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Aluminum Coating Influence on Nitride Layer Performance Deposited by MO-CVD in Fluidized Bed on Austenitic Stainless Steel Substrate

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Abstract. The modification of surface properties by duplex treatments, involving the overlapping of two surface treatment techniques, has been established as an intelligent solution to create new applications for the substrate metallic material. There are driveline components operating under very tough wear and corrosion conditions, with high temperature and humidity variations. Such components are usually made of high Cr and Ni stainless steel and for the hardening of surfaces it is recommended a thermo chemical treatment. Since stainless steels, especially austenitic stainless steels, are difficult to nitride, experimental studies focus on increasing the depth of the nitride layer and surface hardness. Achieving the goal involves changing active layer chemical composition by introducing aluminum in the surface layer. In order to find a solution, a new surface treatment technique is produced by combining aluminum thin films by MO-CVD in a fluidized bed using a triisobutylaluminum precursor with a thermo chemical nitriding treatment.

1. Introduction

The surfaces of components used in some equipments construction must withstand stresses where the combination of multiple properties, such as over-wearing resistance, over bearing capacity, fatigue and corrosion, is absolutely necessary. Unfortunately, such properties cannot always be possessed by the base metal used.

The surface properties modification by thermo-chemical/deposition treatments has been established as an intelligent solution to create new applications for the substrate metallic material. Surface properties that directly meet the requirements of the mode and conditions of use for treated component can be obtained.

Experimental studies focus on increasing the depth of the nitride layer and surface hardness for nitride austenitic stainless steels by duplex heat treatments [1-4]. Duplex treatments involve overlapping of two surface treatment processes on the same base material to obtain superior mechanical properties compared to the mechanical properties of the substrate.

Achieving the objective involves changing surface chemical composition by introducing in active layer aluminum (Al), an residual element in the stainless steel, knowing the fact that aluminium favor the formation of a hardly nitride surface layer. To find solutions, we approach a new surface treatment technique by combining thin aluminum layer deposition by MO-CVD in a fluidized bed using a triisobutylaluminum (TIBA) precursor with thermo-chemical nitriding treatment [5-7].



2. Experimental

2.1. Materials

Choosing material for experiment (raw material, deposition element – aluminum, gas precursor – triisobutylaluminum) and procedures.

2.1.1. Raw material. For this experiment stainless steel X5CrNi18-10, W1.4301, was used, which chemical composition is shown in Table 1. The composition was determined by means of a Foundry Master spectrometer. The samples were cut with laser beam at 12 mm x 10 mm with a thickness of 2 mm.

Table 1. Chemical composition of X5CrNi18-10, W 1.4301 steel.

Element	C	Si	Mn	Cr	Ni	S	P	Fe
Percent	0.12	0.71	0.42	16	9.41	0.026	0.042	Balance

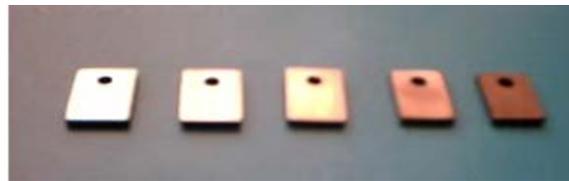


Figure 1. Samples used for experiment.

2.1.2. Aluminum deposition by MO-CVD- precursor. In order to obtain aluminum deposits on austenitic stainless steel supports, a triisobutylaluminum precursor has been used, TIBA is a metalorganic chemical agent with the molecular formula $[(CH_3)CHCH_2]_3Al$ having molecular weight 198.32, boiling point $86^\circ C$, melting point at $4 - 6^\circ C$ and a density of 0.786 g/l at $25^\circ C$. The precursor will be heated to the vaporization temperature ($86^\circ C$) and the vapor-carrier gas (nitrogen) mixture is introduced into the fluidized bed heating system where the steel samples are positioned [8]. During contact with the fluidized bed particles at temperatures between $250-500^\circ C$, the triisobutylaluminum molecules dissociate, resulting in active $Al +$, which will be deposited on the surface of the metallic samples immersed in the fluidized bed. The thermal decomposition of TIBA can be represented by the reaction from Figure 2 [9]:

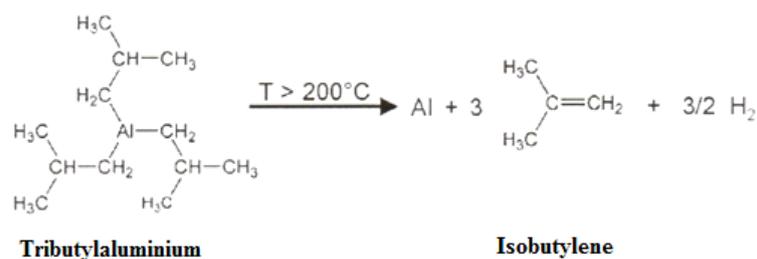


Figure 2. The decomposition reaction for Tributylaluminium.

2.2. Aluminum deposition by MO-CVD with fluidized bed heating

2.2.1. Experimental procedure. The technological solution we are focus is CVD process based on metalorganic compounds, MO-CVD (Metalorganic CVD), in this way the reaction temperature can be greatly reduced. Thereby aluminum (Al) layers can be obtained at temperatures just below $400^\circ C$ [10].

The use of the fluidized bed deposition method has a many advantages especially temperature uniformity and very efficient heat transfer. However, the feed rate of the precursor is limited by the saturation capacity of carrier gas with precursor vapor and in the same time by the relative volatility of precursor which, until reaching the reaction zone, must be maintained below reaction or decomposition temperature [11-15].

2.2.2. Deposition installation. An experimental MO-CVD deposition installation with fluidized bed heating was used to perform the experiment. The fluidization chamber is made of a quartz tube with a diameter of 30 mm and a length of 300 mm and exterior heating resistance. The external protection is made by another quartz tube with a diameter of 75 mm and a length of 400 mm (see Figure 3).

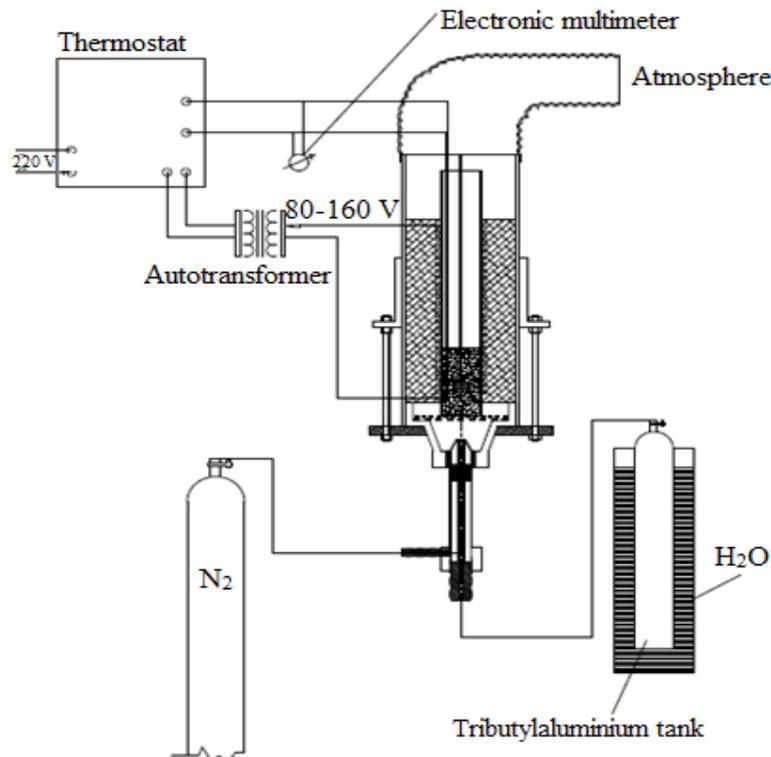


Figure 3. Schematic presentation of MO-CVD in fluidized bed deposition installation.

The feeding of TIBA was made directly from a special cylinder which was introduced into a temperature control tank heated up to 86°C. The carrier gas (nitrogen) pressure was 1.2 bar, sufficient to ensure the fluidized bed operation, the flow was measured by means of a rotameter. Vapor-gas mixture is introduced after the reactor reaches the constant temperature regime. The reactor temperature was maintained at 320°C for 35 minutes during the experiment.

2.3. Sample analyzes after aluminum deposition

The samples were analyzed by microstructure point of view by means of a scanning electron microscope (SEM and EDX) after deposition (2D and 3D). Rugosity influence on MO-CVD deposition was also presented in this study.

2.4. Analyses of nitride stainless steel with aluminum deposition by MO-CVD

- SEM Microstructural analysis of nitride samples; XPS analysis of nitride samples; Microhardness analysis.

3. Experimental results

3.1. Aluminium deposition by MO-CVD on stainless steel support

Stainless steel samples were heated in fluidized bed installation from boundary temperature to 320°C. The maintaining time was 35 minutes. Since the surface absorption of aluminum on the samples during MO-CVD operation is very important, the roughness parameter influence to deposition (absorption) degree has also been observed. In case of a ragged sample, the surface irregularities will

favor the deposition of aluminum (increasing the active surface). For this reason the samples were prepared in terms of different average surface roughness.

3.1.1. Control sample analysis. The control sample was analyzed by EDX by means of a scanning electron microscope. The presence of aluminum is not highlighted.

Table 2. Chemical composition of control sample - percentage by weight.

Element	% C	% Cr	% Ni	% O ₂	% Fe
Percent	0.14	16.93	8.14	0.84	balance

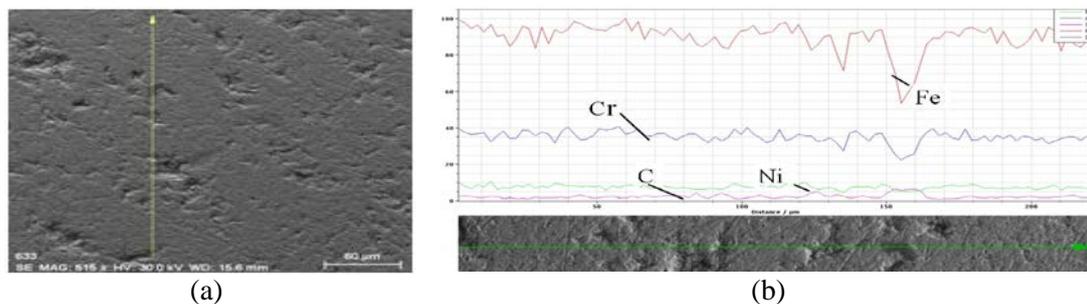


Figure 4. Line analysis for the control sample to highlight the distribution of surface chemical elements (a) Marking of the EDX analyzed area; (b) Line analysis with percentages of Fe, C, Cr and Ni.

3.1.2. Sample $R_z = 0.6 \mu\text{m}$. For sample $R_z = 0.6 \mu\text{m}$ Al was deposited in 0.478 % on the surface, small percentage due to low surface roughness which does not favor MO-CVD deposition.

Table 3. Chemical composition of sample 1 superficial layer.

Element	C	Cr	Ni	Si	Al	Fe
percent	0.12	18.44	7.33	0.84	0.47	balance

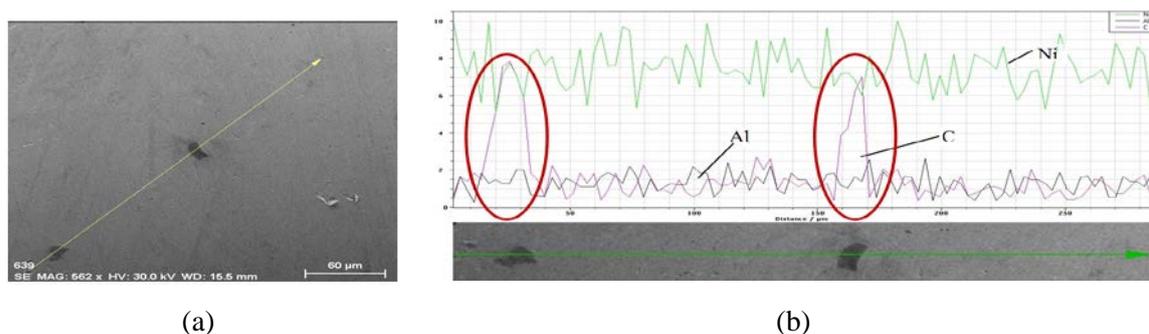


Figure 5. Line analysis for sample $R_z = 0.6 \mu\text{m}$ to highlight the surface chemical elements distribution: (a) Marking of the EDX analyzed area; (b) Line analysis with percentages of C, Al and Ni.

3.1.3. Sample $R_z = 3.2 \mu\text{m}$. For sample $R_z = 3.2 \mu\text{m}$ Al was deposited in 1.363 % on the surface, high percentage due to high surface roughness which does not favor MO-CVD deposition.

Table 4. Chemical composition of sample $R_z = 3.2 \mu\text{m}$ surface layer.

Element	C	Cr	Ni	Al	Fe
Percent	0.13	15.65	8.03	1.36	balance

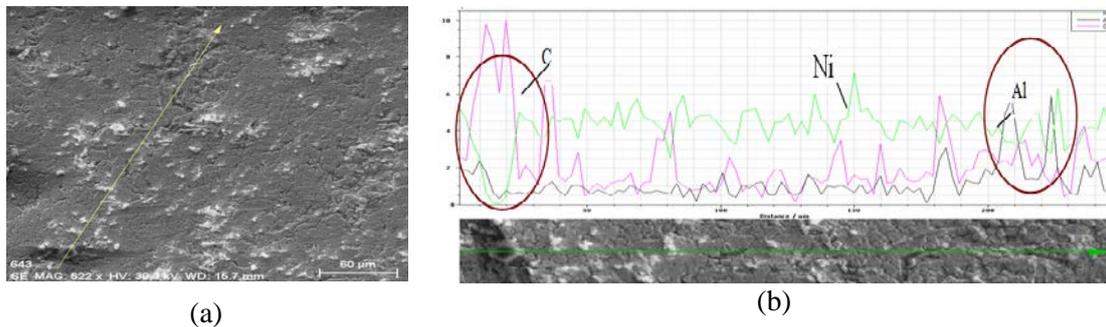


Figure 6. Line analysis for sample $R_z=3,2 \mu\text{m}$ to highlight the surface chemical elements distribution: (a) Marking of the EDX analyzed area; (b) Line analysis with percentages of C, Al and Ni, possible Al_4C_3 formation highlighted in rounded zone.

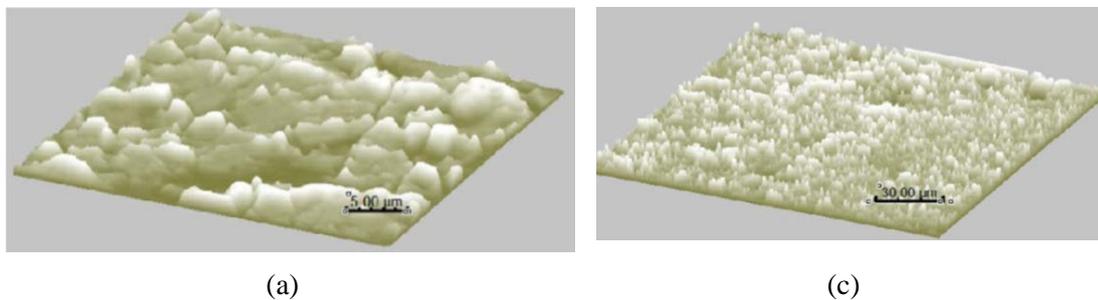


Figure 7. 3D surfaces for sample $R_z = 3,2 \mu\text{m}$ after deposition of Al in fluidised bed by MO-CVD technology: (a) sample $5 \mu\text{m}$ scale (b) $30 \mu\text{m}$.

3.2. XPS analysis of samples after duplex heat treatment (MO-CVD and nitride)

For this analysis an X-ray photoelectron spectrometer, PHI 5000 Versa Probe-XPS, ULVAC-PHI-INC, is used.

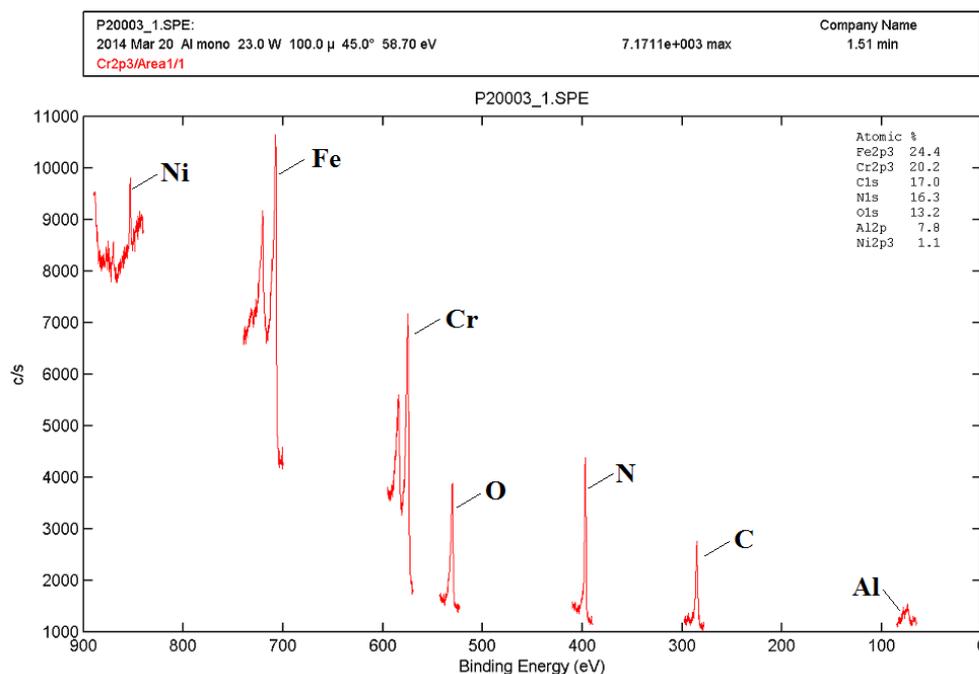


Figure 8. Characteristic XPS spectrum and orbitals.

The exposure time has been increased to remove the effects of contamination because elements such as Si, C and O occur in large quantities, due to surface absorption, either during deposition or subsequent contamination.

For each chemical element the energetic bonds were studied, i.e. the chemical compounds appeared in the layer, and for this purpose enlarged areas from the energy scale were made. Example:

Analyze for Al2p [15], with the band energy between 65 ÷ 85 eV, the peaks in this energy range are observed corresponding to the following chemical compounds: $\text{Al}_{25}\text{Ni}_{75}$, $\text{AlN}_{0,097}$, AlN , $\text{Fe}/\text{Al}_2\text{O}_3$, Al_2FeO_4 , Al_2O_3 , Al_2NiO_4 .

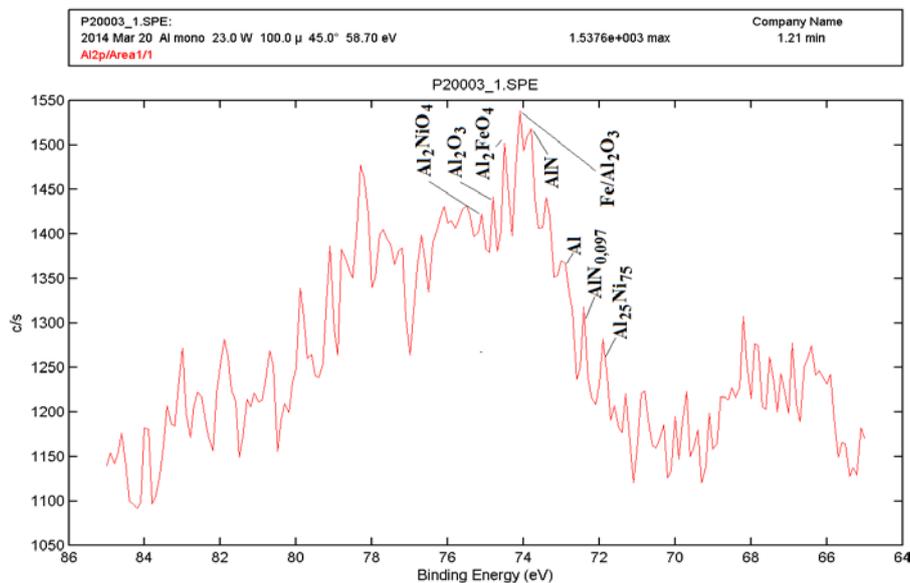


Figure 9. XPS analysis for Al2p for stainless steel sample $R_z = 3,2 \mu\text{m}$, highlighted peaks for following chemical compounds: ($\text{Al}_{25}\text{Ni}_{75}$, $\text{AlN}_{0,097}$, AlN , $\text{Fe}/\text{Al}_2\text{O}_3$, Al_2FeO_4 , Al_2O_3 , Al_2NiO_4).

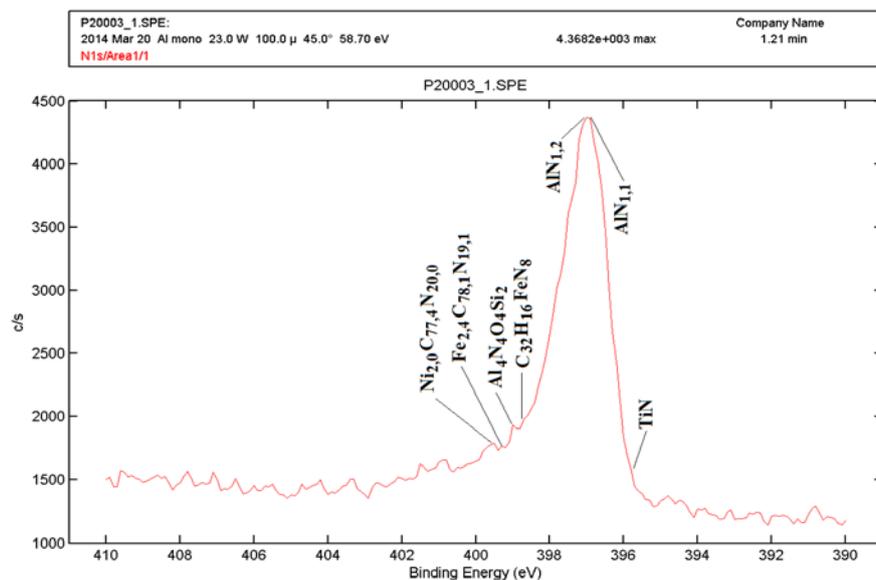


Figure 10. XPS analysis for N1s for stainless steel sample highlighted peaks for following chemical compounds: TiN , $\text{AlN}_{1,1}$, $\text{AlN}_{1,2}$, $\text{C}_{32}\text{H}_{16}\text{FeN}_8$, $\text{Al}_4\text{N}_4\text{O}_4\text{Si}_2$, $\text{Fe}_{2,4}\text{C}_{78,1}\text{N}_{19,1}$, $\text{Ni}_{2,0}\text{C}_{77,4}\text{N}_{20,0}$.

Analyze for N1s [12], with the band energy between 390 ÷ 410 eV, the peaks in this energy range are observed corresponding to the following chemical compounds: TiN, AlN_{1,1}, AlN_{1,2}, C₃₂H₁₆FeN₈, Al₄N₄O₄Si₂, Fe_{2,4}C_{78,1}N_{19,1}, Ni_{2,0}C_{77,4}N_{20,0}.

Aluminum participates in the formation of simple and complex nitrides, AlN_{0,097}, AlN, AlN_{1,1}, AlN_{1,2}, Al₄N₄O₄Si₂, in surface structure. The nitrated surface layer is formed of nitrogen and alloying elements present in steel compounds, namely Al, Cr, Ni, Fe (Al₄N₄O₄Si₂, Cr₂N, Fe_{2,4}C_{78,1}N_{19,1}, Ni_{2,0}C_{77,4}N_{20,0}), not of α (nitroferrite), γ' (Fe₄N), ϵ (Fe_{2,3}N) and ξ (Fe₂N) as in classical ionic nitration, which give a excellent tribological behavior.

3.3. Microhardness testing

Experimental microhardness determinations were performed by means of NAMICON CV Instruments 400 DM. Measurements was performed with 50 gf for control and MO-CVD samples and 200 gf for duplex treated samples (MO-CVD + nitride).

Because the thickness of the deposited layer was very small, indentations were made on the sample surface. This type of measurement gives information about deposited aluminum layer on stainless steel substrate. For each sample, three indentations were performed. The results are shown in Table 5.

Table 5. Vickers microhardness measurements.

Sample	Microhardness after Heat treatment/MO-CVD	Average HV50	Microhardness after nitride	Average HV200
	HV50		HV200	
Heat treatment control sample + NI	239.00	241.00	595.00	594.66
	259.00		602.00	
	225.00		587.00	
MO-CVD control sample	218.10	216.67		
	208.70			
	223.20			
Sample R _z = 0.6 μ m	218.10	216.67	964.30	981.77
	208.70		957.90	
	223.20		1023.10	
Sample R _z = 3.2 μ m	216.90	213.37	988.30	950.63
	222.20		914.40	
	201.00		949.20	

4. Conclusions

The steel used is a high Cr and Ni alloy stainless steel with austenitic structure and about 0.1 % C. Alloying elements create a good austeniticity slowing the penetration of nitrogen.

In order to improve the stainless steel behavior at nitrating, an MO-CVD deposition with a triisobutylaluminum (TIBA) precursor was performed to create aluminum / compact microarea wich favor the absorption of nitrogen in the surface layer.

It has been found that the surface roughness influence the deposition quality, the deposited layer depth increase with the increase of surface roughness.

XPS analysis of duplex-treated austenitic stainless steel components (MO-CVD aluminum deposition and nitride) indicates the presence of complex nitrides and carbonitrides, TiN, AlN_{1,1}, AlN_{1,2}, C₃₂H₁₆FeN₈, Al₄N₄O₄Si₂, Fe_{2,4}C_{78,1}N_{19,1}, Ni_{2,0}C_{77,4}N_{20,0}.

According to Table 5 thermally treated and nitride steel presents low hardness values. After Al deposition by MO-CVD, microhardness decreases up to 10%, but after MO-CVD + nitride duplex treatment, surface hardness has a clear increase.

The thermal regimes applied for the duplex treatment used has a great advantage, because it dosen't affect the physico-mechanical properties of heat treatead substrate.

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