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Research of Coatings Obtained in the Activated Thermo-Chemical Condensate Deposition Method, Al-O System

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Nanocrystalline γ-Al_2O_3 type coatings of 20 µm thickness were obtained in the activated thermo-chemical condensate deposition method, without special preparation of the surface being coated, without formation of an underlayer and without extra thermal processing, on the steel X15Ю5 (Russian standard) plates of 40 µm thickness, which temperature did not exceed 250 °C during coating formation. The article presents investigations of the system: coating-substrate, thermally processed at different temperatures (discrete range of temperatures 100, 300, 500, 700, 900 and 1100 °C), adhesion, phase composition, size of crystallites, microstrain, cross-section, topography. The tests are given for 50-cycle resistance of coated test pieces to thermal shock: heating up to 1000 °C – sudden cooling in water. Preliminary, comparative resistance of the system "coating – substrate" is shown for long-term chemical effect in solutions of alkali NaOH and acids H_2SO_4, H_3PO_4, HNO_3, HCl, HCl-HNO_3, during the tests of 300 hours.

Keywords: γ-Al_2O_3, coatings, adhesion, X-ray diffraction, thermal shock, resistance to acids.

1. INTRODUCTION

System Al-O includes plenty of oxygen combinations with aluminium [1]. The most important is aluminium oxide Al_2O_3, that is found in the crystal state as mineral corundum α-Al_2O_3 and as aluminium oxide hydrates. Aluminium hydroxides are the most widespread raw material for aluminium oxide (Al_2O_3), that itself is found in different meta-stable polymorphous states (transition aluminium oxides) and in thermodynamically stable α-Al_2O_3 (corundum) state [2].

There are some modifications of aluminium hydroxide: gibbsite, bajerite, bemite (cubic crystal structure) and diaspore (hexagonal crystal structure). Gibbsite is made of 65.4 % Al_2O_3 and 34.6 % H_2O. Bemite is made of 85 % Al_2O_3 and 15 % H_2O [1]. The structures of all aluminium hydroxides consist of stacked double layers of oxygen atoms in which the aluminium cations are located in octahedral coordination in the interstices.

During thermal treatment of aluminium hydroxides, the following transformations take place [2]:

1. Gibbsite γ-$Al(OH)_3$ → (150 °C – 200 °C) → bemite γ-AlOOH → (300 °C – 450 °C) → κ-Al_2O_3 → (500 °C – 900 °C) → γ-Al_2O_3 → (1000 °C – 1050 °C) → χ-Al_2O_3 → (1050 °C – 1100 °C) → θ-Al_2O_3 → (1100 °C – 1120 °C)→ α-Al_2O_3.
2. Bajerite β-$Al(OH)_3$ → (150 °C – 200 °C) → bemite γ-AlOOH → (250 °C – 450 °C) → η-Al_2O_3 →(950 °C – 1050 °C) → θ-Al_2O_3 → (1200 °C – 1250 °C) → α-Al_2O_3.
3. Diaspore α-AlOOH → (300 °C – 550 °C) → α-Al_2O_3.

The transition aluminas (especially the γ-form) have fine particle sizes and high surface areas with enhanced catalytic surface activity of their surfaces, and find industrial applications as adsorbents, catalysts or catalysts carriers, coatings and soft abrasives [3]. Adsorbents unavoidably change during operation due to reagents in chemical reactions, and therefore, chemical stability of absorbents is important [4].

γ-Al_2O_3 has lower strength than corundum, but it is more porous, has 1 % – 2 % of structurally bound water in itself. Own surface area is (120 – 150) m^2/gr. Full γ- → α-transformation is followed by volume decrease of 14 % – 18 %. Transformation rate remains stable during time under given temperature. Temperature increase from 1025 °C up to 1200 °C speeds up the transformation more than 100 times. Own surface area ≈ 1 m^2/gr [2].

Thermal stability of the transition aluminas depends on their morphology and crystallite sizes. α-Al_2O_3 (corundum) is obtained during melting of γ-Al_2O_3 or gibbsite, bemite, diaspore at 2100 °C. Corundum has thermal, mechanical and chemical stability, and it is possible to obtain from it a range of ceramics: from non-porous sintered to high-porous (thermal isolating).

In order to get ceramic coatings on metal substrates (for adequate adhesion), substrates are made of Cr, Ni stainless steel or other corrosion-resistant MCrAlY type alloys [5]. Substratum, resistant to thermal shock, is made of aluminium titanate – trialite [6].

When aluminium hydroxides are coated on cold metal substrates (plasma method), γ-Al_2O_3 with 10 % – 20 % α-Al_2O_3 admixture is obtained. When the substrate is heated (before coating) above γ- → α- transformation temperature, the sprayed coating is made only of α-Al_2O_3 [1].

When gas-flame spray with aluminium is carried out, the obtained coating is made of γ-phase, with small quantity of θ- and α-phases [7]. When a thin coating is sprayed in plasma method, it is made of θ- and δ-phases with small quantity of γ- and α-phases, and when a thick coating is sprayed (e.g. 0.25 mm), it is made of α- and γ-phases with very small quantity of δ and θ. When such coating is heated above 1250 °C, held for 2 hours and cooled slowly, it is made only of stable α-Al_2O_3 phase. The structure of this coating depends greatly on spraying conditions.

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The activated thermo-chemical condensate deposition method is based on these principles:

During coating, thermodynamic probability of chemical reaction is described by decrease of system free energy, and kinetics is described by energetic barrier, that is passed by atoms during transition from one stable state to the other (reaction activation energy) [7]. There are three main stages of the process: appearance of physical contact, activation of contact surfaces, and chemical reaction of materials in the separation area of phases (volume reaction), that is a limiting stage of coating. Substrate heating before coating increases greatly adhesion of a coating because there is a more rapid physical-chemical reaction between a coating and a substrate, and corresponding formation of residual stresses. According to Brunauer physical adsorption isotherms, a condensation process goes as follows: the amount of absorbed stream rises steadily in all cases when relative pressure is increasing, and it reaches a monostratum at a definite point. Polimolecular adsorption goes on afterwards, and a condensed phase appears.

Purpose of the work:

a) to find the influence of thermal processing of coatings, obtained in the activated thermo-chemical condensate deposition method, to the change of thickness and mass of a coating, to adhesion, phase structure, morphology, crystallite size, micro-stresses in a crystal lattice;

b) to investigate resistance of the system “coating--substrate” to thermal shock up to 50 cycles and resistance to alkalis and acids during the period of 300 hours.

2. EXPERIMENTAL TECHNIQUE

γ-Al_2O_3 type coating of 20 micrometers thickness was obtained in the activated thermo-chemical condensate deposition method on the steel X15Ю5 (Russian standard) plates 90 mm × 90 mm of 40 micrometers thickness, which temperature did not exceed 250 °C during coating formation. The surface for coating was immediately cleaned during technological process, the physical and chemical activation, as well as condensate deposition, were carried out, without separate formation of a substratum (Fig. 1).

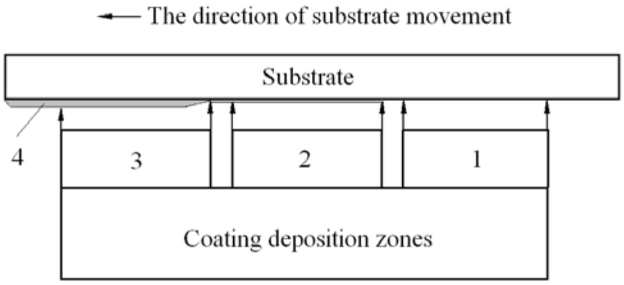


Fig. 1. The principal scheme of the activated thermo-chemical condensate deposition system: 1 – physical contacts zone, 2 – contact surfaces activation zone, 3 – volume reaction zone, 4 – coating

Coating formation system ensured a sufficient speed, yield, and pressure of thermal particle streams to the processed surface. The necessary thickness of a coating was grown up by repeating this cycle, only the first 2 stages of the process were used for activation of the previous stratum. This process can be carried out at atmospheric pressure but it is similar to vacuum coating deposition at discharge of electric arc when ion beams of noble gas are used additionally for cleaning substrate [8].

Afterwards, test pieces of the system “coating-substrate” passed thermal processing at six different temperatures: 100, 300, 500, 700, 900 and 1100 °C. Test pieces were exposed for two hours at the given temperature and cooled slowly with a furnace.

Coated test pieces passed the following research with the device:

1. Adhesion in the “scratch” method when the designed adhesion gauge was used [8].
2. Research of morphology and cross-section of surface when scanning electronic microscopy (SEM) with device JSM 5600 was used.
3. The percentage change of thickness and mass of a coating when thermal processing was carried out in the furnace SNOL 1.6.1-11, and coating thickness gauge (Minitest 600FN), as well as analytical balance VLR-200, were used
4. Phase identification of a coating was carried out with PDF-2 date base [9], when X-ray difractometer DRON-6 with Cu K_α radiation was used in the Braag – Brentano geometry.
5. Size and microstrain of crystallites in γ-Al_2O_3 coating when fundamental parameters approach X-fit program were used [10].
6. 50-cycle thermal shock tests of the system “coating-substrate” (heating up to 1000 °C and sudden cooling in distilled water of 20 °C) when the furnace SNOL 1.6.1-11, a bath of 1 m^3 volume, and a special manipulator for transfer of a test piece unit were used. The test pieces, thermally processed at all six temperatures, were tested at the same time.
7. Resistance tests for long-term 300 hours chemical effect in solutions of alkali NaOH and 60 % acids H_2SO_4, H_3PO_4, HNO_3, HCl, and 20 % acid mixture HCl and HNO_3 (relation 3 : 1), carried out with standard chemical equipment and technically clean reagents.

3. RESULTS AND DISCUSIONS

Measurements of adhesion showed that rather strong bond between a coating and a substrate increases constantly up to 500 °C, remains stable up to 700 °C, and then, rapidly increasing, reaches 58 N value at 1100 °C (Fig. 2).

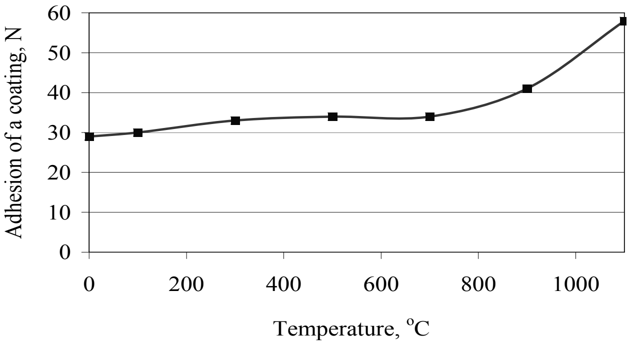
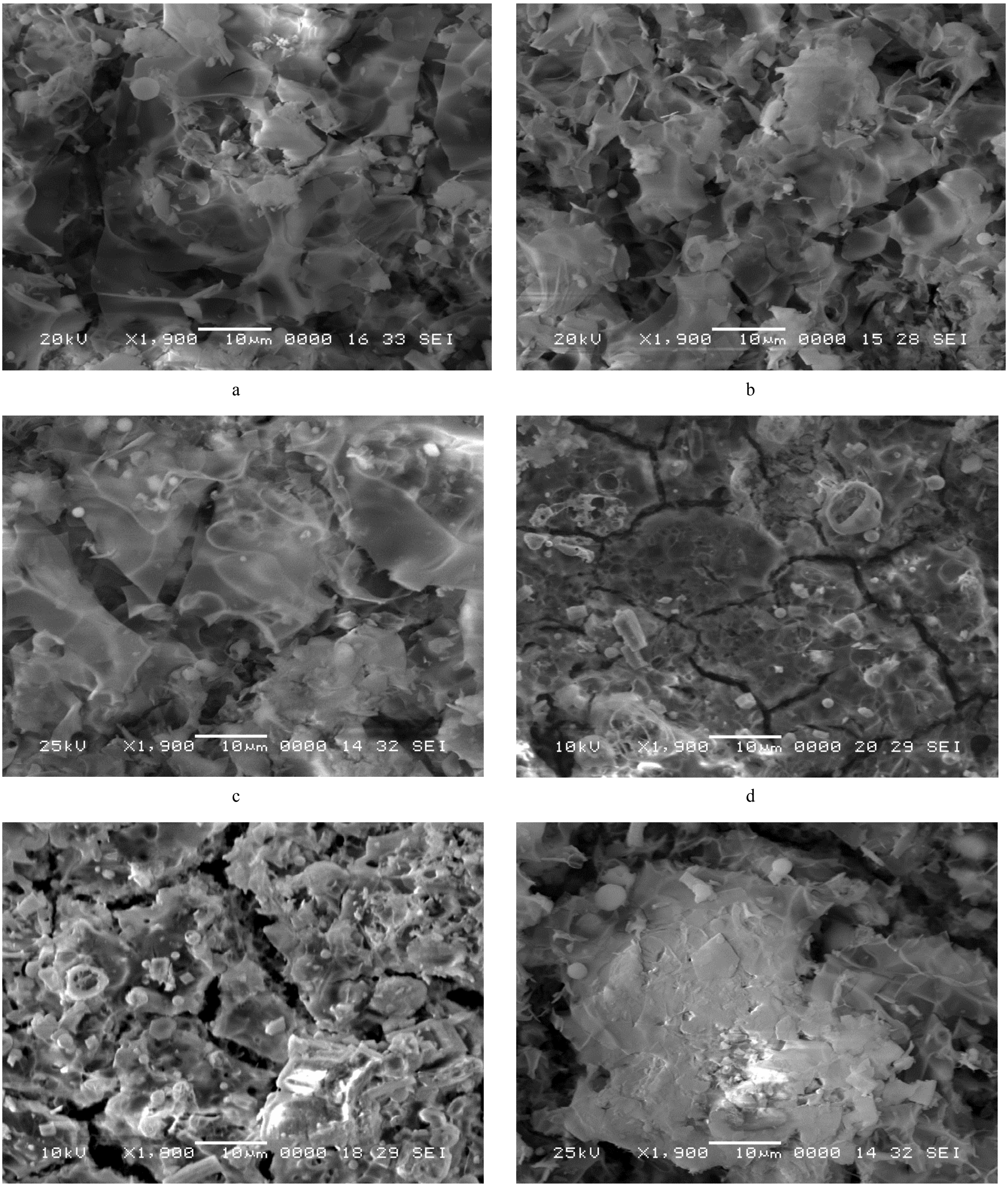


Fig. 2. Adhesion of a coating

For a comparison the aluminium coating of the same thickness obtained in thermal spray method (e.g. high velocity oxygen fuel – HVOF method) has 20 % – 30 % smaller adhesion.

Morphological research shows that a coating is not monolithic at different temperatures of thermal processing, and it has typical surfaces cracks, not reaching the separation surface “coating-substrate” (Fig. 3). The more distinct changes of surface appear at 900 °C (Fig. 3, e) and at 1100 °C (Fig. 3, f), when some areas of surface become denser, making new combinations. Diagonal cross-section of the system “coating-substrate” shows a narrow, especially small-grained interface – separation line (Fig. 4).



a b

c d

e f

Fig. 3. Morphology of a coating after heat treatment: a – 100 °C, b – 300 °C, c – 500 °C, d – 700 °C, e – 900 °C, f – 1100 °C

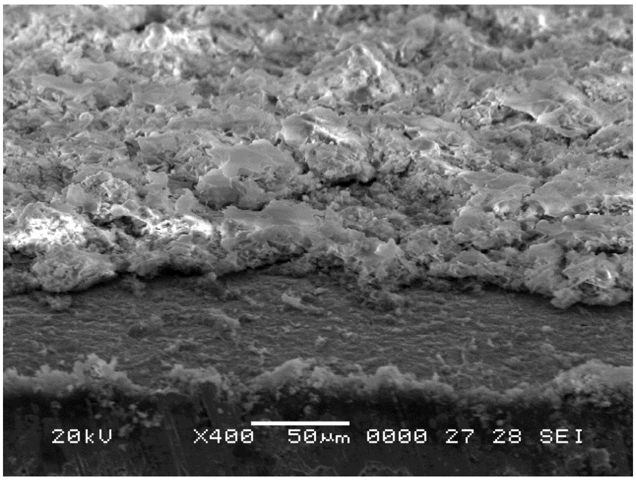


Fig. 4. Diagonal cross – section of the system “coating-substrate” after heat treatment – 500 °C

X-ray diffraction qualitative phase analysis method shows that a coating is made only of nanocrystalline γ-Al_2O_3 phase after coating and thermal processing up to 800 °C (Fig. 5). Above 800 °C, γ-Al_2O_3 phase begins to decrease, θ-Al_2O_3 phase appears (that remains up to 1000 °C), as well as α-Al_2O_3 phase, which crystallization degree increases, especially at 1200 °C. Besides, when temperature goes up to 1000 °C, rather distinct diffraction peaks of a substrate disappear at all.

Thickness of γ-Al_2O_3 coating, during thermal processing, increases constantly up to 500 °C, falls at 700 °C, and remains stable until above 900 °C, then decreases remarkably. Thickness change of a coating reaches 24 % at the temperature range of 500 °C – 1100 °C (Fig. 6).

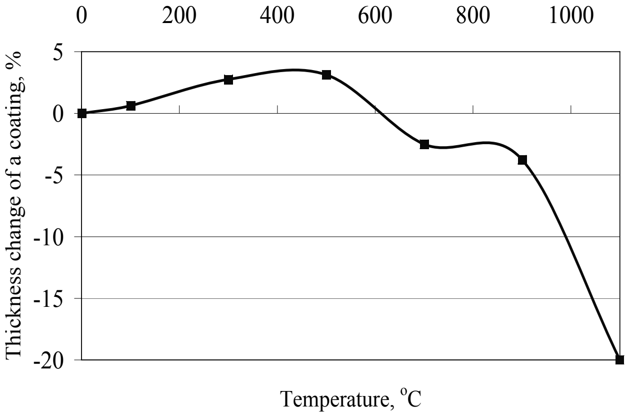


Fig. 6. Thickness change of a coating

Mass loss of a coating takes place a little bit more intensely up to 300 °C, but then decreases and reaches 14 % at 1100 °C (Fig. 7).

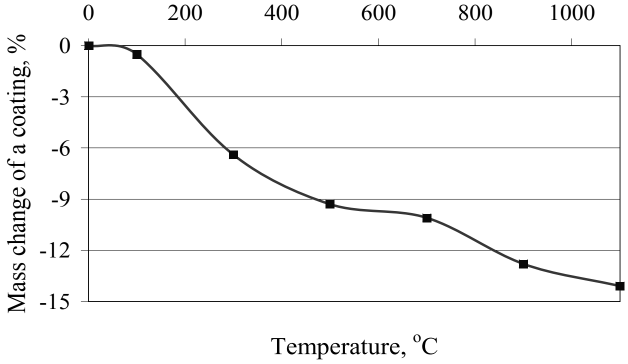


Fig. 7. Mass change of a coating

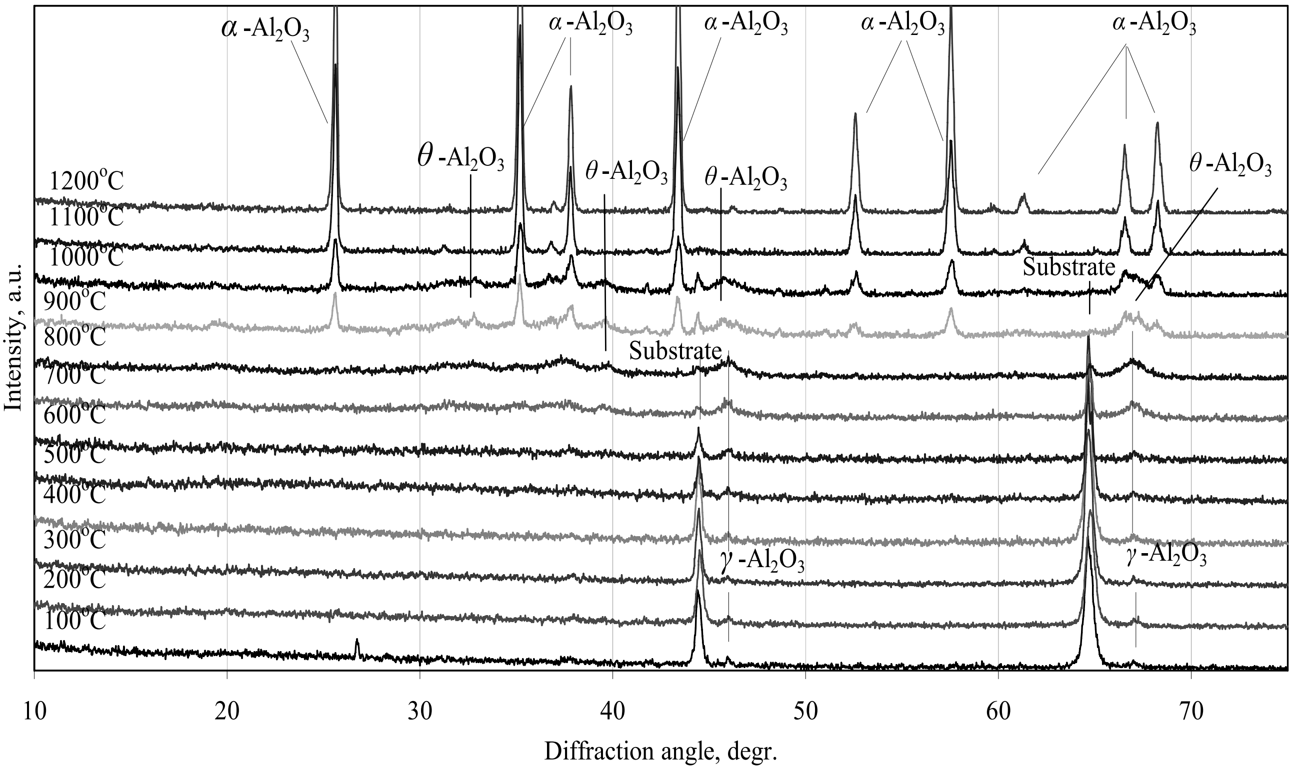


Fig. 5. X-ray diffraction patterns of a system “coating-substrate”

Crystallite size of γ-Al_2O_3 coating according to $2\theta \approx 67°$ angle of X-ray (Fig. 8) curves is the biggest during thermal processing of 100 °C and makes 191 nm, and it is the smallest at 800 °C and makes 10 nm (Fig. 7). Crystallite size was between 10 nm – 27 nm at the temperature range of 200 °C – 900 °C.

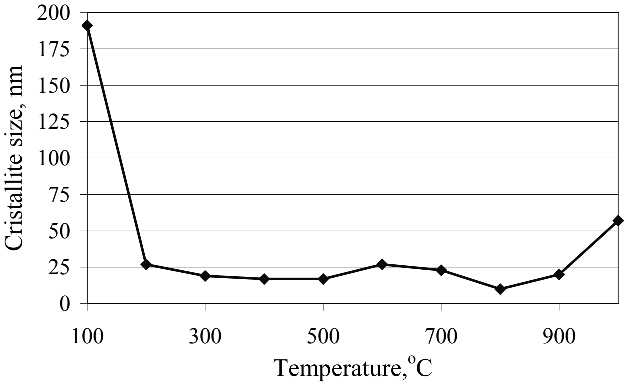


Fig. 8. Crystallite size distribution of γ-Al_2O_3 coating

Microstrain in γ-Al_2O_3 coating are the highest at 900 °C and make 0.75 % (Fig. 9). Microstrain in γ-Al_2O_3 crystal lattice do not exceed 0.005 % at the temperature range of 200 °C – 800 °C. The obtained nanostructural γ-Al_2O_3 coating is structurally stable at a wide temperature range.

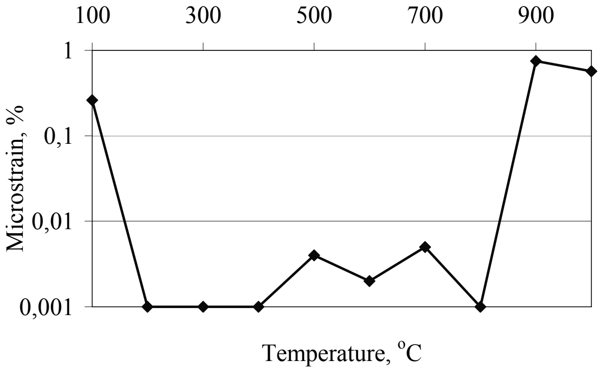


Fig. 9. Distribution of microstrain in crystal lattice of γ-Al_2O_3 coating

50-cycle thermal shock tests of the system "coating-substrate" (heating up to 1000 °C and sudden cooling in distilled water of 20 °C) were carried out under the condition the test pieces were dried at 200 °C for 2 hours after each test series (Fig. 10). Mass loss of the system "coating-substrate" after one and after three cycles of thermal shock is not perceived. After 5 cycles, in the worst case, it reaches 0.19 %, after 10 cycles – 0.78 %, after 20 cycles – 2.84 %, after 30 cycles – 3.68 %, and it goes up to 16.7 % after 50 cycles for a coating with thermal processing at 300 °C. Besides, no cases were perceived that the coating separated from the substrate.

Resistance of the system "coating-substrate" to thermal shock after 50 cycles with thermal processing at 900 °C and 1100 °C is equal to mass loss of a coating – 4.6 % and 4.4 % respectively.

For a comparison aluminium coatings of the same thickness obtained in thermal spray method (e.g. HVOF method) and oxidized thermally in the same way, have 33 % – 83 % coating mass loss after 5 cycles, 47 % – 98 % mass loss after 10 cycles, 47 % – 98 % mass loss after 20 cycles, 63 % – 100 % mass loss after 30 cycles, 99 % – 100 % mass loss after 50 cycles.

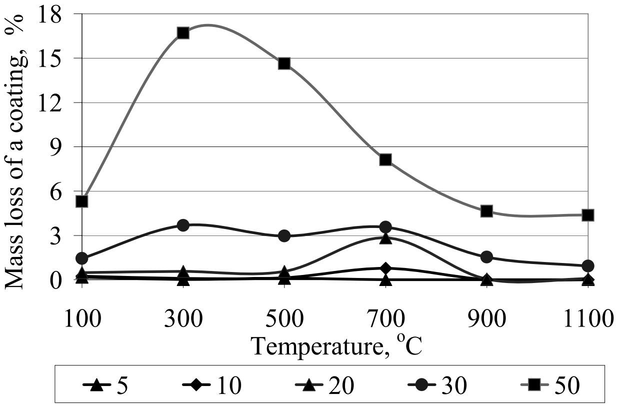


Fig. 10. Resistance of the system "coating-substrate" to thermal shock

1 M and 5 M NaOH had no effect on the system "coating-substrate" during the period of 300 hours, while the aluminium coating of the same thickness, obtained in thermal spray method (e.g. HVOF method) and oxidized thermally in the same way at 1100 °C, kept for 20 – 30 minutes in the best case.

20 % solution of acids HCl and HNO_3 (relation 3 : 1) had influence first of all (after 20 – 22 hours) on the test pieces, thermally processed up to 500 °C. This time reached 35 hours at 700 °C, and the system "coating-substrate" disintegrated completely at 900 °C after 63 hours. Remarkable resistance of the system "coating-substrate" to this solution appeared for the test pieces, thermal processed at 1100 °C, and it reached 220 hours (Fig. 11).

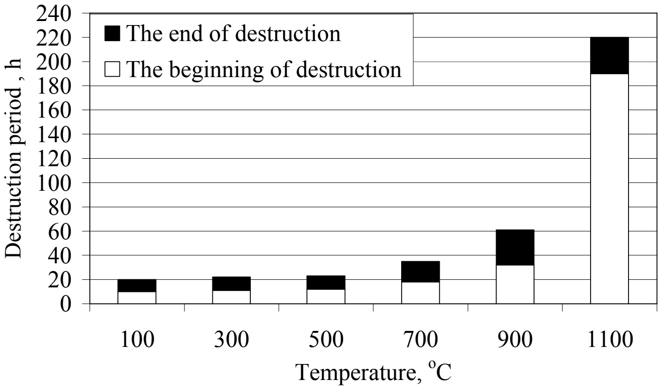


Fig. 11. Resistance of the system "coating-substrate" to 20 % acids HCl and HNO_3 (relation 3:1)

60 % acids HCl, H_2SO_4, HNO_3 and H_3PO_4, destroyed the system "coating-substrate" completely after 260, 268, 282, and 297 hours, correspondingly (Fig. 12). Weight of test pieces began to change remarkably at the time when the substrate began to disintegrate, and it caused the complete disintegration of the system "coating-substrate".

An especially strong chemical connection is assured in the system "coating-substrate". No cases were perceived that the coating separated from the substrate in bigger patches, the solution had only sediment.

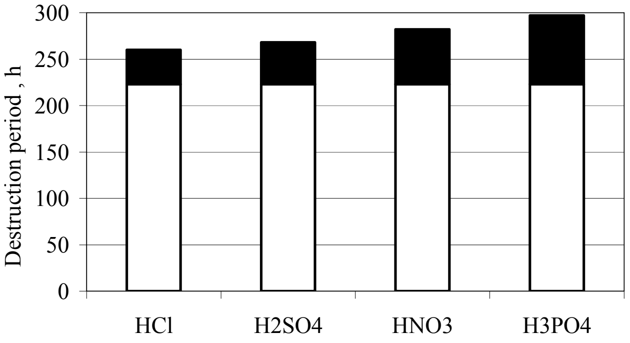


Fig. 12. Resistance of the system "coating-substrate" to 60 % acids HCl, H_2SO_4, HNO_3, H_3PO_4

For a comparison aluminium coatings of the same thickness, obtained in thermal spray method (e.g. HVOF method) and oxidized thermally in the same way at 1100 °C, kept in the above mentioned acids from 1 to 6 minutes.

CONCLUSIONS

1. System Al-O coating, obtained in the activated thermo-chemical condensate deposition method when substrate temperature during coating formation did not exceed 250 °C, is made only of γ-Al_2O_3 nanocrystalline phase, that does not change during thermal processing of test pieces until 800 °C temperature.
2. When thermal processing temperature rises from 100 °C up to 1100 °C, cracking of coating surface and material density increase, adhesion of a coating increases up to 58 N, thickness of a coating decreases down to 24 %, and mass of a coating decreases down to 14 %.
3. Inertness of the system "coating-substrate" to chemical effect it did not react to 1 M and 5 M sodium alkali during the period of 300 hours, and the system began to react to 60 % acids: HCl, H_2SO_4, HNO_3 and H_3PO_4, not earlier than after 230 hours.
4. The system "coating-substrate" of this type is worth using in the especially aggressive high-temperature chemical environment, under thermal cycling conditions.
5. The system "coating-substrate" is chemically rather passive. When coatings are formed, elementary substrates are worth trying and using, e.g. simple low-carbon steels.
6. The activated thermo-chemical condensate deposition method allows forming of binomial, trinomial or multinomial oxide systems practically of any single elements or their combinations and coatings type "sandwich" by chemical elements composition. Porosity of coatings can be controlled.

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