

DEPOSITION OF THIN-FILM HYBRID SYSTEMS ON FE-CR-AL-STEEL SUBSTRATE AND TESTING THEIR CATALYTIC PROPERTIES

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Abstract

Metal foils play more and more important part in production of catalytic converters for exhaust and industrial gas. The deposition of the active phase on the foil surface makes it possible to create the optimum conditions for the catalytic process and obtain the high-duty converters resistant to vibrations and thermal shock.

The work was focused on the new thin-film technique designed for depositing the laminar and hybrid oxide systems obtained as a result of the high-temperature oxidation of the foil made of OH18J5 heat resisting steel, using a mixed oxygen-argon atmosphere with equal volume fractions, and then they were coated with Al₂O₃ nano-films by sputtering the α Al₂O₃ monolithic target with the aid of an r.f magnetron.

Both the oxide layers without coating and the layers coated with Al₂O₃ nano-films were deposited with Pt coats by sputtering the metal target from a d.c magnetron. The thickness of each sputtered Al₂O₃ and Pt film did not exceed 25 nm.

The catalytic activity of the obtained coatings and their acidic-basic properties within the range of temperatures 523-673 K were determined on the basis of a 2-methylol-3-butyn-2-ol decomposition reaction.

1. Introduction

The chemical properties of mechanical catalysts (oxide layers) are affected by physicochemical properties of the catalyst carrier (oxide films), and mostly by activated catalytic elements (e.g. Pt) and their dispersion on the surface. Polymorphic modifications θ and γ - Al₂O₃ and their concentration in film systems with Pt demonstrate a great activity.

Opinions on the mechanism of forming the oxide films made of Al₂O₃ scale deposited on FeCrAl ferrite steel are divergent and concern mainly two ways of their interpretation. In one of them, the occurrence of Al ion diffusion from the core is assumed, however the other one interprets the growth of the film by oxygen diffusion towards the core [1,2,3]. Therefore, it is

not out of the question that two mechanisms of forming the Al_2O_3 scale can occur at the same time.

It follows from experimental investigations that scale generated by thermal oxidation at SO_2 atmosphere may contain a small amount of an θ Al_2O_3 phase, as well as γ - Al_2O_3 and more part of α - Al_2O_3 phase [4,5]. It causes them to show the catalytic basic properties and slight acidic ones. These formations are marked by their discontinuity on steel surface, which have an influence on coherence and adhesion between the whole scale and substrate.

2. Experimental procedure

2.1. Methods of the deposition of hybrid nano-film systems

The film systems were produced on the basis of Al_2O_3 extended surfaces obtained by oxidation of OH18J5 (Fe-Cr-Al) steel at the atmosphere Ar and O_2 at the proportions 1:1, with total flow 2mls^{-1} , at temp 840°C and 860°C , within 20-24 hours.

Nano-films were produced in the following way:

1. Metal foil was coated with a nano-film of platinum or aluminum and then it was oxidized.
2. A platinum nano-film deposited on metal foil was coated with aluminum and afterwards the coating was oxidized.
3. An aluminum nano-film deposited on metal foil was coated with platinum and afterwards the coating was oxidized.
4. The oxidized foil was coated with Al_2O_3 or platinum.
5. The oxidized foil was coated with Al and subjected to further oxidation.

Films having a thickness of: Pt-6nm, Al-8nm, Al_2O_3 - 5 and 15 nm, were produced by PVD methods applying the technological parameters described in ref. [4]. The specimens subjected to a catalytic test are listed in Table 1.

The thickness of the deposited films was determined using an atomic force microscope AFM, type: Autoprobe CP, made by Scientific Instrument in reference to the measurement of the offsets on specially prepared mono crystal lattices of Si, which were fixed to the sheets of metal foils being deposited. Examples of typical "scans" of the measured thickness are presented in Fig.1.

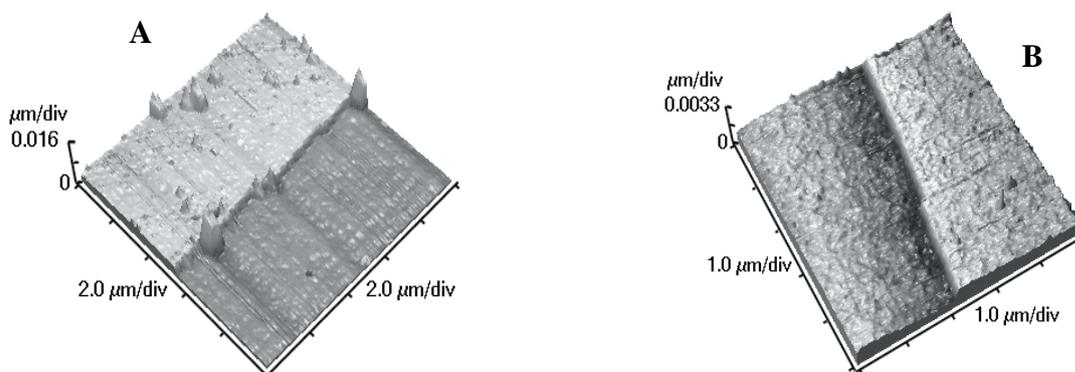


Fig. 1. AFM images of amorphous Al_2O_3 (A) and Pt (B) films obtained by PVD methods

Table. 1. List of specimens subjected to a catalytic test

Item	Specimen specification	Specimen symbol
1	Raw foil	R
2	Foil with oxide coating (840°C)	S840
3	Foil with oxide coating (860°C)	S
4	Foil with oxide coating (860°C)+ 6 nm Pt	S/Pt6
5	Raw foil +6nmPt, oxidized at 860°C	R/Pt6+ox860
6	Raw foil +6nmPt+8nmAl oxidized at 860°C	R/Pt6/Al8 +ox860
7	Raw foil +8nmAl +6nmPt, oxidized at 860°C	R/Al8/Pt +ox860
8	Foil with oxide coating (860°C)+ 15 nm Al ₂ O ₃ (RF)	S/ Alu15
9	Raw foil +5nm Al ₂ O ₃ (RF)	R/Alu5
10	Foil with oxide coating (860°C)+ 15nm Al ₂ O ₃ +2nmPt	S/Alu15/2Pt

Microscopic examinations of film structure

The surface of scale was observed by JSM 5500 scanning electron microscope at 10kV (SE). The microstructure observations were performed using Philips CM20 TWIN (200kV) transmission electron microscope equipped with EDAX Phoenix EDS system. The thin foils were prepared presenting alumina scale and magnetron sputtered material in *cross-section* using mechanical polishing, dimpling and finally ion milling with Gatan Duomill 600 at 5kV.

Catalytic test

The catalytic activity of Al₂O₃ and Pt films was determined by catalytic tests, where model 2-methylol-3-butyn-2-ol particle-probes were used. The tests were carried out in a micro-reactor linked “*on line*” with a gas chromatograph of an SRI 8610C type within the 475-675K range of temperature.

The catalytic properties of alumina are determined by O²⁻ and Al³⁺ ions of different coordination, and also the structural defects and hydroxyl groups occurring in their structure [6,7]. Therefore, the Al₂O₃ surface can include both Brönsted’s acidic sites, and Lewis’s basic sites. Especially high catalytic activity of alumina in these reactions results from the occurrence of θ and γ Al₂O₃ phases. Platinum also exhibits basic sites. However, an α Al₂O₃ phase shows relatively lower catalytic activity in the reaction of 1-propanol conversion. 2-methylol-3-butyn-2-ol on the basic sites underwent the conversion into acetone and acetylene, however on the acidic sites it dehydrated into 2-methylol-1-buten-3-yn [4, 5].

Testing the film adhesion to substrates

Considering the small thickness of Al₂O₃ and Pt films (not exceeding 17nm), additionally being deposited on the scale produced by FeCrAl foil oxidation, where the size of whiskers did not exceeded 1000nm, the tests on mechanical properties were limited to testing the adhesion to metal foil:

a) scales, b) scales with additionally deposited Al₂O₃ and Pt films, c) scales with deposited Al₂O₃ film.

For this reason, the scratch test was applied with aid of a Swiss-made Revetest CSM tester. Due to a very small thickness of the substrate made metal foil (0.05mm), the specimens 20 x 25mm were cut from oxidized flakes, and then they were stuck to a polished steel disk with chemo-setting adhesive, which allowed for a possibility of reducing the deformation of foil by the action of an indenter. A Rockwell diamond cone was used as an indenter. The indenting force was linear in character from 0.005N do 21.43N growing with a speed of 19.52 N/min, on a distance of 11 mm and at a travelling speed of 10.04 mm/min. Adherence characteristics were taken from analysis of changes in the friction force F_c and from the visual examination of the assigning the changes in film continuity to the load N leading to chips, spilling or cracks of the film.

3. Results

Structure

The scale obtained due to the selection of the oxidizing atmosphere, the reaction temperature and the process duration was like a lawn in appearance Fig. 2A. Its characteristic feature is marked by the occurrence of crystalline forms in the shape of whiskers and pyramids showing a non-isometric and isometric direction of growth, Fig. 2B,C,D. These structures, despite their diversified distribution on the foil surface creating aggregates, form the entirely well extended surface.

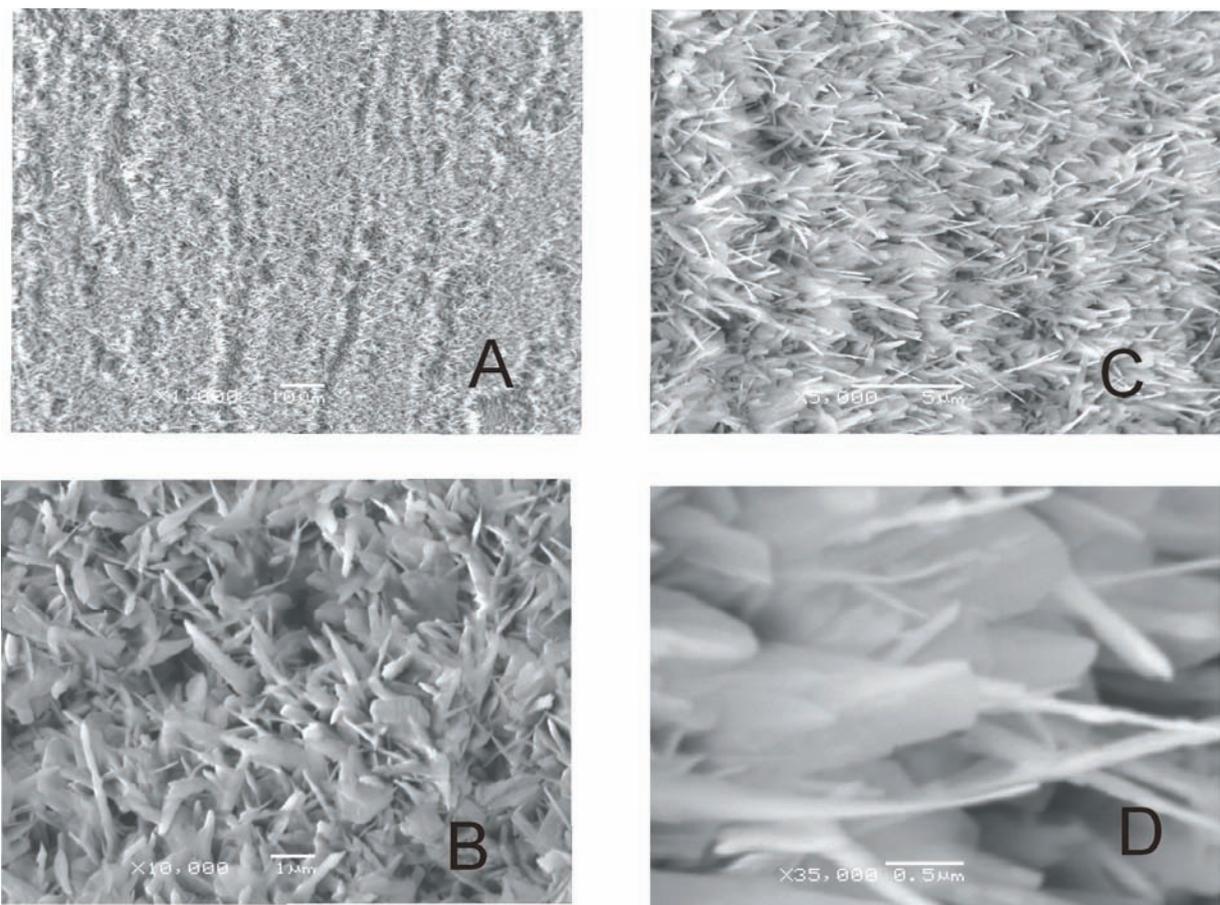


Fig. 2. Oxide forms produced on the surface of FeCrAl foil by thermal oxidation; A – general view of the surface, B,C, - whiskers, D – conical oxide forms providing the under layer for whiskers

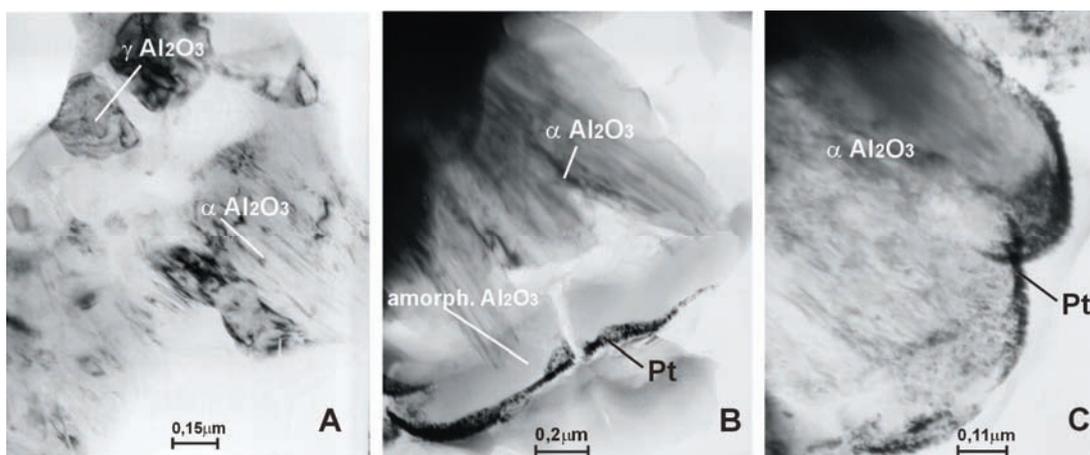


Fig. 3. TEM image of scale cross-section:

A - with crystallites of $\gamma\text{Al}_2\text{O}_3$ and $\alpha\text{Al}_2\text{O}_3$ phases, B - with a Pt nano-film and an amorphous Al_2O_3 film coating the whiskers, C - platinum nano-film directly deposited on the surface of the whiskers

Examinations of a hybrid layer system carried out using a transmission electron microscope revealed the occurrence of $\gamma\text{Al}_2\text{O}_3$ forms in cubic layers, and large crystallites of $\alpha\text{Al}_2\text{O}_3$ phase (Photo 3A). They are similar to structures determined earlier by electron diffraction [5]. It was found that the surface zone also included an amorphous Al_2O_3 film with a very thin film of crystalline Pt coating the whiskers (Photo 3B) and the whiskers coated only with a discontinuous Pt film (Photo 3C).

Catalytic activity

The catalytic activity of the obtained laminar systems is presented in Fig. 4A-4E. It results from trade-off studies of foils oxidized at temp 840°C and 860°C (Fig. 4A) that the oxide film obtained at a lower temperature do not change their catalytic activity in reference to raw foil (R). This activity increases not until the temperature of oxidation increases to 860°C , as a result of a significant development of the oxide film. An increase in the oxidation temperature of the film brought about a decrease in a ratio of the active sites of acetylene to the 2-methylol-1-buten-3-yn sites ($r_{\text{acet}}/r_{\text{byn}}$), i.e. an increase in concentration of acidic sites in reference to the total activity of Al_2O_3 coating. It is connected with a relatively higher concentration of $\gamma\text{Al}_2\text{O}_3$ phase in the oxide film.

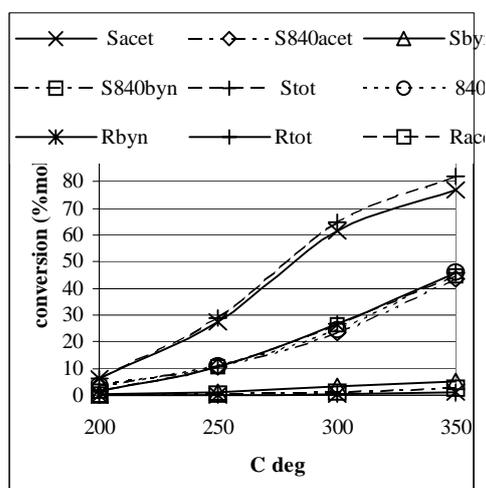


Fig. 4A. Conversion for scales obtained at 840 and 860 C deg

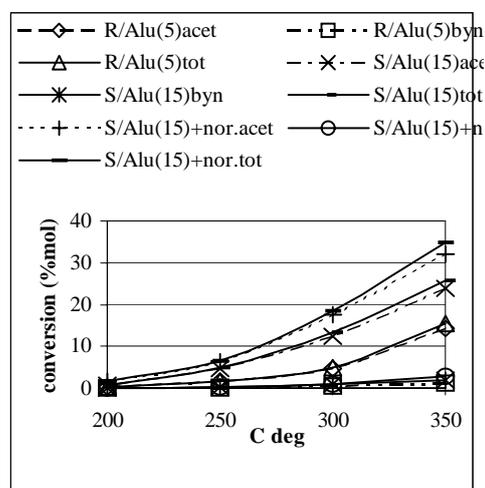


Fig. 4B. Conversion for systems foil (R and S) coated by AL_2O_3 (ALUMINA) layers

By coating the raw foil with a nano-film of amorphous Al_2O_3 (R/Alu(5)) the catalytic properties were decreased due to the locking of the active sites (Fig.4B). The higher activity was observed in case of layer systems (S/Alu(15)) of the oxide obtained on foil by thermal treatment and additionally coated with an Al_2O_3 nano-film. An additional increase in activity of the system was obtained by its heating at temp 400°C for 0.5 hour (S/Alu(15) + norm).

It follows from extension of the surface and its development likely to the partial recrystallization of amorphous Al_2O_3 .

In case of oxidation of the layer system (Fig.4C) produced by coating the substrate with an Al-nano-film and then a Pt-nano-film (R/Al8/Pt6) the high activity of the hybrid system was obtained, because platinum (Fig.3D) deposited on the surface was involved in the process along with the Al_2O_3 film obtained by B-ynol catalysis.

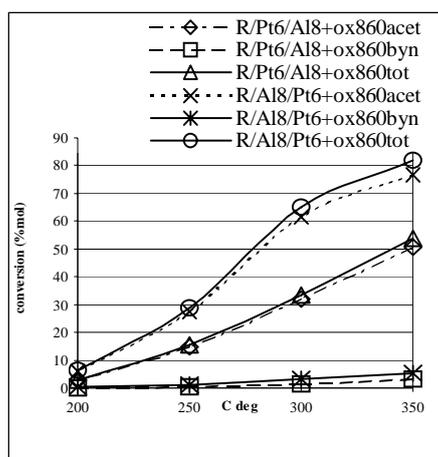


Fig. 4C. Conversion for raw foil coated by Pt and Al layer and then oxidized and coated by Al and Pt films and oxidized

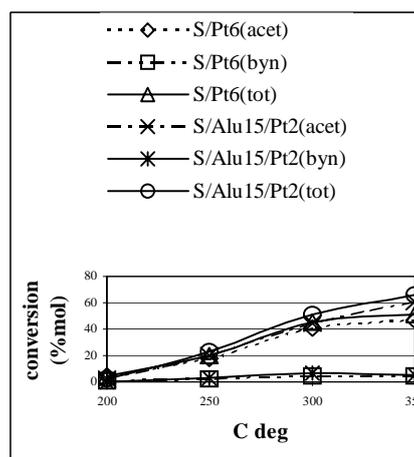


Fig. 4D. Conversion for foil with scale, coated by Pt and alumina and Pt layers

This activity was not obtainable for the systems with films deposited in a reverse order (R/Pt6/Al8) due to locking the platinum fraction in the process of catalysis by an Al_2O_3 nano-film obtained by oxidation of aluminum. Relatively lower activity results from catalysis of B-ynol mainly in active sites of a crystalline Al_2O_3 nano-film.

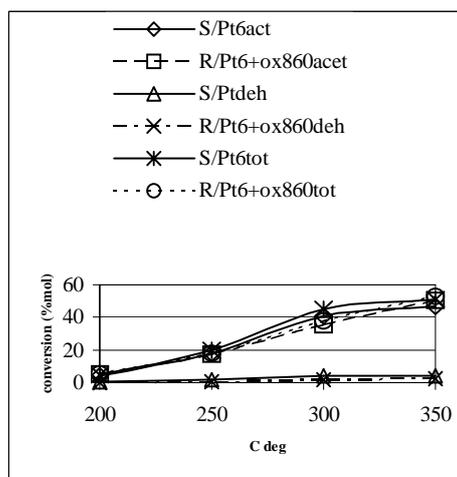


Fig. 4E. Conversion for S/Pt6 & R/Pt6+ox860

It follows from the comparison (Fig.4D) that the development of the oxide film on foil by deposition of amorphous Al_2O_3 (S/Alum15/Pt) has an influence on the system activity, because the system where Pt was deposited directly on the crystalline Al_2O_3 (S/Pt) film showed the relatively lower catalytic activity within the whole temperature range of analysis.

One can assume that the higher activity of a three-layer hybrid system is connected with an increase in the development of the Al_2O_3 film surface.

It follows from the results (Fig.4E) that a platinum nano-film deposited on foil and deposited on raw foil subjected to oxidation is not locking the activity of the crystalline oxide (S/Pt6) and is not locking the oxidation process of foil (R/Pt6+ox860), because these systems revealed similar catalytic activity.

Adhesion

From the comparison of the scale adhesion (2,6 N) Fig. 5a with the adhesion of scale with Al₂O₃ and Pt Fig. 5b and scale with Al₂O₃ (4,12 N) Fig.5c, one can observe a slight increase in the failure load from 4N to 9N. Such the increase likely results from the mutual consolidation of crystals and the spongy structure with the amorphous film of Al₂O₃ and Pt.

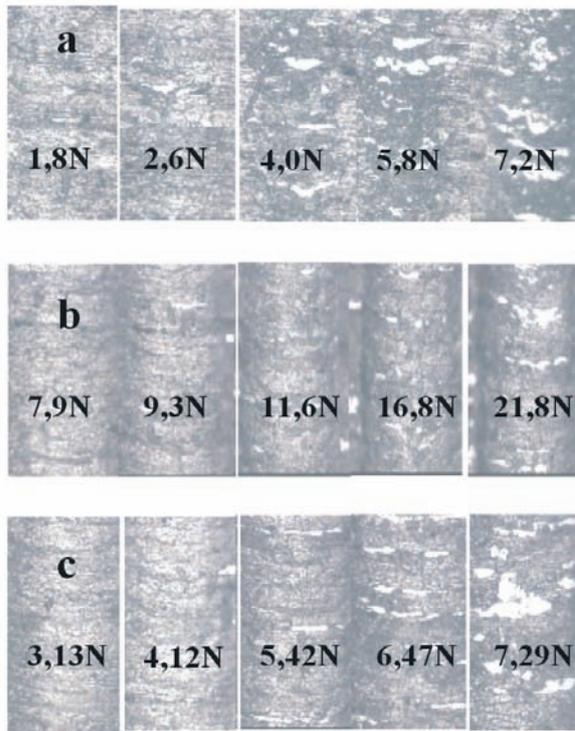


Fig. 5. Microscopic observation of the states of changes in the surface caused by loading the diamond cone in the scratch test: a) foil with scale, b) foil with scale coated with amorphous Al₂O₃ and the with Pt-film, c) foil with scale coated with Pt-film

4. Conclusions

1. The process of thermal oxidation of FeCrAl foil under Ar/O at a flow rate ratio 1:1 makes it possible to obtain the oxide films with the structure similar to the technology in which the SO₂ atmosphere was applied [4,5].
2. The occurrence of γ Al₂O₃ crystallites separated in the film and α Al₂O₃ crystallites growing from the substrate indicates the mechanism of growth based on out-diffusion of aluminium and in-diffusion of oxygen through newly formed scale.
3. Crystalline Al₂O₃ obtained during the oxidation under Ar/O at flow rate ratio 1:1 is basic in character and the concentration of acidic sites is minimal.
4. By coating the foil with a platinum nano-film the process of foil oxidation is not hampered (it is only slightly weakened), and platinum in the course of growing the oxide film remains on the surface of hybrid system increasing its catalytic activity.
5. Coating Pt-film with an amorphous Al₂O₃ nano-film causes the active Pt sites to be locked.
6. Additional coating the oxidized metal foil with the Al₂O₃ and Pt nano-films increases the laminar system adhesion to steel substrate over two times.

5. References

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