

Influence of Substrate Local Heating on Morphology of Al and Al₂O₃ Nanofilms

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Experimental investigations presented in this work were focused on the execution of a carousel system with its usability for step-by-step revolutions and the mechanism for clamping the heater, which made it possible to heat substrates individually within the range from 25 °C to 300 °C. This system was used for depositing the metallic Al films by the magnetron sputtering method on foil made of FeCrAl steel, which found application in the production of metallic catalytic reactors. It was found that in the case of not-heated foil the polycrystalline continuous Al film, which is separated from steel by an amorphous oxide nanofilm obtained spontaneously under influence of weather conditions, was created. The deposition of aluminium on foil heated to the temperature of 300 °C caused the film marked by fine grains integrated with small forces to be formed. These differences had an influence on the morphology of the oxide films.

PACS: 68.55.jm, 68.55.J–

1. Introduction

Comparing metallic monoliths based on FeCrAl steel with ceramic ones applied to catalytic converters, one should emphasize an opportunity to produce alumina films on their surface being directly bonded with metallic substrate [1, 2]. A suitably formed alumina film is able to provide a carrier for catalytically active elements or could be used as an interlayer for increasing the adhesion between other oxide films deposited for surface development. Due to the limited aluminium content (< 6%) in FeCrAl steel to retain the suitable high-temperature creep resistance, the increased content of aluminium required to produce its oxide could be obtained by the deposition of additional Al-film prior to the process of high-temperature oxidation [3]. The growth of oxide films and especially the formation of hybrid crystalline system from aluminium obtained from steel are affected by the metallic nanofilm structure.

The state of surface i.e. the occurrence of physical defects and impurities in the form of naturally formed oxides and especially the temperature required to deposit Al-films are key factors that affect the condensation of particles and their transition as finally films are formed. In the case of vacuum equipment used for depo-

sition of metallic films by magnetron sputtering methods, the complicated and expensive solutions are required for preheating the substrates that are mounted in carousel fixtures. The present work describes a model of a step mechanical-electrical system that is able to preheat the substructure in contact while turning the carousel. The operation of the system was verified by comparing the Al-nanofilms deposited on FeCrAl foil substrates at 25 °C with the films deposited on substrates at 150 °C. The morphology of oxide films obtained by oxidising the foils coated with these nanofilms was also compared.

2. Experimental procedures

2.1. Deposition of metallic Al-films

For depositing the Al-films, the vacuum apparatus [4, 5] fitted with two magnetron constant-current sources, where the targets made of aluminium plates (purity 99.99) were used. The deposition of films was carried out on pieces of foils 35 mm × 35 mm × 0.005 mm in dimension made of Fe20Cr5Al steel. The targets were situated at the distance of 45 mm from the substrates; the process of sputtering was carried out for 60 s at the pressure of argon $p_{Ar} = 3.3\text{--}3.5$ Pa and the power of magnetron sources 0.2–0.54 kW. A special design for a carousel (Fig. 1) made it possible to fix 16 pieces of foil.

The pieces of foil were coated at the temperature not exceeding 25 °C and preheated to 150 °C. The preheating of the foil occurred when the leading roll of a rotating carousel during the heating was at recess 2, then the

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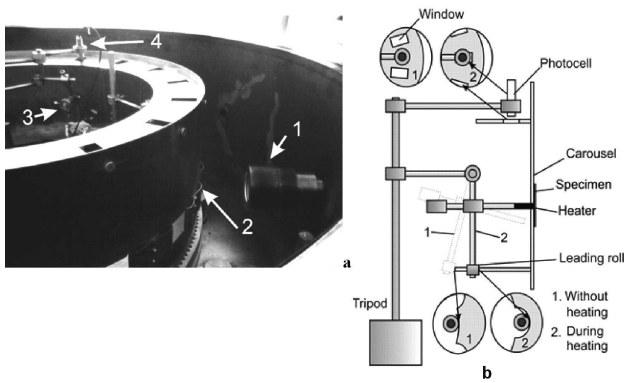


Fig. 1. A carousel system for step revolution for pre-heating the individual substrates: (a) general view: 1 — magnetron, 2 — fixtures of substrates mounted on a carousel, 3 — back part of a heater, 4 — photocell, (b) diagram of substrate preheating: 1 — positions where the heater is retracted from substrates, 2 — positions, where the heater is in contact with the substrate.

heater was at position 2. This time the revolution of the carousel was switched off by the photocell — position 2. The repeated movement of the carousel caused the leading roll to be moved to position 1 and the heater to be retracted to position 1 (without heating). Due to positioning the photocell at position 1 it was possible for the carousel to be turned and to take the position by a new piece of foil opposite the target. At the time the leading roll took position 2, the revolution of the carousel and the magnetron were again switched on.

2.2. Foil oxidation

The foil oxidation was carried out at 860 °C for 24 h at a flow rate of the argon and oxygen mixture at atmospheric pressure where the oxygen content was 67.6% and the total gas flow was $Q_{(O_2+Ar)} = 53.2 \text{ cm}^3/\text{min}$. The oxygen purity of $O_2 = 99.95\%$ and the argon purity of $Ar = 99.995\%$ were applied to the process of oxidation. The oxidising equipment included an electric furnace with a vertically positioned quartz tube [5]. A temperature controller allowed the temperature to be stabilised in a reaction zone precisely $\Delta \pm 5 \text{ }^\circ\text{C}$. The sample after oxidising was subjected to slow cooling under argon for 120 min in the furnace chamber to the ambient temperature, approximately 22 °C.

3. Results

3.1. Metallic Al films

As follows from the observations by scanning electron microscopy (SEM), the foil surface coated with an Al nanofilm at the temperature not exceeding 25 °C did not show any significant morphological differences compared to the uncoated foil. However, when the foil was heated up to 300 °C there were formed films insular in character (Fig. 2). Small grains were probably formed due to the

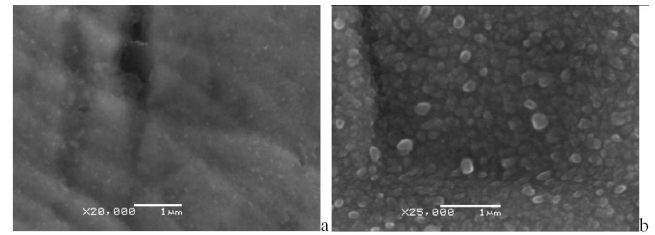


Fig. 2. SEM images of FeCrAl foil surface coated with Al nanofilms: (a) at the temperature not exceeding 25 °C, (b) at the temperature of 300 °C.

conditions favourable to migration of aluminium particles being deposited.

As follows from the cross-sectional view of an Al surface in the bright field (STEM-BF), the coat continuous in character, composed of three zones where the middle one revealed features of crystalline structure, was formed by deposition of pure Al (Fig. 3). However, the films formed below and above the middle zone did not reveal any features confirming the crystalline structure.

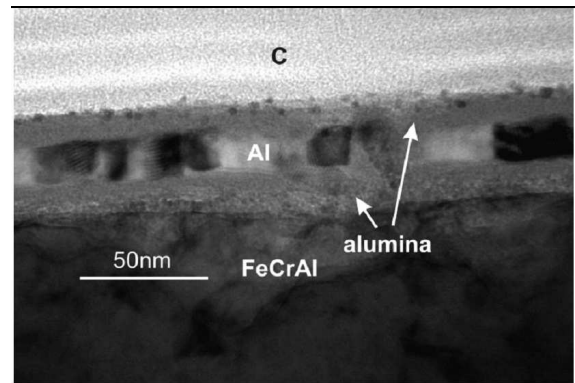


Fig. 3. STEM-BF image (scanning transmission microscope — bright field) of FeCrAl foil cross-section coated with the Al film: Al — polycrystalline Al film, C — carbon film produced by the CAPD method in order to reinforce the films being tested during preparation of the specimen.

From a distribution of elements in the places marked with a line (Fig. 4a) one can see that these zones could form Al_2O_3 oxides. It was indicated by two small superimposed maxima (arrows 1 and 2, Fig. 4b) corresponding to the aluminium and oxygen lines, adjacent to the substrate surface and outside from the central maximum of the Al line (arrow 3) and minimum of an oxygen (arrow 4), corresponding with a zone of crystalline structure (Fig. 4a). Fe was identified in an alumina zone close to foil (arrow 5). This place was lacking in a maximum of an oxygen line (Fig. 4b) and a spectroanalysis (Fig. 4c) carried out in the middle of the crystalline zone (the place marked with a local cross, Fig. 4a) showed that the signal intensity obtained from aluminium was much higher than that of the oxygen.

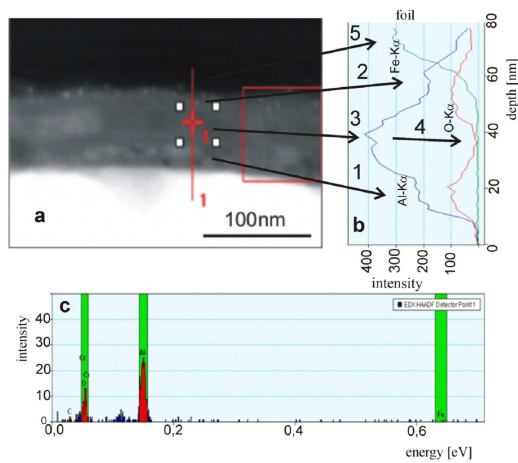


Fig. 4. EDS analysis for the Al film: (a) STEM-BF image, (b) analysis of Fe, Al and O elements distribution along a line, (c) spectrogram of signals obtained from the marked place.

An amorphous form of an oxide film creating a zone adjacent to steel substrate could be explained by a long-lasting process of foil oxidation in open air, at the ambient temperature, prior to the process of Al-film deposition. A nanofilm of amorphous oxide was formed in a natural way and its thickness did not exceed several nanometers ($d \leq 15$ nm). This film in the case of not-heated foil was a basis for crystallite nucleation in a continuous metallic Al film, however, in the case of the elevated temperature it allowed migration to be spread in all the directions, which led to local accumulation and nucleation. A thinner external oxide zone, which was identified in both films, was likely to be formed after completing the process of aluminium film deposition just at the time of aerating the vacuum chamber and contact with oxygen. It followed from a strong chemical affinity between aluminium and oxygen.

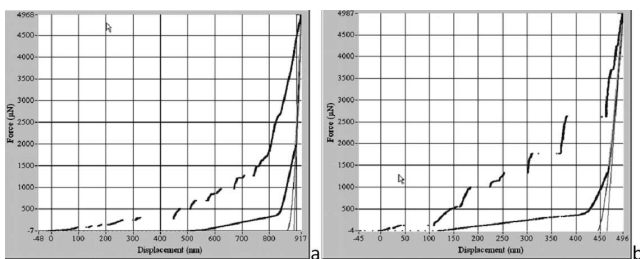


Fig. 5. Hardness test on the films with a nanoindenter hysitron[®] carried out for the Al films deposited FeCrAl foil: (a) at the temperature not exceeding 25 °C, (b) at 300 °C.

The hardness test on the films executed with a nanoindenter hysitron[®] revealed better elastic properties of the films obtained on not-heated substrates, diagram (Fig. 5a) compared to those obtained at 300 °C, diagram (Fig. 5b). It was confirmed by abrupt penetration of an

indenter at constant load. It was caused by insular nature of the film structure and a lack of continuity between individual grains.

3.2. Oxide films on the FeCrAl foil

The occurrence of the oxide in nodular forms, shaped as pyramids (Fig. 6a) and long spike-shaped whiskers protruding above them (Fig. 6b) was the feature characteristic of the scale obtained as a result of oxidising the foil coated with Al films at the temperature not exceeding 25 °C. Sizes of these whiskers are larger than that of the whiskers obtained on the uncoated foil.

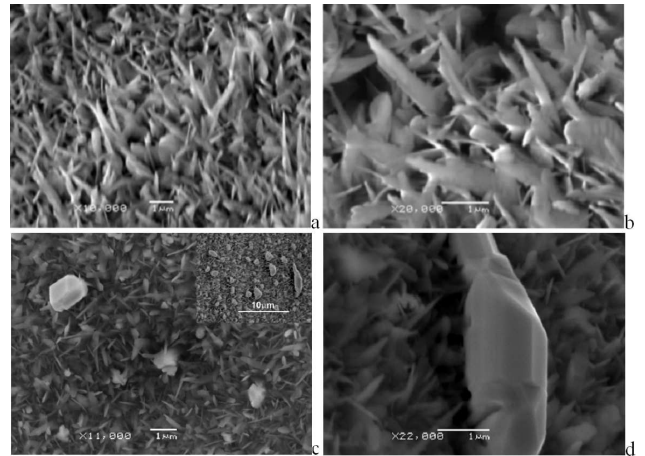


Fig. 6. SEM images of the alumina film obtained by oxidising the foil coated with Al nanofilms: (a, b) at temperature not exceeding 25 °C, (c, d) at 300 °C.

Large spike-shaped whiskers grow among nodular forms and have orientation, however, finer whiskers are in the form of “loose coniferous mat” (Fig. 6b).

There is constituted a laminar system, where a lower film is more compact. The investigations revealed [6] that nodular crystallites formed an α - Al_2O_3 phase, whereas a θ - Al_2O_3 phase was crystallizing into the form of whiskers.

The scale obtained as a result of oxidising the Al-coated foil at 300 °C was marked by the occurrence of large crystalline forms α - Al_2O_3 scattered over the whole surface (Fig. 6c). The outward features indicated highly defected monocrystals. They were seated on the alumina whiskers whose dimensions were smaller but their shapes were similar to those obtained on the not-heated foil. The mechanism of their formation is not known; one may assume that in the course of oxidising the foil at 860 °C there occurred dislocation and compounding of individual Al grains, as well as transformation into oxide crystals. This process was assisted by the whiskers growing from the steel substrate and the growth-oriented nodular crystals, as it occurred in case of not-heated foil. The smaller sizes of whiskers were probably due to restraining reaction of a grained Al film at the initial stage of oxidation, caused by oxygen consumption by this film.

4. Conclusions

1. The system of step-by-step shifting the carousel and the mechanism for clamping the heater made it possible to run the process of thin-film deposition on heated substrates individually up to a given temperature, within the range from ambient temperature to 300 °C.

2. As a result of foil heating up to 300 °C the Al film of granular structure, showing the higher plastic deformability in hardness tests than the film deposited on not-heated foil, was formed. It was due to weak bonding within the granular structure of a film, which consequently was conducive to more free access of oxygen atoms to aluminium atoms.

3. The occurrence of the oxide film obtained under influence of weather conditions on the steel foil and the granular structure of a metallic Al film were conducive to the coagulation of Al particles and the formation of crystalline α -Al₂O₃ forms. They were connected with whiskers of alumina, which was simultaneously obtained

from aluminium included in steel and aluminium deposited on foil. The hybrid system of alumina crystallites of different morphology from the films obtained by oxidising the not-heated foil was formed in this way.

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