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CHARACTERIZATION OF ALUMINA SCALE FORMED ON FeCrAl STEEL**CHARAKTERYSTYKA WARSTWY ALUMINY UTWORZONEJ NA STALI FeCrAl**

In this paper the morphology of the oxide scale formed at 850°C on the foil surface of FeCrAl steel is described. Two types of samples have been used: one covered with an Al nano-layer and the second without. Microscopic observations of the cross-sections of scales have demonstrated that in the case of foil without Al nano-layer there is a remnant of an amorphous Al_2O_3 nano-layer, from which γ and θ crystallites of Al_2O_3 have been grown. In the case of foil covered with the Al nano-layer, α - Al_2O_3 phase is present and θ -phase forms a forest of whiskers on the surface.

Keywords: A. steel, B. TEM, B. SEM, C. oxidation, alumina

W pracy opisano morfologię warstw tlenkowych, które powstały na folii FeCrAl pod wpływem jej utleniania w temperaturze 850°C. Badania dotyczyły folii pokrytej nanowarstwą Al oraz nie pokrytej. Przekroje warstw i podłoża stalowego badane za pomocą transmisyjnej mikroskopii elektronowej wykazały, że w przypadku folii nie pokrytej warstwą Al występuje pozostałość amorficznej nanowarstwy Al_2O_3 , z której następuje wzrost krystalitów γ i θ - Al_2O_3 . W przypadku folii z osadzoną nanowarstwą Al stwierdzono obecność fazy α Al_2O_3 oraz występującej na powierzchni folii fazy θ - Al_2O_3 , w postaci lasu whiskerów.

1. Introduction

The formation of compact aluminium oxide scale on steels at high temperatures is related to a number of factors and in particular temperature and gas composition as well as the amount of impurities in the steel. All these factors may exert an influence on the morphology of the scale forming at high temperatures, which can change from whisker formations through lamellar and pyramidal structures to the formations of poorly developed crystalline structures [1]. One of the crucial questions related to the structure of the aluminium oxide scale is the fact that aluminium oxide may exist in various polymorphic forms. The presence of various polymorphic forms of aluminium oxide is connected with temperature. It was assumed that at high temperatures of about 1000°C the α -form constitutes the stable form, whereas at lower temperatures the metastable γ -, θ - and δ - aluminium oxide phases are formed [2-6].

The results obtained in a number of scientific centres did not indicate that a particular crystalline form of the oxide is attributed only to one of polymorphic Al_2O_3 form, and hence Al_2O_3 may take different crystalline forms [7, 8]. It was assumed that the metastable γ -, θ - and δ - Al_2O_3 crystals assume the form of pyramids, columns, and whiskers. The growth mechanism of these phases takes place as a result of the outward cations diffusion, whereas the stable α - Al_2O_3 phase is

formed due to the inward oxygen diffusion and is most frequently present in the form of oval bodies and/or small grains [9].

On the basis of TEM experiments and electron diffraction analysis it was established in the present paper that particular phases of aluminium oxide are formed in different way, assuming diverse crystalline forms which result from the various mechanisms of their formation.

2. Material and methods

The analyses were performed on two types of samples:

1. on commercial Fe-Cr-Al steel foil (Thyssen-Krupp-VDM) of 0.005 cm thickness;
2. on commercial Fe-Cr-Al steel foil (Thyssen-Krupp-VDM) of 0.005 cm thickness, covered with a thin Al nano-layer.

All samples were 3.5×3.5 cm in size and were cut out from the foil and degreased. The process of the Al nano-layer deposition was carried out with the PVD method with the application of a Magnetron KO1 device [10, 11]. The coating process was carried out under argon pressure equal $2 \cdot 10^{-2}$ mbar. The nano-layer thickness was measured by X-ray reflectometer (XRR). The average thickness of nano-layer was 25 nm. The cross-section of the Al nano-layer is shown in Fig. 1.

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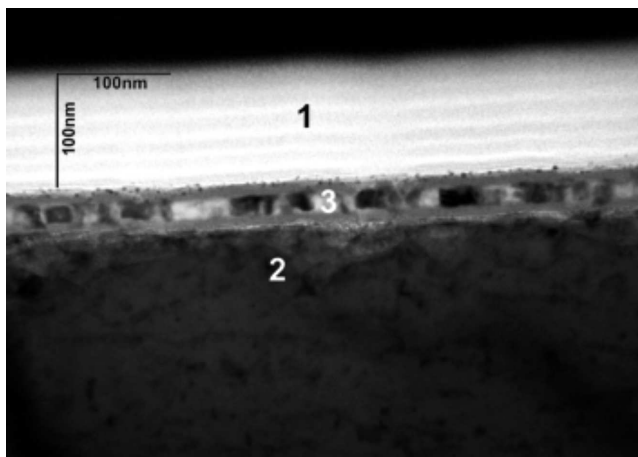


Fig. 1. STEM BF image showing a cross-section of the Al nano-layer deposited on FeCrAl foil. 1 – carbon coating strengthening the Al layer during cross-sectioning, checking the accuracy of the description of layers; 2 – FeCrAl base; 3 – Al nano-layer

Oxidation processes were carried out in a stream of Ar + 67.6% O₂ gas mixture under atmospheric pressure at 850°C. The flow rate of this atmosphere amounted to 53.2 cm³/min. The oxidation time was 24 h. The samples were placed in the furnace and heated in high purity (99.995%) argon atmosphere. After the requirement temperature was reached, the gas mixture (Ar + 67.6% O₂) was introduced. After oxidation, the sample surface was analysed by SEM (JEOL 6500LV) and TEM (Philips CM20 TWIN) together with electron diffraction. Samples were prepared in Quanta 3 set, equipped with Omniprobe manipulator, by ion etching method with FIB technique. Table 1 presents the chemical composition of the steel.

TABLE 1

Chemical composition (wt. %) of Fe20Cr5Al steel

Elements	Fe	Cr	Al	Si	C	Other
According to certificate	75.65	19.5	4.6	–	0.05	0.2
According to EDS (average of 7 measurements)	73.1	21.0	5.4	0.2	–	0.3

3. Results and Discussion

SEM images obtained after oxidation from the surface of the FeCrAl steel samples with and without Al nano-layer are shown in Figures 2, 3, and 4. In both cases the formation of the scale on the steel surface was observed. The surface was covered with crystallites in the form of pyramids, needles, and flat lamellae.

The surface of the scale formed on the samples without the Al nano-layer is characterized by highly different crystals of Al₂O₃. In the region of the foil defects, most frequently spongy forms of α -Al₂O₃ phase are observed (Fig. 5). On the steel surface free from physical defects, the formation of lamellae, pyramids, and whiskers with different sizes are formed. The phase composition of these oxidation products shows also different forms. The presences of θ - and α -Al₂O₃ phases have been found (Fig. 2). Columnar crystals

and whiskers in the form of elongated needles belong to the θ -Al₂O₃ phase, whereas lamellar as well whiskers forms belong to α -Al₂O₃ phase. Dark streaks suggesting the presence of tightly-adjacent crystals between the whiskers or the channels of 0.01 μ m in width inside the whiskers of θ -Al₂O₃ phase (Fig. 3).

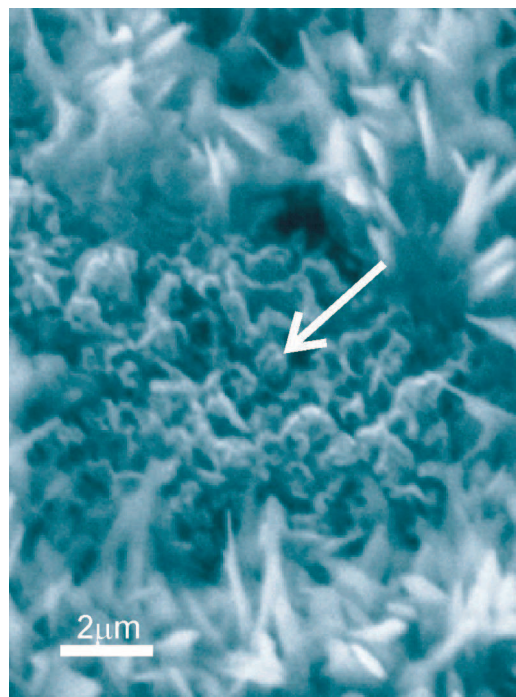


Fig. 2. SEM image showing a fragment of the foil surface after 24 h of oxidation in the atmosphere of Ar + 67.6% O₂ at 850°C, spongy structure of oxide which appeared in the place of the rolled 'chip'

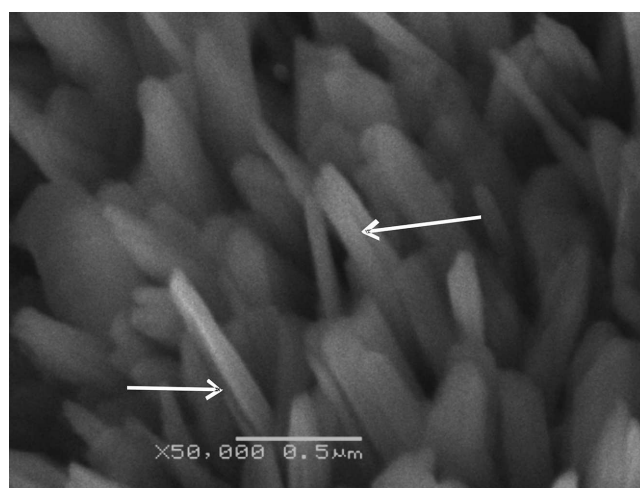


Fig. 3. SEM image showing the morphology of whiskers obtained after 24 h oxidation of the foil in an atmosphere of Ar + 67.6% O₂ at 850°C; crystal dividing lines (ducts) are marked with arrows

The scales formed on samples covered with the Al nano-layer also possess developed surfaces, but they are more homogeneous (Fig. 4). The phase composition of these crystalline forms corresponds to θ - and α -Al₂O₃ phases, however the θ -phase consists of elongated crystallites (whiskers), while the forms in the shape of lumps and columns constitute the α -Al₂O₃ phase.

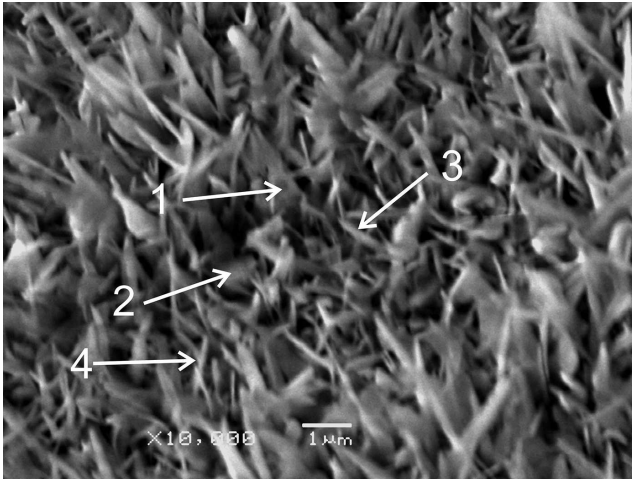


Fig. 4. SEM image showing the structure of the oxide layer obtained as a result of the foil oxidizing covered with an Al nano-layer 19-20 nm in thickness. 1, 2 – lumps and columns of α - Al_2O_3 phase; 3, 4 – pin forms and whiskers of θ - Al_2O_3

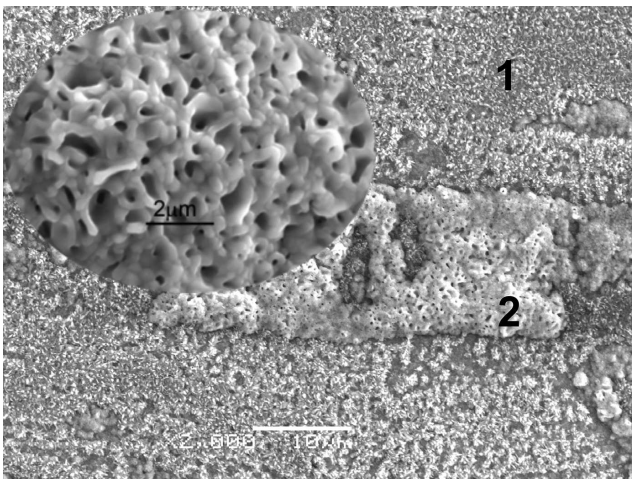


Fig. 5. SEM image showing oxide forms which appeared in places of mechanical defects (scratching) of foil. 1 – undamaged place; 2 – spongy form of oxide (magnified)

TEM analyses of Al_2O_3 oxide formed on samples without the Al nano-layer indicate that whiskers grow from inside the scale. Small columns are usually built of α - Al_2O_3 phase. Inside the scale layer the α -phase leads to the formation of spherical grains or columns. The α -phase is usually formed on the surface of the metallic core; nevertheless, isolated crystallites of α -phase in the form of columns were also identified inside the scale layer, not having however any contact with the metallic core, growing above the scale surface (Fig. 6). Aluminium oxides crystallize in hexagonal structure. It was established that their columnar growth occurs along the crystallographic c axis [12-14].

The θ - Al_2O_3 phase forms a “forest” of whiskers (Fig. 7) on the outer surface of the scale. Inside the scale θ - Al_2O_3 phase forms crystals in the shape of columns and they are generally bigger than the α -phase. Sporadically, θ - Al_2O_3 phase were identified on lump grains of the γ -phase which are in contact with the surface of the metallic core (Fig. 6a, b). The γ - and θ -phases are growing as a result of the outward diffusion of cations. The nuclei of the metastable γ -phase are forming in the first stage of the oxidation process. It was found

that the θ -phase is formed on the surface of γ -phase and it may result from the transition of γ to θ .

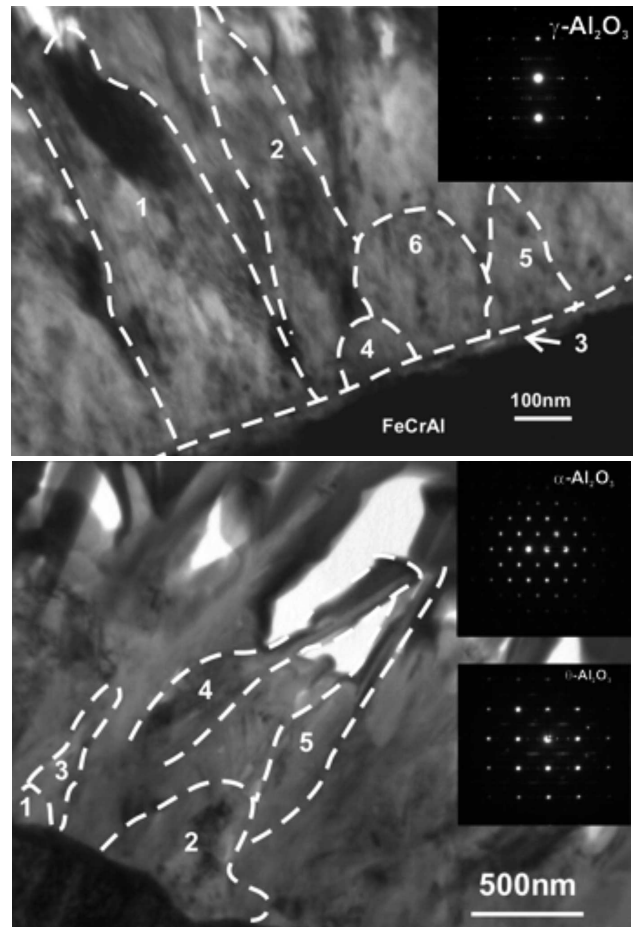


Fig. 6. TEM-BF image showing fragments of oxide layer obtained in the atmosphere of 67.6% O_2 +Ar at 850°C for 24 h on a sample without an Al nano-layer: a) 1, 2 – columnar structures of θ - Al_2O_3 phase; 3 – amorphous layer sticking to base; 4, 5 – places where γ - Al_2O_3 phase is present; 6 – places where α - Al_2O_3 phase is present, b) 1, 2 – places where γ - Al_2O_3 phase is present; 3, 4, column and whisker of θ - Al_2O_3 phase; 5 – whisker of α - Al_2O_3 phase growing from inside the scale

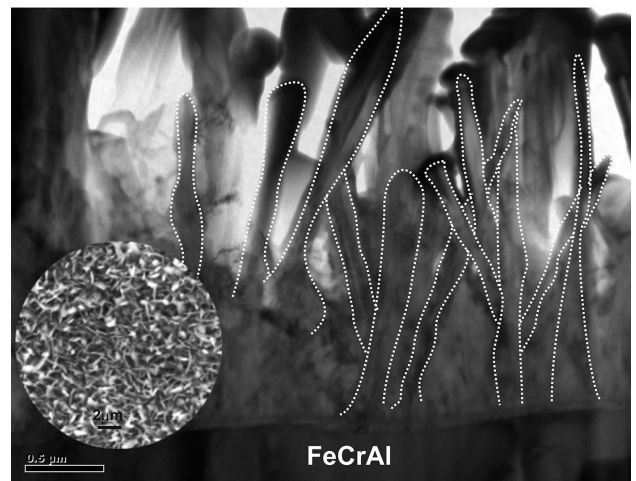


Fig. 7. TEM-BF image showing whiskers of θ - Al_2O_3 phase growing from the inside of oxide layer. SEM image showing a fragment of the foil surface after oxidation in an atmosphere of Ar + 67.6% O_2 at 850°C for 24 h

Scales formed on the surface of samples covered with the Al nano-layer possess a similar structure to scale formed on the samples not covered by Al nano-layer; Al_2O_3 oxides had form of lump, pyramids, and long columns protruding above the surface in the form of whiskers (Fig. 8). The sizes of these whiskers are bigger than those observed on foil samples without the Al nano-layer, it can be connected with higher concentration of aluminium. Large spiky whiskers grow among lump forms and are positioned perpendicularly to the surface. Small whiskers are chaotically oriented towards the surface. Phase analyses revealed that $\alpha\text{-Al}_2\text{O}_3$ phase constitutes lump forms located on the surface of the metallic core, whereas whiskers are built of $\theta\text{-Al}_2\text{O}_3$ phase. The θ -phase grows both from the metallic base and from the inside of the oxide layer. Similarly to the samples without Al nano-layer, the presence of columnar crystals of $\alpha\text{-Al}_2\text{O}_3$ reaching the scale surface. The presence of $\gamma\text{-Al}_2\text{O}_3$ phase was not identified throughout the oxide layer (Fig. 9).

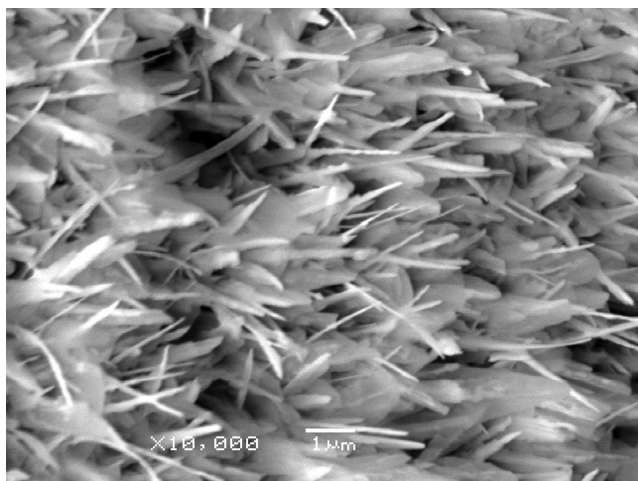


Fig. 8. SEM image showing scale formed on foil surface covered with Al nano-layer before oxidation in an atmosphere of Ar + 67.6% O_2 at 850°C for 24 h

On the basis of the above analyses one may put forward a hypothesis that the formation of $\alpha\text{-Al}_2\text{O}_3$ phase within the scale is formed as a result of two mechanisms:

At the initial stage of the oxidation process namely the nuclei of different $\alpha\text{-Al}_2\text{O}_3$ phase on the surface of the metallic core are growing as a result of inward transport of oxygen in the oxide [9,15-17]. Due to the extremely low concentration of point defects in $\alpha\text{-Al}_2\text{O}_3$ phase, the lattice diffusion of aluminium and oxygen does not virtually participate in the increase in the size of the oxide. Therefore, crystallites of $\alpha\text{-Al}_2\text{O}_3$ phase do not reach large sizes (Fig. 9).

The second mechanism refers to the presence of $\alpha\text{-Al}_2\text{O}_3$ phase both, inside the oxide layer and on the scale surface (column). The presence of these particles result of form the phase transformation of θ to α . Growth stresses existing in the inner scale layer tend to phase transformation resulting in annihilation of phase smaller molar volume (14%) [17,18]. Crystallites formed in such a way may assume considerable sizes as the transformation processes are not controlled by diffusion.

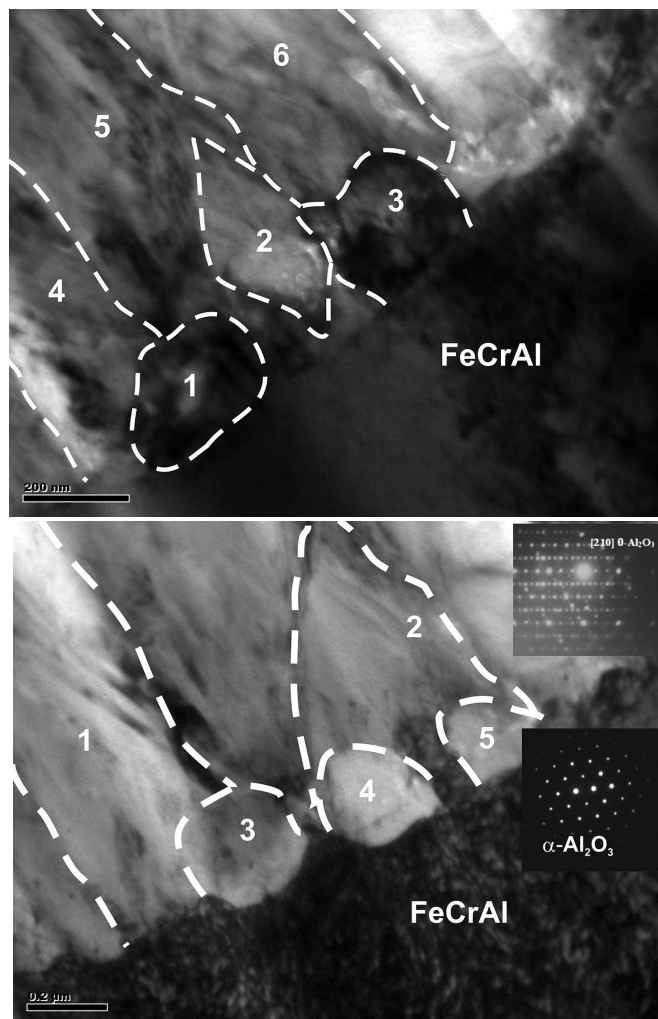


Fig. 9. TEM-BF image showing fragments of the oxide layer obtained in the atmosphere of Ar + 67.6% O_2 at 850°C for 24 h on a sample with Al nano-layer: a) 1, 2, 3 – lump crystals of $\alpha\text{-Al}_2\text{O}_3$ phase and 4, 5, 6 – columnar crystals of $\theta\text{-Al}_2\text{O}_3$ phase connected with them, transforming into whiskers on the scale surface, b) 1, 2 – columnar crystals of $\theta\text{-Al}_2\text{O}_3$ phase partially deposited directly on the steel base and partially deposited on polycrystals of $\alpha\text{-Al}_2\text{O}_3$ 3, 4, 5 phase

In the case of samples covered with the aluminium nano-layer the presence of the γ -phase was not identified. It is possible that this phase forms only during the initial stage of the reaction, but as a result of significantly higher concentration of aluminium in the base it quickly undergoes transformation into the θ -phase. The possibility of the formation of θ -phase on the metal surface without a phase transition cannot be excluded (Fig. 10). The $\theta\text{-Al}_2\text{O}_3$ phase is more stable than the γ -phase at the reaction temperature. Aluminium oxides crystallizing in the hexagonal structures setting; it was found to form columnar crystals increase along the crystallographic c axis [12-14].

It was not proved that the crystals of all identified phases should have privileged crystallographic directions. The crystallographic surfaces identified in this work were different in each phase. Therefore, reconstruction of the lattice during the transformation $\gamma \rightarrow \theta \rightarrow \alpha$ is not of epitaxial character, as might be expected from the observation of places of their formation (Fig. 6).

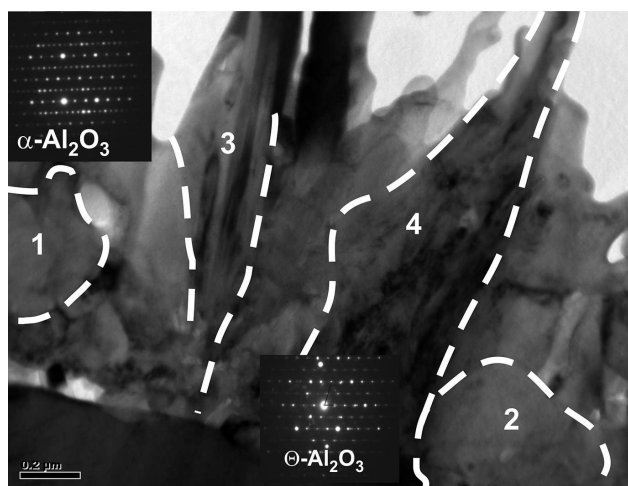


Fig. 10. TEM BF image of a cross-section of an oxide layer fragment showing direct contact with the α -phase Al_2O_3 crystals (1, 2) and θ -phase Al_2O_3 crystals (3, 4) with the base

4. Conclusions

Basing on the results described in the present paper the following conclusion can be formulated:

1. High-temperature oxidation of Fe20Cr5Al steel foil in the of Ar + 67.6% O_2 gas mixture leads to the formation of a scale which is morphologically very complex, being composed of crystallites of γ -, θ - and α - Al_2O_3 phases.
2. It was established that physical defects on the surface have an impact on the formation of Al_2O_3 oxides with a foamy structure, composed mainly of α - Al_2O_3 phase.
3. Covering the foil with nano-layer of crystalline aluminium prior to oxidation resulted in a much larger increase of Al_2O_3 crystallites with pyramid and needle forms than in the case of foil without an Al nano-layer.
4. Microscopic observations of scale layer cross-sections revealed that in the case of the foil without Al nano-layer there exist remnants of an amorphous Al_2O_3 nano-layer from which γ - and θ -phase Al_2O_3 crystallites grow. In the case of the foil covered with the Al nano-layer the presence of amorphous nano-layer of the oxide and the γ - Al_2O_3 phase was not found. However, it was established that there is direct contact of θ - Al_2O_3 crystals with the metallic base.
5. The presence of crystals of α - Al_2O_3 phase in the form of spherical nano-lumps which are in contact with the metallic base is a characteristic feature for both states of the foil surface (with and without a nano-layer).

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