], it should be stated that the Ni-based layers, and particularly the Ni(Cr) interlayer seems to be more beneficial because of lower amount of pores in the boundary with the substrate.

5. Conclusions

1. The Ni(Al) interlayer obtained by the process of gaseous spraying deposition contained basically pure nickel with a small fraction of NiAl phase. The Al oxide based amorphous phase was observed in this area in the form of bands. Subgrains which grown directionally from the substrate were identified as pure Ni. The part of the layer was built of cellular AlNiO oxide, whose grains solidified at lower rate than those on the substrate from the partially melted interlayer in the process of detonation spraying.

2. The boundary of the Ni(Al) layer and the substrate revealed porosity and brittle particles of the presence of amorphous phase, which lowers the adherence of the interlayer to the substrate.

3. The Ni(Cr) interlayer detonation deposited onto the Ni(Al) layer basically contained Ni of subgrain morphology. Pure chromium in the Ni matrix appeared in the vicinity of Fe-Al coating in the shape of bow-like bands, parallel to the coating. The amorphous phase based on AlNiO was also observed in the vicinity of Cr rich areas. Fe and Al were identified in the neighbourhood of the coating, apart from Ni. The further away from the coating, the amount of Fe decreased, while content of Ni and Al grew.

4. The boundary between the Ni(Cr) layer and the Fe-Al coating revealed abrupt decrease of the Ni content in the coating at simultaneous rapid increase of the Fe amount. The coating contained basically intermetallic phases of the Fe-Al type. The area of the boundary revealed only few pores originated from the process of detonation spraying.

5. Improper Al/Cr ratio within the Ni matrix seems to by responsible for formation of Al-oxides and the bands of almost pure Cr in the Ni(Cr) layers and resulting decrease of interlayer adherence.

Acknowledgements

The authors tank Profesor Paweł Zięba with the Institute of Metallurgy and Materiale Science for profitable discussion and remarks.

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Received: 10 August 2010.