The influence of the Al deposition by MOC-CVD method on stainless steel thermal conductivity depending on the substrate roughness

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This paper studies the influence deposition of aluminum pellicular layers partially compact, by MOC-CVD method on stainless steel, in order to improve the nitriding capacity of these materials. The study was done for alloys used in aerospace construction (motion elements), which must withstand large temperature variations (must have a low expansion coefficient), able to withstand the corrosion and wear. Deposition was performed on samples of base material with different roughness, resulting different Al layer thickness, therefore different conductivities. Depending on the material conductivity they behave differently to thermochemical plasma treatment, meaning ion nitriding.

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1. Introduction

Thin layers are of great importance, leading to materials performance increase for technological, functionally and economically purposes, always present and of great interest to manufacturing. Surface properties modification by deposition methods imposes itself as a smart solution to separate basic material properties, which is the substrate, most of the volume, with those of the deposited material, required for a given application. The material is chosen according to its mechanical, structural and thermal or possibly the electric properties without forgetting the economic criteria. Due to the wide variety of procedures for the protection of surfaces by diffusion and deposits treatments, which allows new properties compounds obtaining, the nature of the material can be completely different from that of the surface. It is possible to obtain optimum properties of the surface, which directly address the requirements arising from the manner and conditions of use (wear) for the treated component, [2-8].

The paper addresses the topic for obtaining aluminum depositions on austenitic stainless steels. The alloy has good corrosion resistance, but has a high wear resistance and therefore it is necessary to apply an ion nitriding operation to remedy this disadvantage. Since the diffusion of nitrogen in the chosen material is difficult to be obtained and cannot achieve a required quality service layer (hardness and depth of penetration), chemical vapor deposition method (CVD) was used for aluminum deposition at low temperatures, using the fluidized bed combustion technique (C-CVD), with the precursor an metalorganic product (MOC-CVD), [12-15]. Under this form of deposition (noncompact deposition) aluminum acts as a catalyst to increase the nitrogen diffusion on the part section in ion nitriding process. Deposition was performed on samples of base material with different roughness, resulting different Al layer thickness, therefore different conductivities. Depending on the material conductivity, they behave differently to thermochemical plasma treatment, meaning ion nitriding, [9-11].

2. Materials and deposition method

The substrate on which deposition occurs must meet the condition that its structure do not change irreversibly at deposition temperature and possess sufficient corrosion resistance to the gases used in the process.

The base material is an austenitic stainless steel, X5CrNi18-10, DIN 1.4301, whose chemical composition is shown in Table 1. This composition was determined using the spectrometer Foundry Master.

Table 1. Chemical composition of X5CrNi18-10 stainless steel, [%]

Chem. Elem.	Fe	C	Si	Mn	Cr	Ni	S	P
%	Bal.	0,12	0,71	0,42	16	9,41	0,02	0,04

The stainless steels Cr-Ni corrosion resistance depends mostly on the presence of chromium carbides in structure, whether there is an austenite with a high degree of homogeneity.

The adhesion of the layer to the substrate and microhardness, are two of the most important characteristics that determine efficiency of coating.

The deposition element is aluminum, which intends to facilitate the diffusion of nitrogen in the layer, to increase

the thickness of the ion nitrided layer, its hardness and thus the characteristic wear resistance.

For the experimental deposition of the thin metal layers was adopted chemical deposition from vapor estate method, using aluminum by the organometallic precursor combustion - triizobuthylaluminum (TIBA). The carrier gas must not interact chemically with the precursor. Technical nitrogen was used at a working pressure of 1.2 bar, which is sufficient to operate the fluidized bed, [1].

For the experiment was used an apparatus that can fluidize by blowing gases (air, reagents + carrier gas, sand so on) into an neutral powder environment (granular aluminum oxide). The heating fluid bed chamber (CVD reactor) is constructed of a quartz tube with a diameter of 30 mm and length 300 mm.

The electrical resistance is arranged circumferentially, outside of the enclosure, and is made of 1 mm diameter kantal. The thermal insulation material is made of oxides (aluminum oxide in the form of fibers and glass wool). Outside a tube of quartz with a diameter of 75 mm protects the oven.

3. Results and discussions

Before the chemical deposition of aluminum, the samples were polished on sandpaper with grain sizes from 400 up to 4000.

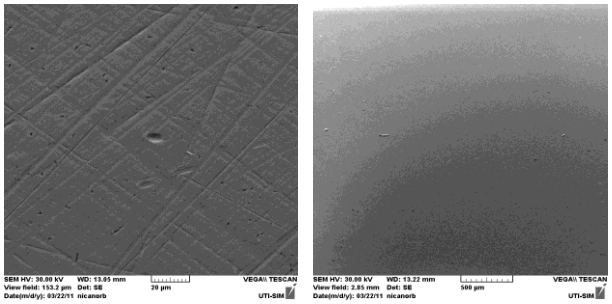
- Samples type P. 1 – polished up to 4000 grain size (mirror)
- Samples type P. 2 – polished up to 2000 grain size
- Samples type P. 3 – polished up to 400 grain size
- Samples type P. 4 – chemical engraved samples: 34%H_2SO_4+12% HCl+water.
- Samples type P. 5 – chemical engraved samples: 20% NaOH.
- Samples type P. 6 – deposited control sample

Making differentiated sanding aimed at highlighting the degree of roughness influence on the level of deposition of aluminum. This was achieved by using in the final stage both the metallographic papers, with different grain size and chemical etching in NaOH solution.

Different degrees of roughness was revealed using SEM photographs. Absorption of aluminum to the surface was revealed by EDX sample analysis. For each sample were also performed 3D images for viewing the surface roughness used for the deposition of MOC-CVD method with reactions in fluidized bed.

3.1. SEM micrographs for P.1 sample

In the case of samples type P. 1 which was polished up to mirror gloss, 4000 grain size.



a) b)

Fig.1. SEM micrographs for P.1: a) 500 μm; b) 20 μm.

Can be observed that aluminum was deposited 0,478% on the surface, a small amount due to a decreased roughness for the surface which does not favors the combustion CVD method. The reaction during the process creates the prerequisites for physico-chemical depositions on the surface in majority around the burrs of the surface.

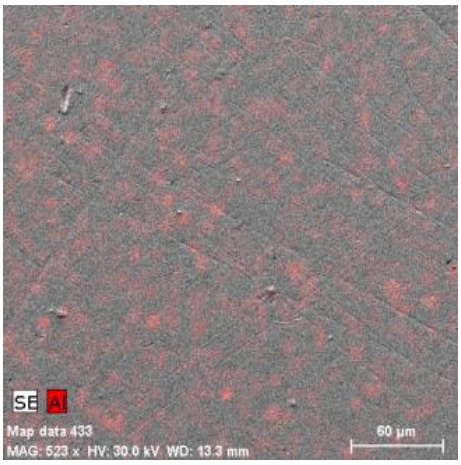


Fig. 2. The EDX analysis for highlighting the Al distribution on the P.1sample surface.

This is emphasized by the photos of EDX analysis (Figure 2) where is observed aluminum deposition areas on micro depressions left from paper sanding.

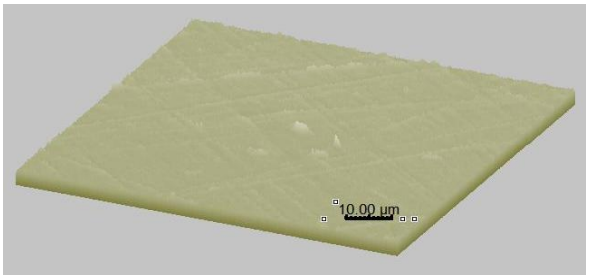
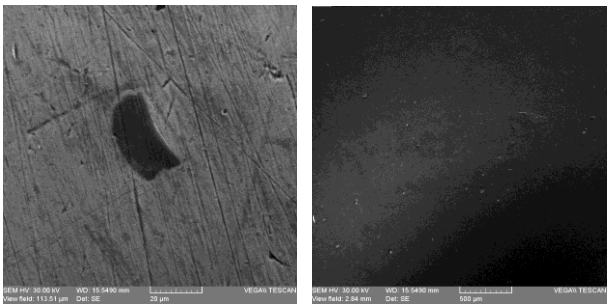


Fig. 3. P.1 sample - 3D image after Al deposition with fluidized bed technology MOC-CVD: 10 micrometers landscape-scale.

3.2. SEM micrgraphs for P. 2 sample

This sample has a good degree of polishing (2000 sanpaper grain size).



a) b)

Fig.4. SEM micrographs for P.2: a) 500 µm; b) 20 µm.

The sample was subjected to TIBA deposition for 10 minutes at 320°C and during that time the CVD reaction occurs – combustion in quartz sand fluidized bed, gas bubbled with precursor. After deposition, an disrupted Al layer is formed on the sample, whose thicknesses was influenced by the temperature and the reaction time.

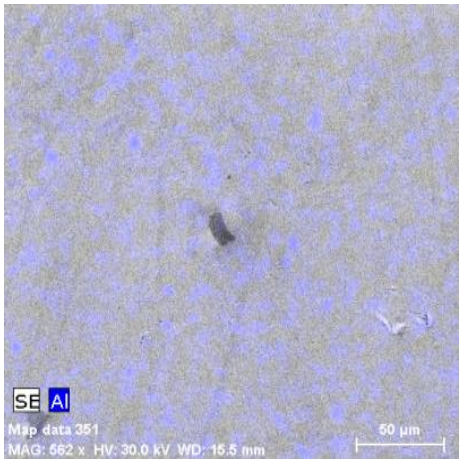


Fig. 5. The EDX analysis for highlighting the Al distribution on the P.2 sample surface.

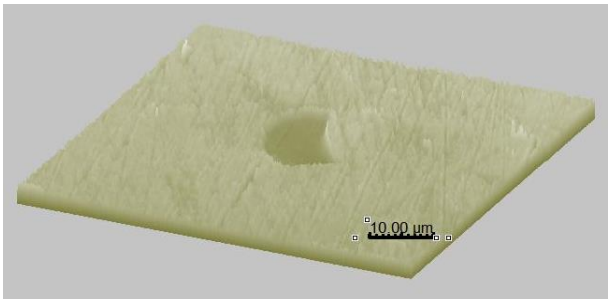
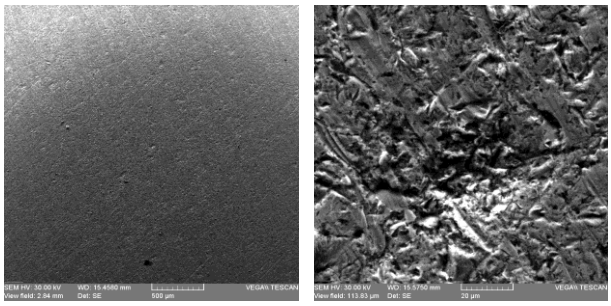


Fig. 6. P.2 sample - 3D image after Al deposition with fluidized bed technology MOC-CVD: 10 micrometers landscape-scale.

3.3. SEM micrographs for sample P.3

The sample type P. 3 was polished up to 400 grain size and then subjected to a MOC-CVD deposition method using as deposition agent the triisobuthylaluminum, and thed it was analysed on the SEM microscope.



a) b)

Fig.7. SEM micrographs for P.3: a) 500 µm; b) 20 µm.

After SEM analysis, from Fig. 7 can be observed that deposited Al is increased, compared to the previous two ones, due to the higher roughness of the sample.

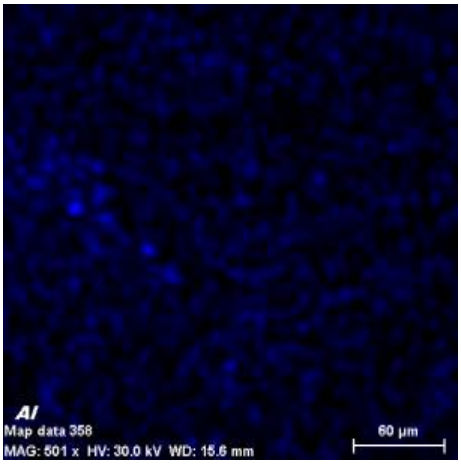


Fig. 8. The EDX analysis for highlighting the Al distribution on the P.3 sample surface.

The chemical reaction from the surface are focused on the scratches, dents, bumps and bobbles that represents a concentrators effect for physico-chemical deposition of aluminum. Aluminum deposition occurs mainly on the workpiece surface irregularities and less on smooth areas.

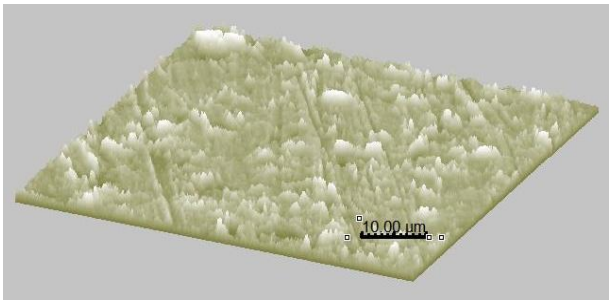
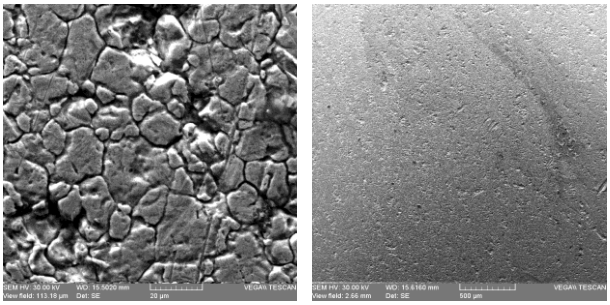


Fig. 9. P.3 sample - 3D image after Al deposition with fluidized bed technology MOC-CVD: 10 micrometers landscape-scale.

3.4. SEM micrographs for P.4 sample

The sample type P. 4 was chemical engraved in a mixture of acids 34%H_2SO_4+12% HCl+water for 30 minutes at 65°C.



a) b)

Fig.10. SEM micrographs for P.4: a) 500 µm; b) 20 µm.

SEM microscopic analysis shows that chemical attack reveals granular formations of steel by grains edges corrosion. This fact influences aluminum particle deposition on the sample surface, deposition reactions taking place on a larger area.

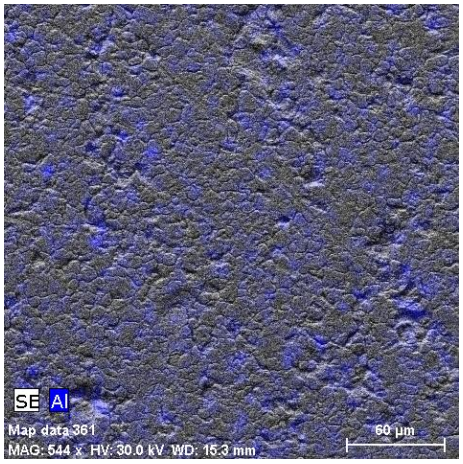


Fig. 11. The EDX analysis for highlighting the Al distribution on the P.4 sample surface

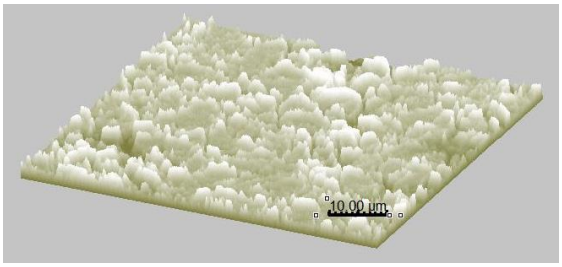
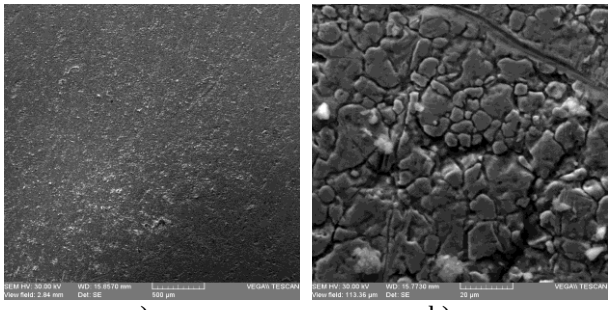


Fig. 12. P.4 sample - 3D image after Al deposition with fluidized bed technology MOC-CVD: 10 micrometers landscape-scale.

Can be observed that Al deposition takes place in the areas were the Fe and Cr quantity on the surface is decreased but not the C. The EDX analysis shows a 1,434% Al concentration on the surface.

3.5. SEM micrographs for the P. 5 sample

The samples type P. 5 was subject to Al deposition using the MOC-CVD method in fluidized bed after the chemical engraving with a solution 20% NaOH.



a) b)

Fig.13. SEM micrographs for P.5: a) 500 µm; b) 20 µm.

It is noted that, in contrast to the other samples due to the chemical attack on the surface, it shows the type of grain by etching boundaries between grains. Studying EDX analysis to the surface there is a relatively uniform distribution of aluminum on the surface, at the rate of 1.363%.

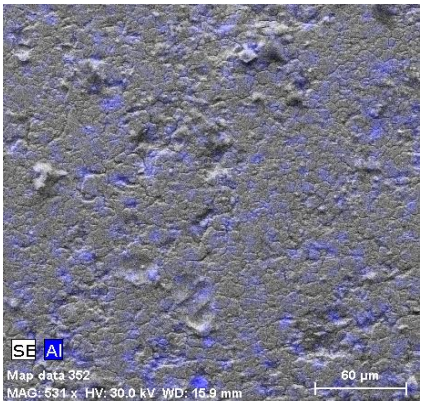
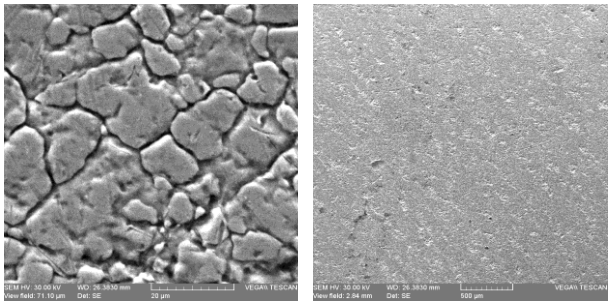


Fig. 14. The EDX analysis for highlighting the Al distribution on the P.5 sample surface.

Fig. 15. P.5 sample - 3D image after Al deposition with fluidized bed technology MOC-CVD: 10 micrometers landscape-scale.

3.6. SEM micrographs for P.6 sample

P.6 sample was not prepared mechanically to the surface. From EDX analysis can be identified areas with major Al deposition on sample surface, with higher Al concentration on the dimples (highlighted grain edges). Film deposition are achieved but with discontinuities occurring in the roughness peaks areas.



a) b)

Fig.16. SEM micrographs for P.6: a) 500 µm; b) 20 µm.

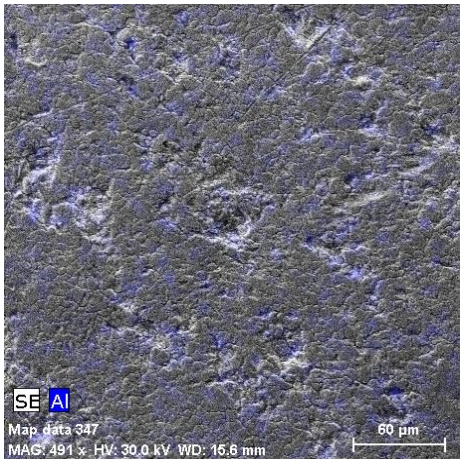


Fig. 17. The EDX analysis for highlighting the Al distribution on the P.6 sample surface.

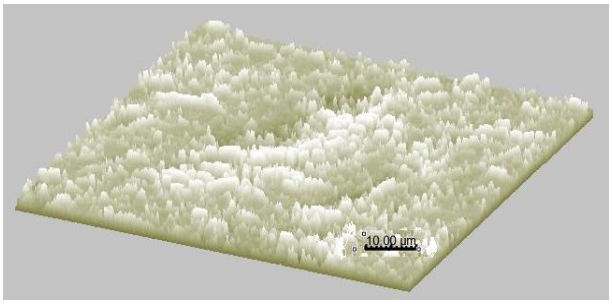


Fig. 18. P.6 sample - 3D image after Al deposition with fluidized bed technology MOC-CVD: 10 micrometers landscape-scale.

3.7. Roughness measurements

Roughness measurements for samples were made using the apparatus Perthometens M1. With this apparatus, for each sample on a specific distance (standard for this machine) 5.6mm, were determined the following parameters: R_z (the vertical distance from the highest peak to the lowest valley), R_a (arithmetic average of the roughness profile) şi R_{max} (the highest peak).

The measurements are registered in the table 2, and the general graph for the aluminum deposition depending on the roughness value is presented in fig. 19. In this table is presented also the deposition rate in percent on the samples surfaces.

Table 2. Sample roughness

Crt. No.	Sample	**R**a [µm]	**R**z [µm]	**R**max [µm]	% Al deposited
1	P.1	0,038	0,450	0,620	0,478
2	P.2	0,036	0,320	0,460	0,503
3	P.3	0,389	4,640	5,370	3,024
4	P.4	0,216	1,880	2,660	1,434
5	P.5	0,069	0,930	1,780	1,363
6	P.6	0,449	4,130	5,670	1,300

It is observed that along with roughness increasing also increases and the percentage of Al deposited by CVD combustion.

Due deposition conditions, more difficult on roughness peaks and easier in the recesses, and the existence of an erosion process generated by the fluidizing medium that virtually blasted the surface, roughness deposited layer cannot be a yardstick of the working procedures.

We conclude that the coating has a high degree of compactness and no constant thickness, being made a substantial deposition in the recesses and a lower deposition to the peaks.

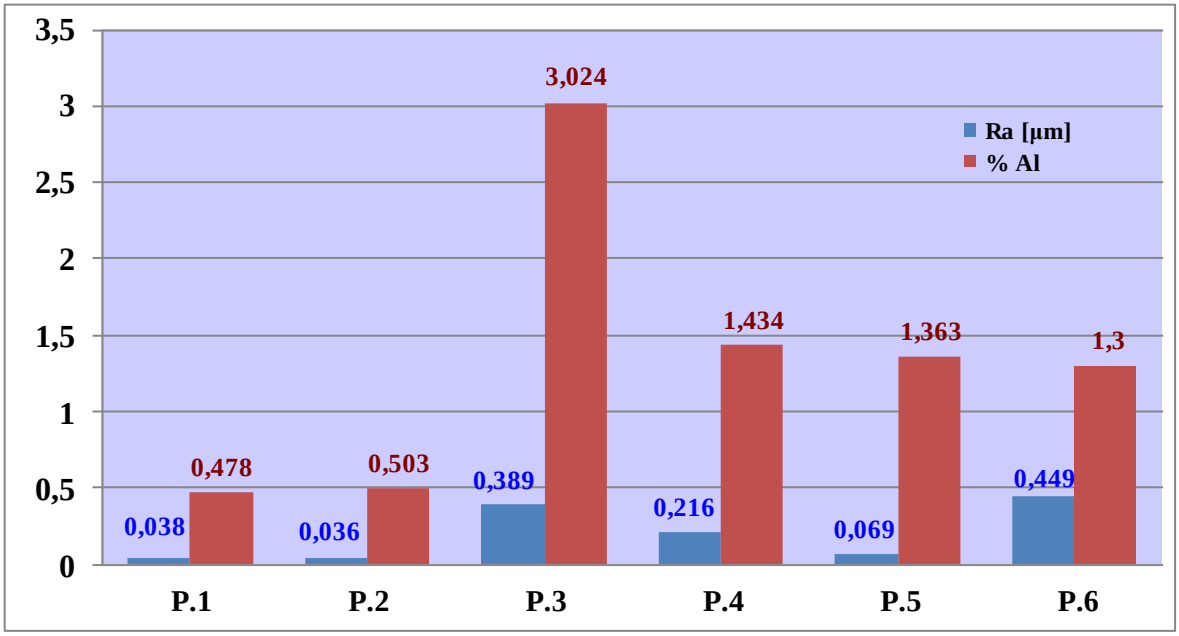


Fig. 19. Roughness influence over aluminum deposition by MOC-CVD method.

4. Conclusions

Deposition of aluminum on austenitic stainless steel substrate requires CVD - combustion working method, if it wanted that physical, mechanical and chemical properties of the substrate are not adversely affected.

For the experimental deposition of the thin metal layers was adopted the organometallic precursor combustion - triizobuthylaluminum (TIBA). The choice was made for economic reasons.

Austenitic stainless steel samples (with small dimensions) were mechanically prepared on the deposition surface in order to study the effect of roughness of the surface layer on the mechanism, kinetics and dimensional characteristics of the depositions.

Quality surface roughness expressed qualitatively and quantitatively influences the Al deposition. Thus, areas which provide a roughness comparable to the one obtained by grinding roughing, finishing turning ensure consistent deposition of aluminum.

From 3D figures we see that large roughnesses corresponding to low surface qualities are beneficial to intake of Al embedded on the surface of the workpiece as drops anchored by microalloying mainly, in areas of roughness depth and less on peaks.

In general, the aluminum layer deposited by MOC-CVD on the austenitic stainless steel support is very thin, discontinuous, leading to accumulation of aluminum in the cavities of the surface. It can be classified as an island growth layer deposition, model Volmer – Weber, [16]. At the level of such deposited layers, deposited atoms (in this case aluminum) are better linked between them or with other atoms, which are not substrate atoms.

The structure and morphology of the aluminum layer deposited on austenitic stainless steel support enable thermochemical treatment of ion nitriding which would aim to improve surface hardness in the active system and to maintain the chemical stability.

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