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STRUCTURE MORPHOLOGY OF Fe-Al COATING DETONATION SPRAYED ONTO CARBON STEEL SUBSTRATE

MORFOLOGIA POWŁOKI Fe-Al NATRYSKIWANEJ DETONACYJNIE NA PODŁOŻE ZE STALI WĘGLOWEJ

The morphology of Fe-Al type intermetallic coatings produced by detonation spraying on a 045 steel substrate was described based on the microstructure analysis using transmission electron microscopy (TEM), and selected area electron diffraction (SAED) techniques as well as an analysis of chemical composition in microareas (EDS). The TEM was useful in establishing the coating structure in the vicinity of the interface between the substrate and the coating up to the depth of 10 m. Starting from the boundary with the substrate, an amorphous phase (A), then columnar crystals (CC) followed by crystalline grains of Fe_3Al were observed. Farther on, the amorphous phase again and grains of the FeAl2 phase were localized. The Fe_2Al_5 and Fe_3Al phases lay close to the coating surface. The phase transformations were completed with calorimetric analysis, which showed heat effects typical for magnetic transformations and ordering.

The results indicated to the mechanism of coating formation which consisted in partial melting of the Fe-Al starting powders and the formation of the amorphous phase, unidirectional solidification of the columnar phases and the deposition of the remaining not melted Fe-Al powder. Next, partially melted material was deposited.

Keywords: barrier coatings, detonation spraying, Fe-Al crystallites, phase transformations

W pracy przedstawiono morfologię struktury powłoki faz typu Fe-Al. naniesionej przez natryskiwanie detonacyjne na podłoże ze stali węglowej 045. Morfologię opisano na podstawie analizy mikrostruktury metodą transmisyjnej mikroskopii elektronowej(TEM), dyfrakcji elektronowej (SAED) oraz analizy składu chemicznego w mikroobszarach (EDS). Badania przemian fazowych uzupełniono analizą kalorymetryczną. Metodą TEM ustalono budowę części powłoki w pobliżu granicy powłoka/podłoże do odległości ok.10 m. W bezpośrednim sąsiedztwie granicy z podłożem zaobserwowano fazę amorficzną (A) oraz kryształy kolumnowe (CC), następne ziarno krystaliczne składające się z fazy Fe_3Al. Dalej fazę amorficzną i ziarno fazy FeAl2. W pobliżu powierzchni powłoki zidentyfikowano fazy Fe_2Al_5 i Fe_3Al. Badania kalorymetryczne wykazały efekty przemian magnetycznych oraz uporządkowania. Wyniki analizy wskazują na mechanizm tworzenia powłoki polegający na nadtopieniu się częściowym wyjściowego proszku faz typu Fe-Al. i tworzeniu fazy amorficznej, kierunkowym krzepnięciu faz kolumnowych oraz osadzaniu pozostałości nie stopionego ziarna Fe-Al. Dalej osadza się następne, częściowo nadtopione ziarno.

1. Introduction

The intermetallic protective coatings of Fe-Al type detonation-gas sprayed (DGS) onto a substrate of typical constructional materials like carbon steel 045 or superalloy Ni-Cr-Al reveal very good exploitation properties. They are resistant to high-temperature corrosion and thermal shocks. They have good mechanical and lubricity properties, positive adhesion and little porosity, but first of all excellent resistance to abrasive wear [1, 2]. A high energy transmitted to the Fe-Al particles of the coating material during gas-detonation spraying brings about the formation of the layer morphology of flattened grains [3] as well as a partial melting of the $FeAl_3$, $FeAl_2$ and FeAl phases as an effect of collisions at high velocity [4].

The present work has been aimed at the explanation of the mechanism of the coating formation in the course of solidification after the detonation spraying and its possible modification.

2. Experimental

The experiments were carried out on a coating obtained by gas-detonation spraying of the Fe_2Al_5, Fe_3 Al

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and FeAl powders of 40-60 μm grain size on the substrate of 045 carbon steel. The deposition of the coatings of about 50 μm thickness was performed through heating the powder up to 100 °C before the deposition. The steel of the substrate was annealed and cleaned after rolling. The specimen was cut out from the coating/substrate area. Thin foils for the TEM observations were obtained using Tecnai G^{2}F20 (200kV) microscope by thinning the sample with focused Ga ion beam (FIB) in Quanta 200 3D instrument. The TEM analyses were conducted on crossections. The images were taken in bright field (BF) basing on mass and diffraction contrast. A local analysis of chemical composition was performed using the scanning transmission electron microscopy (STEM) technique, which made use of so called Z-contrast: brighter areas contained heavier elements, while darker areas the lighter ones. Calorimetric studies were carried out on a calorimeter of Universal V4.1D TA Instruments type.

3. Results and discussion

3.1. TEM microstructure and SAED and EDS analysis

A TEM image of a coating taken at the distance of 5 μm from the interface with the substrate is shown in Fig. 1a. On the right side, the boundary between the coating containing intermetallic phases of the Fe-Al type and the 045 steel substrate can be seen. A 1 μm wide crack is visible about 1 μm from the interface. It comes up to the surface of the substrate under the observed plane. Fine crystalline particles of Fe_3Al phase of size 300-700 nm got there during spraying, which was confirmed by the SAED inserted in the corner of Fig. 1b. The composition analysis of the substrate showed the existence of the steel without other metallic additions (Fig. 1 c). Left side of the image presents the coating with intermetallic phases of Fe_3Al and Fe_2Al_5 type. A 100 nm wide layer of the amorphous phase and a little further such a same phase but of more or less equiaxial shape can be seen in the boundary. The amorphous phase lies next to an area of columnar crystals and a grain of the starting powder.

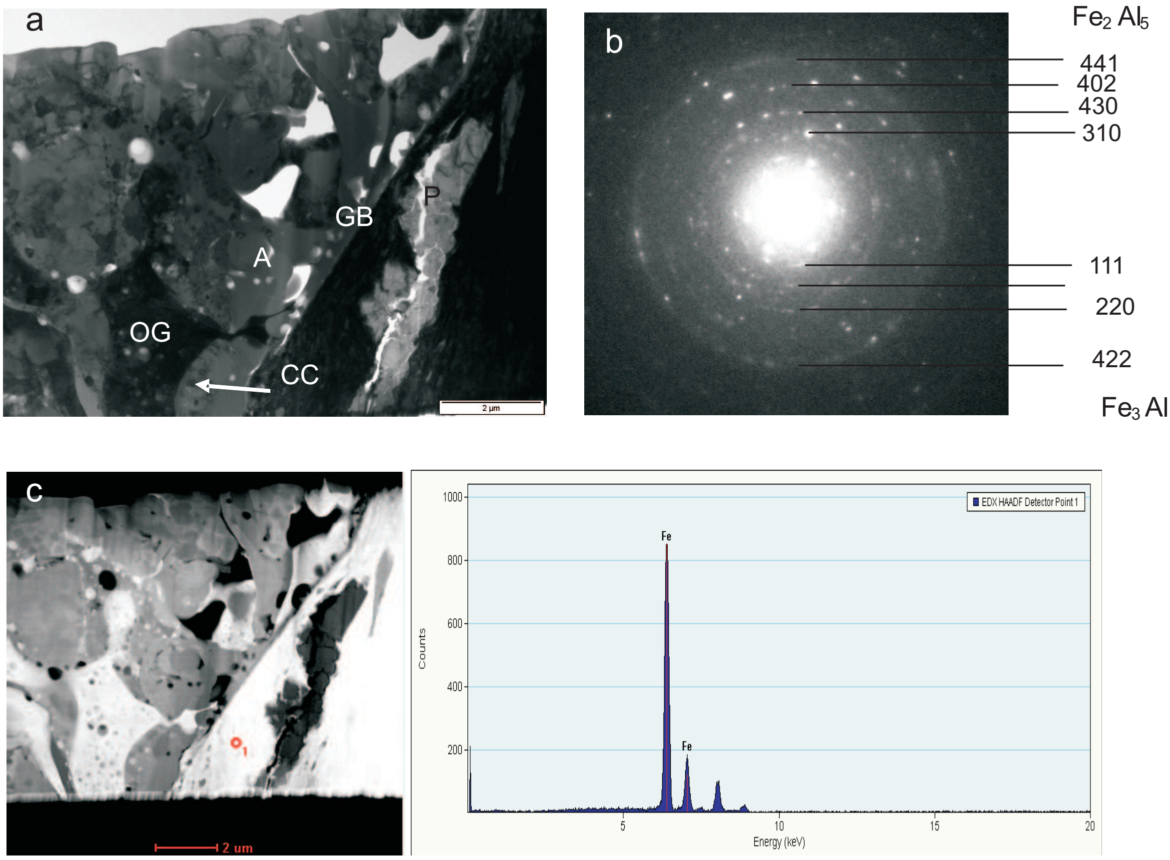

Fig. 1. a) TEM image of the area close to the Fe-Al coating boundary with 045 steel substrate (on the right side): OG – original grain, CC – columnar crystals, A – amorphous phase, GB – coating/substrate boundary. Visible crack in the substrate with the Fe_3Al phase; b) SAED of the Fe_3Al particles in the crack; c) STEM with the point of analysis and the EDX analysis of composition of the substrate

Fig. 2 lets us observe the amorphous phase (a) confirmed by the SAED (b). Its composition indicates that it is strongly oxidized O_2(60 at.%) one rich in Fe (12 at.%) and Al (28 at.%) (Fig.2c). The analysis shows that it is a phase with Al/Fe ratio 2.3. It corresponds to the equilibrium composition of the phase, which melted and then solidified into a vitryfied form during rapid cooling.

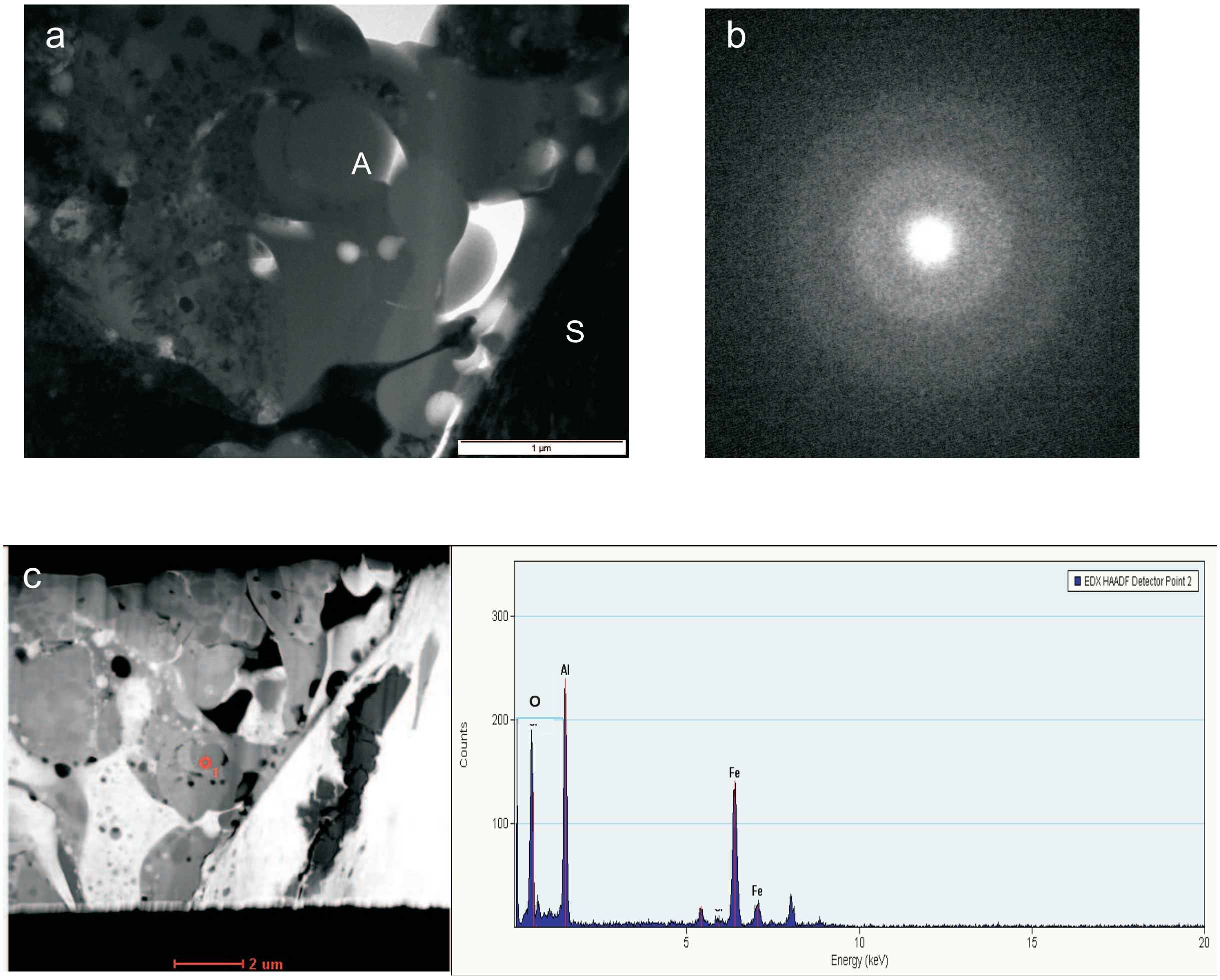

Fig. 2. a) TEM microstructure of the amorphous phase area marked A and substrate marked S, b) SAED from the amorphous phase, c) STEM image together with marked place of analysis, d) analysis of composition from the amorphous phase

Fig. 3 presents a following amorphous phase located at about 2 μm from the coating boundary. Columnar crystals appeared as a result of directional heat flow from the partially melted ε phase can be observed close to the boundary from the not melted side of the crystal. Slower solidification of the ε phase resulted in the precipitation of the FeAl and Fe_2Al_5 phases (according to the equilibrium system) observed also in paper [5].

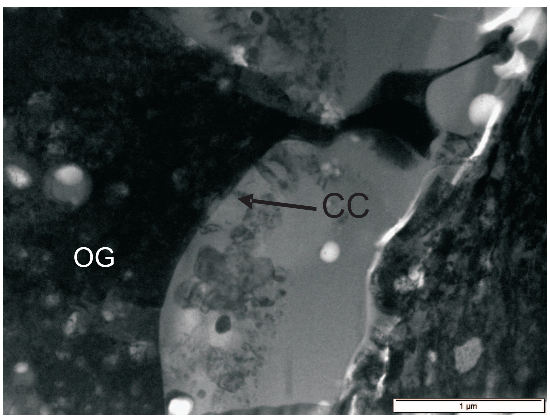

Fig. 3. TEM image of the amorphous phase with visible columnar crystals in its left side, at the boundary with the not melted grain

A flattened crystal about 2 μm can be seen in Fig. 4a at the distance of 3 m from the interface. It was identified as the Fe_3Al phase (based on the SAED shown in Fig. 2 b) within the α Fe, containing a prevailing content of Fe (67 at.%) with 8 at.% of Al and traces of O_2 (25 at.%) according to the analysis shown in Fig. 3 c. It must have undergone flattening when hitting the substrate at high speed during detonation spraying.

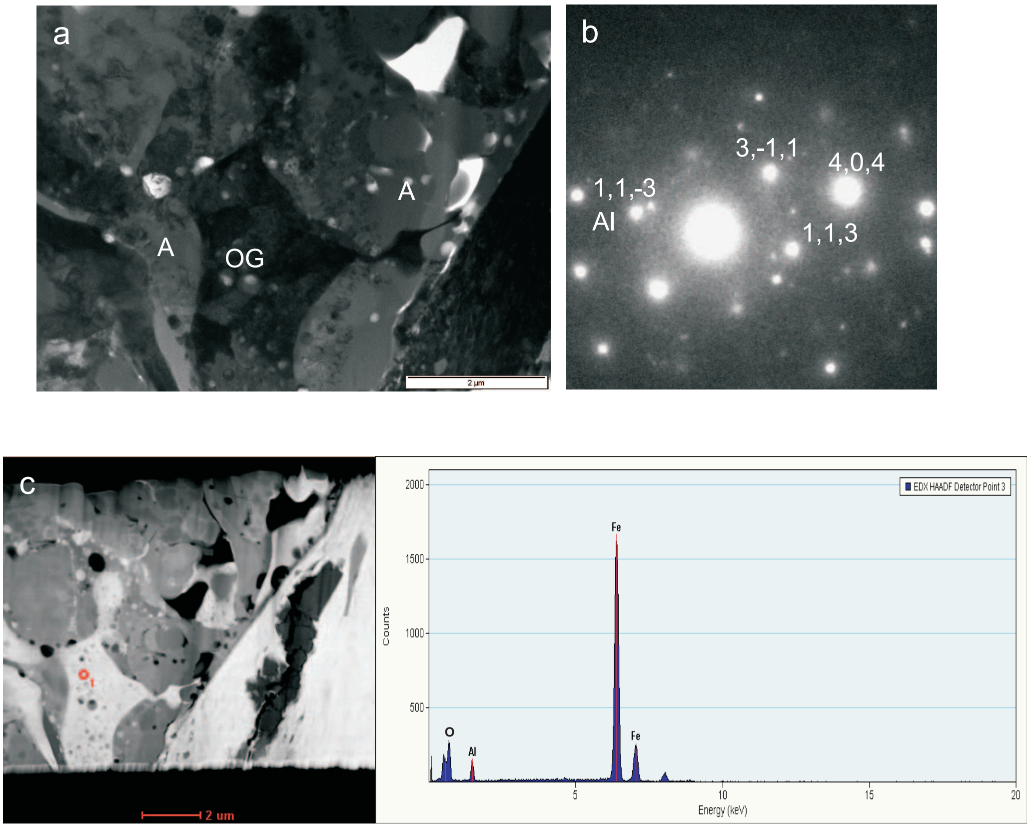

Fig. 4. a) TEM microstructure of the original powder particle (OG) in the centre of the image surrounded with the areas of amorphous phases, b) corresponding SAED from the OG identified as Fe_3Al, c) STEM image and the EDX analysis made from the Fe_3Al phase containing Cr

The microstructure contained in Fig. 5 indicates the presence of crystalline grains apart from the amorphous phases at the distance about 6 μm away from the interface with the substrate. Particles of other phases (Fig. 6 a) were observed further on, at more than 8 μm distance from the substrate, identified as Fe_2Al_5 and Fe_3Al according to SAED shown in Fig. 6 b. The chemical composition of that phase Al(26 at.%), Fe(7 at.%) and O_2 – 67 at.% suggested a highly oxidized Fe_2Al_5 (Al/Fe=3.7) phase.

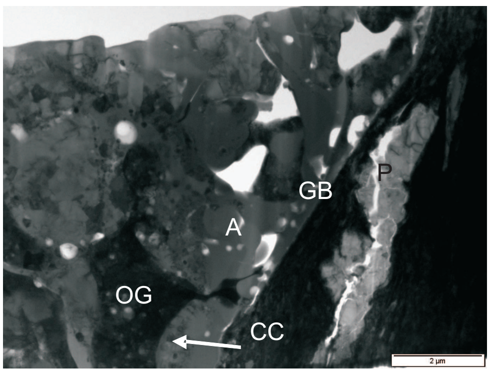

Fig. 5. TEM image of the original grain (OG) in the left upper corner about 6 μm away from the interface with the substrate (S) on the right side

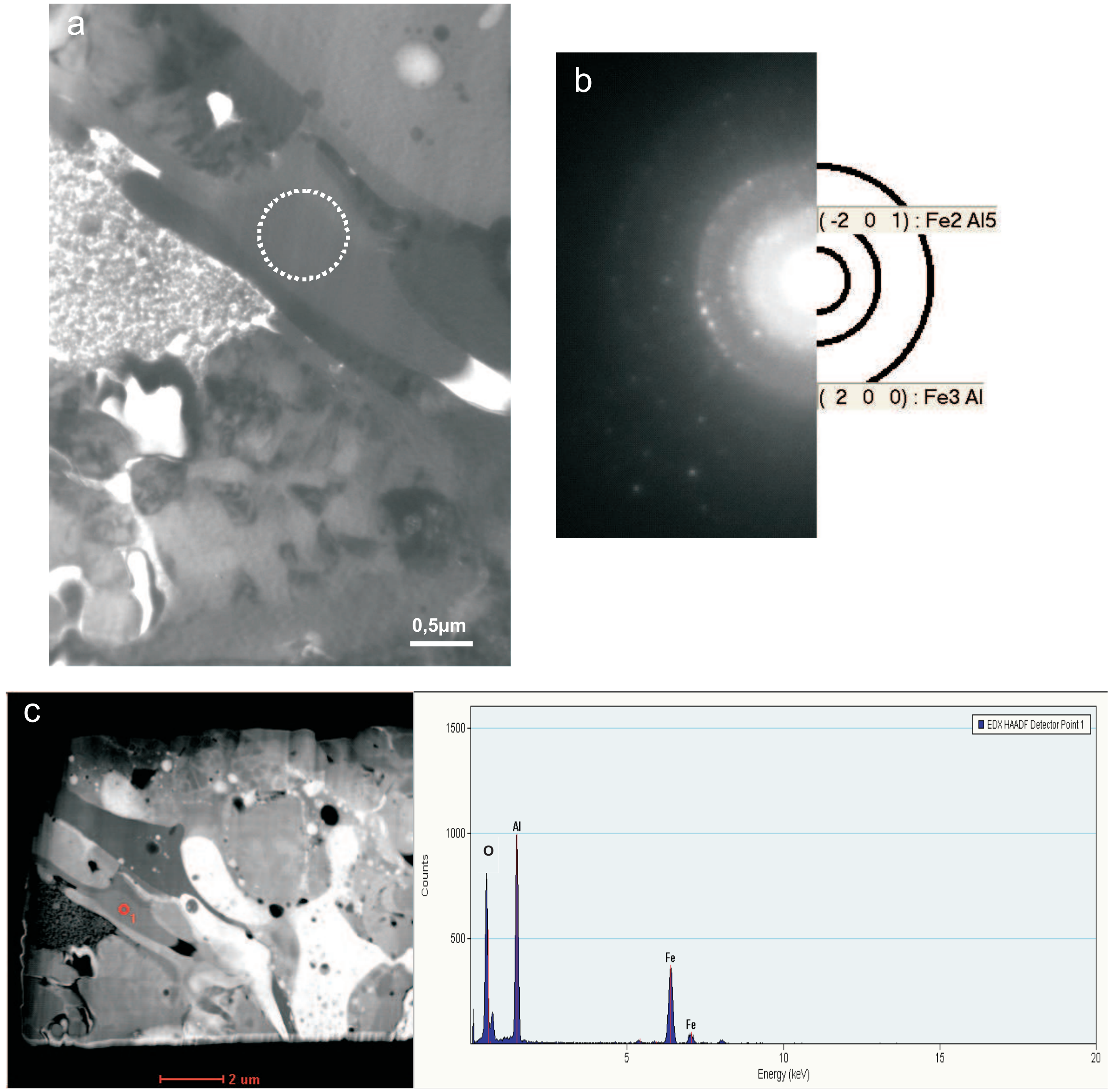

Fig. 6. a) TEM microstructure of the area away from the substrate, b) SAED taken from the place marked with circle, c) TEM image with EDX analysis of the Fe_2Al_5 phase with Cr marked with circle

3.2. Calorimetric analysis

The TEM study of the microstructure was supplemented with calorimetric analysis in order to confirm the phase transformations, which took place in the coating formed during the detonation spraying of the intermetallic Fe-Al phases containing from 2-60 at.% Al.
During heating (curve 1) at 10 deg /min in temperature range 600 °C -1000 °C, a strong endothermic effect at 739 °C as well as a weak exothermic one at 862 °C was observed (Fig. 7). The first effect can be attributed to the magnetic transformation of ferromagnetic phase into paramagnetic one (at about 10 at.% Al), while another to the precipitation of fine crystalline Fe_2Al or Fe_2Al_5 phases from the supersaturated amorphous phase (at about 60 at.% Al).

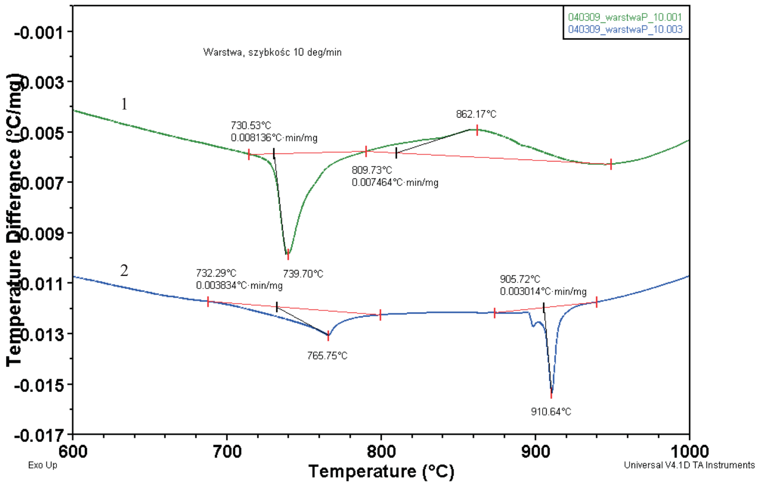

Fig. 7. Calorimetric analysis of the detonation sprayed Al-Fe coating

The sample was then cooled down to 600°C followed by another heating (curve 2) at rate 10 deg/min up to 1000 °C. That time, a strong endothermic effect was observed at 910 °C connected presumably with the transformation of γFe into αFe (Fe-2 at.% Al) and another, but a weaker one at 765.7 °C due to ordering of the α_2(h) phase into α_2(l) one (about 42 at.% Al) of FeAl [6].

Those results supplemented the observations of microstructure by establishing the occurrence of magnetic transformation, ordering as well as partial crystallization of the amorphous phase.

4. Conclusions

1. The amorphous phase solidified as 200 nm wide layers in the closest vicinity of the substrate due to rapid cooling of partially melted ε phase, which changed into equiaxial forms at larger distances from the substrate.
2. Columnar crystals appeared farther away from the interface out of the partially melted ε phase as the effect of directional crystallization from the liquid phase.
3. Strongly oxidized crystals of Fe-Al phase, which did not undergo melting were observed behind the amorphous phase in the flattened shape 2-4 µm wide due to high pressure during the detonation spraying.
4. The secondary crystallization was not observed in the course of TEM investigations in spite of the results of calorimetric analysis, which recorded a partial crystallization of the amorphous phase.
5. The structure morphology exhibited a cyclic mechanism of the coating occurrence. Layers appeared in the following order starting from the substrate/coating interface: amorphous phase, columnar crystals, equiaxial Fe_3Al and Fe_2Al_5 particles. The mechanism of coating formation includes a partial melting of the starting particles.
6. Magnetic transformations and ordering were also observed in the analysed coating.
7. Open cracks about 2 µm wide at the surface of the substrate were observed to be filled with fine crystalline particles of the Fe_3Al and Fe_2Al_5 phases originated from the process of the detonation spraying.

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