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Oxidation and exhaust gas corrosion resistance of the cobalt base clad layers

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Properties

ABSTRACT

Purpose: Purpose of this work is describing the behaviour of the cobalt base cladding layers after treatment in hot air (750°C, 200 hours) and exhaust gases (700°C, two month).
Design/methodology/approach: The layers were produced by two cladding, laser and PTA, cladding technique. Cladding was conducted with a high power diode laser HDPL ROFIN SINAR DL 020 and Plasma Transformed Arc method. The layers consisted of three multitracking sublayers. The cobalt base layers were evaluated by microstructure investigations (optical and scanning electron microscope SEM), chemical analysis and micro hardness measurements.
Findings: The microstructure of the investigated layers did not change much, neither on the top part nor in the clad/steel interface after treatment in both environments. On the outer surfaces the oxide layers were observed which consisted generally of chromium and iron oxides. The compositions of this scales were reviled by the EDS analyze. The changes in chemical compositions before and after oxidation and after corrosion in exhaust gases in the dendritic regions and micro regions were confirmed by the semi-quantitative chemical analysis (EDS). Neither the oxidation nor exposition for two month in exhaust gases did not influence on the morphology of the clad layers in any region however changes in chemical composition were observed. For both sort of clads the oxide layers were observed on the surface. The proposed layers are resistant for the hot exhausted gases.
Research limitations/implications: The future researches should be done on microstructural and kinetic analyze of high temperature corrosion for higher temperature and times of the process.
Practical implications: The clad layers, of this composition, were designed as a method to prolong service time for the ship engine exhausted valve and after this investigation the first valve heads with laser clad layer were installed in working ship engine.
Originality/value: The chemical composition of the powder was new one. Also using the laser cladding technique for ship engine parts subject of interesting.
Keywords: Gas corrosion; Oxidation resistance; Cobalt-base alloy

1. Introduction

During service many parts of machinery or equipments like blades and vanes of gas turbines or valves of the engines are subjected to high thermal stresses and mechanical loads. The big ship diesel engines are subjected the severe work conditions. The exhaust valves are one of theirs crucial points. They have to stand the high mechanical and thermal stresses which are applied. Also they undergo corrosion by the hot gases and wear abrasion and erosion is observed. The presence of sulfur must be taken into consideration because the heavy fuel oil are still the dominant fuel quality for diesel engines. Technical and economical factors lead to the conclusion that longer time of service is necessary. In order to prolong this service time of the valve the hardfacing technology is often used to produce surface layer protecting parts against different kinds of degradation [15, 16; 23]. The typical damages of exhaust valve seat (an example of the damaged valve is presented on Figure 1) are the following:

- Tightness loss due to corrosion pits caused by exhaust gases
- Burnt-out of head plate rims due to the flow of hot gases
- Cracks, scratches and splinters caused by the wear of the seat face top layer

Fig. 1. An example of valve failure during the service

Surfacing the seat face with different techniques and different resisting materials can increase the durability of valves. The used materials and technologies should provide the thin layers presented high mechanical properties and corrosion resistance for acceptable cost. Cobalt-base alloys that are used in the aeronautical industry or in industrial hot processes fulfill the basic demands: oxidation and hot corrosion resistance, wear resistance and high strength at elevated temperature [4, 12, 17]. These properties are connected with chemical composition of this alloys which should to be simple enough to lead to the formation of a limited number of phases. The primary alloying elements are chromium, tungsten and carbon.

- Chromium provides high resistance against oxidation in the high temperature and corrosion by aggressive environment also participates in the formation of carbides.
- Carbon induces the formation of primary and secondary carbides which are provide high mechanical properties at high temperature and creep resistance.
- Tungsten strengthen the alloys by forming a solid solution with cobalt forms carbides.

Cobalt and tungsten also enhancing the resistance to galling in metal-to-metal wear applications by reducing the stacking fault energy. Cobalt base superalloys consist of a continuous fcc matrix and a variety of carbides. Mainly they are primary ones, such as $M_{23}C_6$, M_7C_3, and M_6C. This carbides form during the alloys solidification. In service at elevated temperatures or during aging a large amount of secondary carbide precipitation, commonly $M_{23}C_6$ are formed. This fine secondary carbide precipitates are even more effective in strengthening the alloy matrix [1-3; 8].

For practical use the surface layer should have stable properties during the whole service time. Not much works have been done to evaluate microstructural stability of the cobalt layer in the temperature of the service [5-7, 10, 11; 13; 15; 18, 19].

2. Materials and experimental

For this type of engine, the exhaust valve head are usually made of valve steel which are resistant for high temperature, wear and service environment. For this investigation also the steel forging valve was used. The steel was A-R-H10S2M which is corresponding with an X40CrSiMo10-2 steel. Before cladding the valve face underwent turning. Next some of this experimental valves were cladded with two techniques which were laser end plasma transformed arc (PTA). For laser cladding a high power diode laser HDPL ROFIN SINAR DL 020 with generated beam power of 2.3 kW was used. The PTA cladding was conducted with using EUTRONIC GAP 200 by CASTOLIN equipment. The chemical composition of the powder, which was delivered straight to the melt pool, was as follow: C-1,32%, Si-1,25%, Cr-29,0%, W-5,3%, Ni-2,1%, Mo- <0,1%, Fe- 1,9%, Co as balance. It was an experimental formulation called PG5218. The laser cladding layers consisted of three sublayers with two subsequent laser tracks, overlapped by 3 mm (about 30%). In the PTA case, the clad layer consisted of three sublayers with three tracks overlapped by 3 mm. For both processes the cladded layers were 8,5to 9,0 mm wide and 4,0 to 4,5 mm thick. The proper geometry of the valve face was obtained by turning after cladding. The next step was preparing the samples for oxidation and exhaust gas corrosion. The valves with clad layers were cut into the pieces and underwent the experiment. The oxidation of the samples were performed in air at 750°C for 200 hours using laboratory electric tube furnace (Fig. 2).

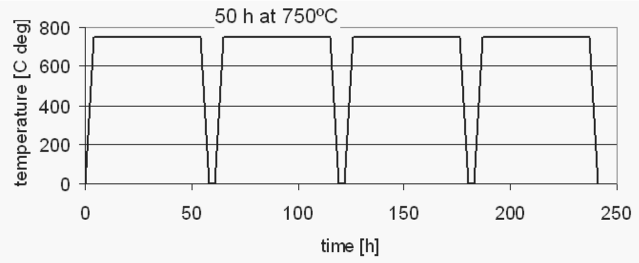

Fig. 2. Thermal cycles of clad layers oxidation process (heating rate ~ 19ºC/h)

The combustion processes produced exhaust gases and their composition depended on many factors for example chemical composition of the fuel and oxygen amount during the combustion. In this experiment the corrosion processes in exhaust gases were carried on the experimental station under the simulative service condition. The exhaust gases were produced by the real ship diesel engine placed in laboratory. The gases came into chamber where they were heating to the temperature about 700°C and react with the valve clad layer. The chemical composition of the gases, which vary in time, were monitoring all the time. The average chemical composition of gases was: CO 2002 mg/m^3, SO_2 20 mg/m^3, NO_x 424 mg/m^3. The exposition on exhaust gases lasted two months, but only 30% of this time in high temperature. On the cross-section of the clad passes the microstructural study was performed after metallographic preparation. Figure 3 presents the way of preparing the sample.

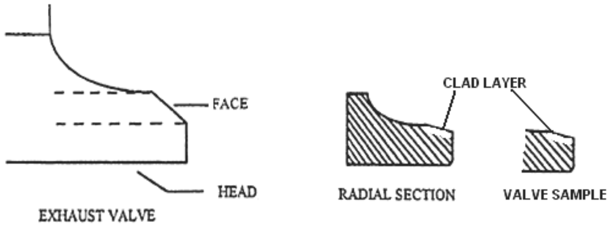

Fig. 3. The preparing of the valve sample

The follow analytical techniques were used to characterize the samples: optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). SEM studies were conducted at accelerating voltages ranging from 15-30 kV in backscattered and secondary electron imaging modes. Hardness measurement on the cross-section represented changes in mechanical properties.

2.1. Morphology

In deposited layers a typical surface welding solidification structures were observed (Figs. 4a, 4d). Microstructure of as-deposited layers consists of α-Co (Co-rich matrix) with a network of carbides and eutectics in the interdendritic regions. The carbides which were observed were identified as mainly $M_{12}C$ (Co_6W_6C) and $M_{23}C_6$ ($Cr_{23}C_6$). Carbides are the most important secondary phase in cobalt alloys and contribute significantly to alloy strengthening. Cross-section EDAX analysis of clad layers revealed that the matrix was enriched in chromium and tungsten while the eutectics were enriched in chromium, tungsten and silicon. Any substantial changes could be observed for both sorts of layers after corrosion processes both in air and in the exhaust gases. The scale layers on the surface of the clad on the cross-section were hardly to notice (Figs. 4b, 4c, 4e, 4f), however the observation of the valve face confirmed the presence of the oxide layers (Figs. 5, 6). Also, there were slightly differences in the appearance of the layer after oxidizing and exposition for exhaust gases. The further examination allowed analyzing the result of investigated cobalt alloys gaseous corrosion.

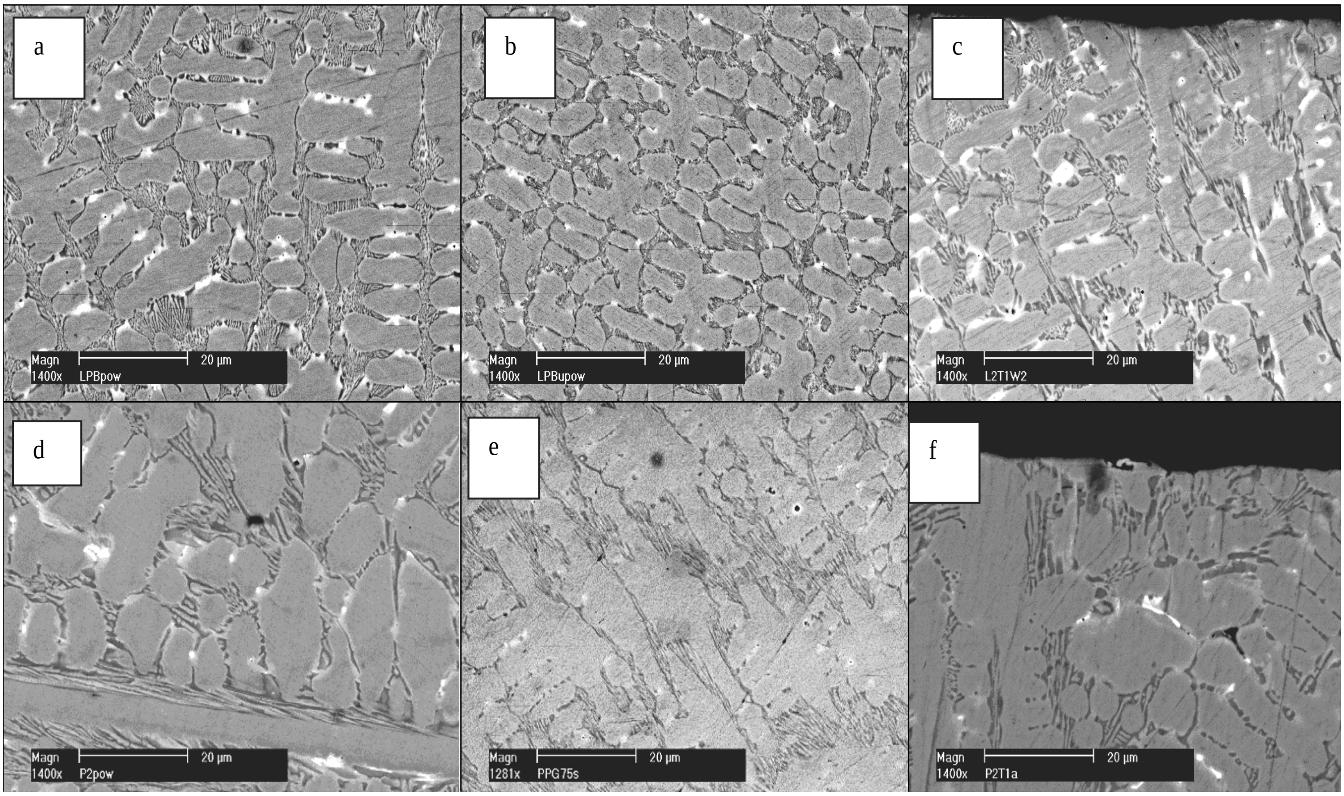

Fig. 4. The structures on the cross-sections of clads; a – laser cladding - as clad; b- laser cladding - after oxidation; c- laser cladding - after corrosion in exhaust gases; d- PTA cladding - as clad; e- PTA cladding - oxidation; f- PTA cladding - after corrosion in exhaust gases

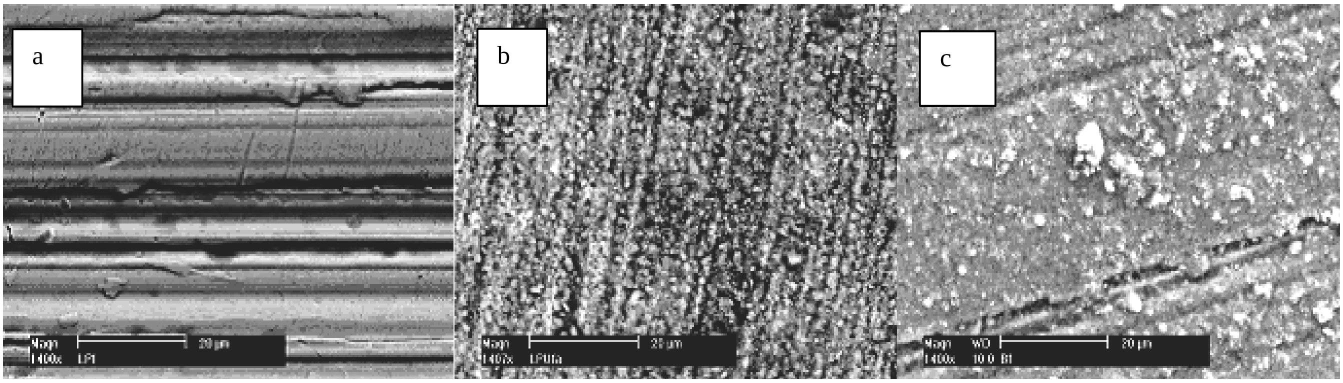

Fig. 5. SEM micrographs showing the surface morphology of valve face coating by laser cladding: a- as clad; b- after oxidation; c- after corrosion in exhaust gases

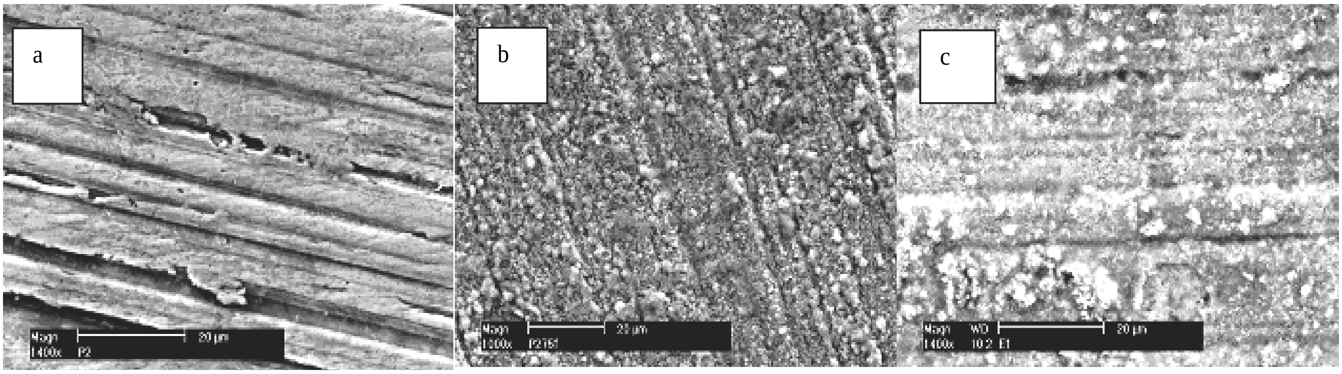

Fig. 6. SEM micrographs showing the surface morphology of valve face coating by PTA cladding: a- as clad; b- after oxidation; c- after corrosion in exhaust gases

2.2. Chemical analyze

EDS analyzes were used to describe the corrosion processes. This analysis were made for the micro regions and for dendritic regions on the cross-section of the clad layers. The micro regions sizes were 100x90 µm and they were situated close to the outer surface of the clad and in the middle part of the clad. These measurements were made for the as clad layer, after oxidation and after corrosion in the exhaust gases. For measurement of single phase region – on the cross section - the big enough dendrits were found and point chemical analysis were performed. The micro regions analyze could provide information about average changes of chemical composition in the different part of the clad layer. The dendritic region investigation could inform only about changes in the single phase regions. The Figs. 7 to 14 are the examples of the obtained results for the layers made by laser cladding. Such investigations were performed for the layers made by both technologies. Presented charts were obtained by measuring in 5 points for each one. Generally, character of changes were similar for each point.

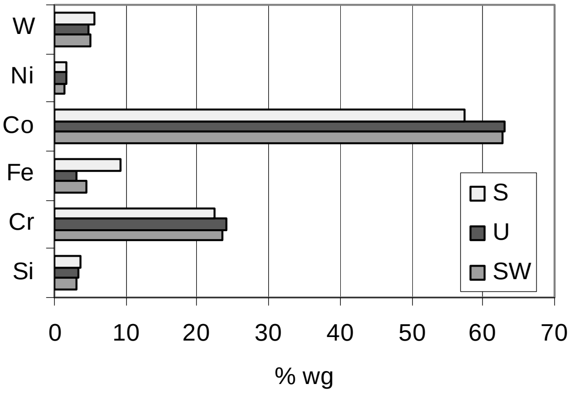

Fig. 7. Chemical analysis (EDS) of the dendritic regions close to the surface of the clad layer made by laser cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

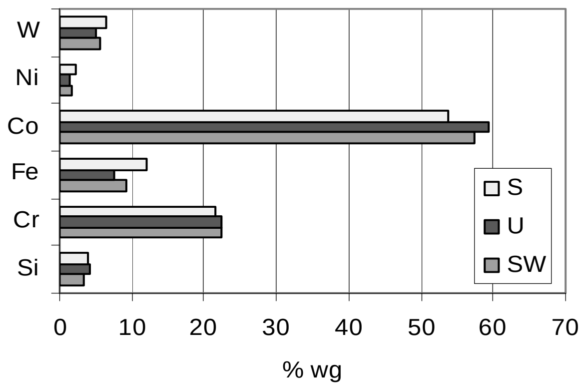

Fig. 8. Chemical analysis (EDS) of the dendritic regions in the middle part of the layer made by laser cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

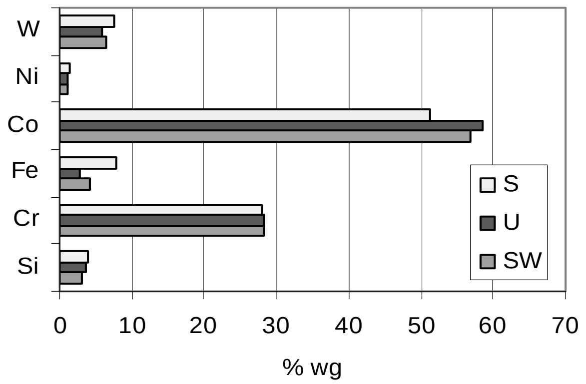

Fig. 9. Chemical analysis (EDS) of the microregions close to the surface of the clad layer made by laser cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

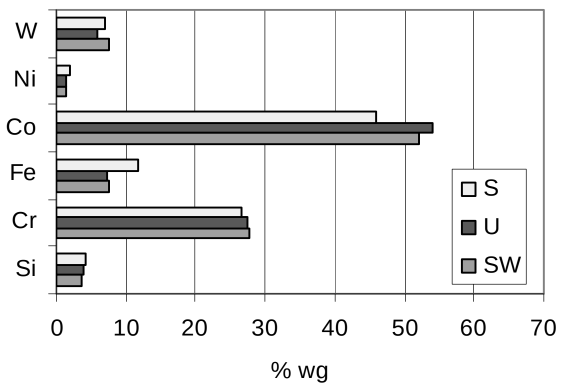

Fig. 10. Chemical analysis (EDS) of the microregions in the middle part of the layer made by laser cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

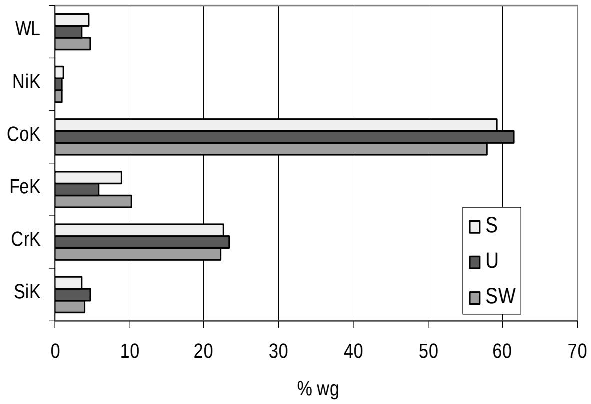

Fig. 11. Chemical analysis (EDS) of the dendritic regions close to the surface of the clad layer made by PTA cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

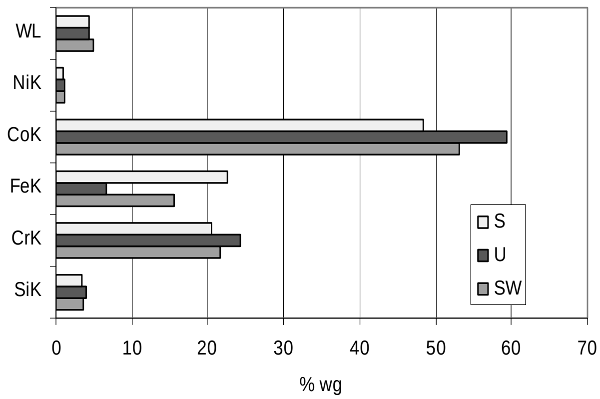

Fig. 12. Chemical analysis (EDS) of the dendritic regions in the middle part of the layer made by PTA cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

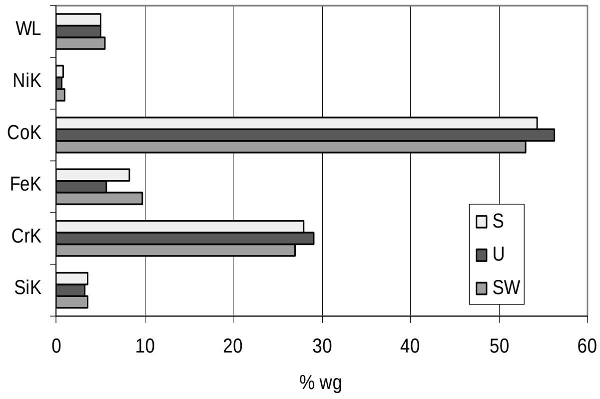

Fig. 13. Chemical analysis (EDS) of the microregions close to the surface of the clad layer made by PTA cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

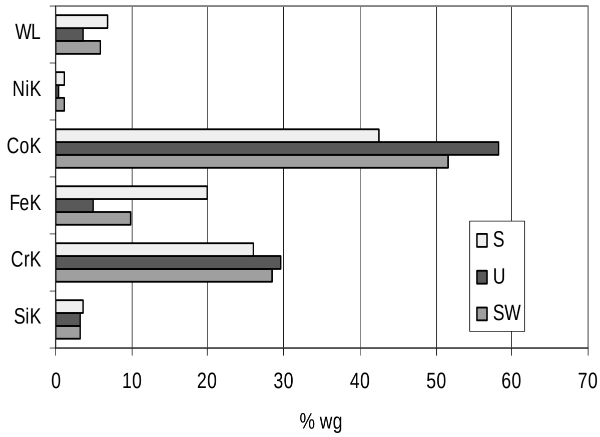

Fig. 14. Chemical analysis (EDS) of the microregions in the middle part of the layer made by PTA cladding; SW –as clad, U - after oxidation, S- after corrosion in exhaust gases

The scale on the valve face was well adherent and very tiny. The chemical composition of the scale layers on the valve face were established by EDS techniques (Figs. 15-18). The scale layer consisted of the elements which had very different atomic weight. This caused that the results should be taken rather as a quality type.

The EDAX analyze was used to characterize the composition of the corrosion products on the valve face. With the help of EDS maps of the elements distribution and given spectrums it was determined as a chromium and eventually iron rich oxide for both type of layers, laser and PTA cladding after oxidation. In the case of the corrosion in exhaust gases beside the oxides the presence of sulfur was corroborated.

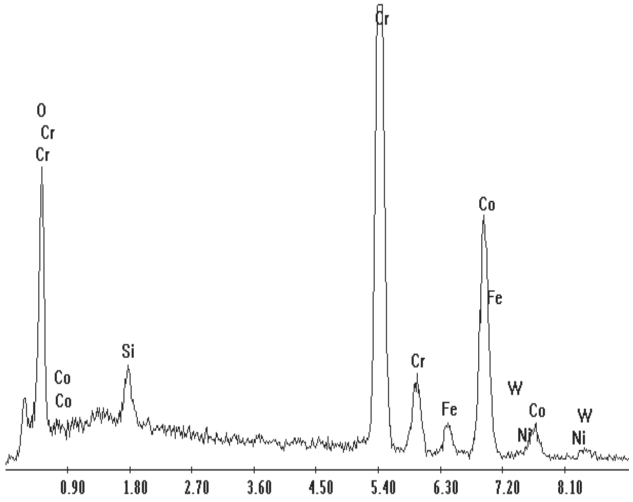

Fig. 15. EDAX spectrum of valve face produced by laser cladding, oxidized in air at 750 ºC for 200 hours

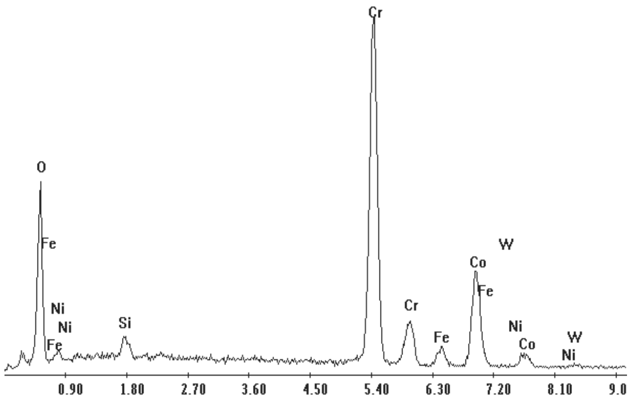

Fig. 16. EDAX spectrum of valve face produced by PTA cladding, oxidized in air at 750 ºC for 200 hours

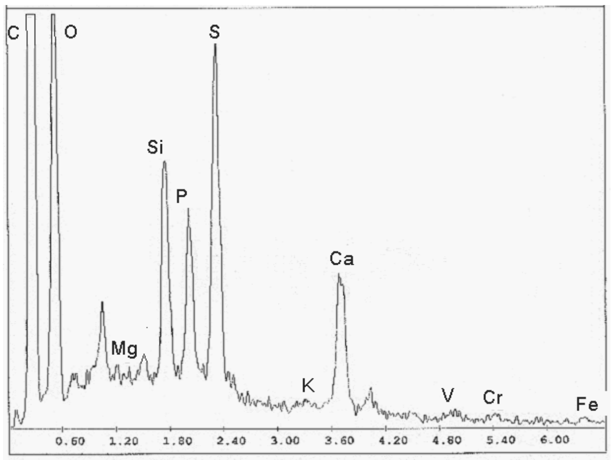

Fig. 17. EDAX spectrum of valve face produced by laser cladding, after corrosion in exhaust gases

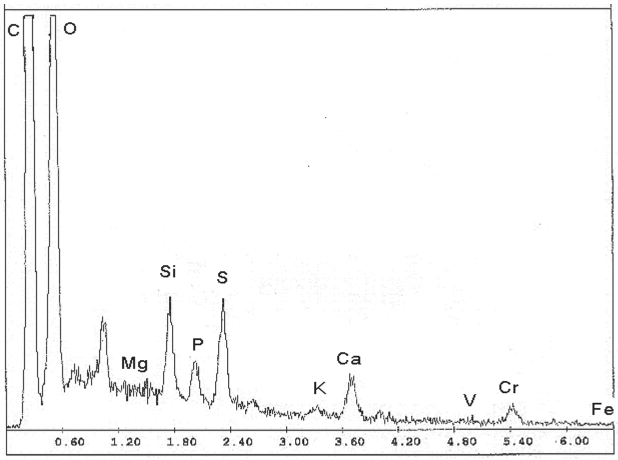

Fig. 18. EDAX spectrum of valve face produced by PTA cladding, after corrosion in exhaust gases

2.3. Hardness measurement

Mechanical properties of the clad layers were represented by their hardness. The hardness was measured for as-clad layers, for sample after cyclic oxidation and for sample after corrosion in exhaust gases. Both type of layers, laser and PTA cladding, underwent the measurement. The average hardness of the original heat-treated steel was 283 HV30. For the layers the Vickers numbers hardness obtained were variable and higher than for steel base. The applied methods of cladding resulted in unstable hardness of the layers which was visible especially for as clad layers.

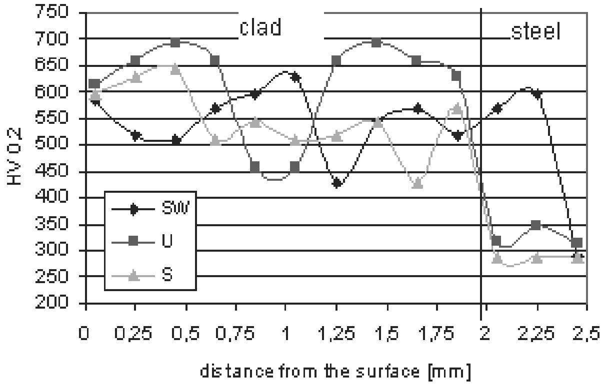

Fig. 19. Micro hardness distribution on the cross section of the clad, perpendicularly to the surface – laser cladding. Symbols: SW – as clad, U – after oxidation, S – after corrosion in exhaust gases

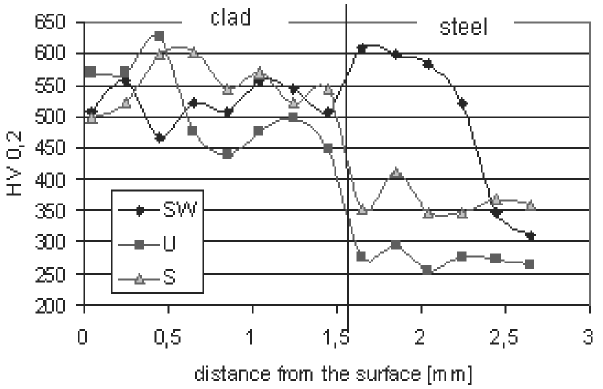

Fig. 20. Micro hardness distribution on the cross section of the clad, perpendicularly to the surface – PTA cladding. Symbols: SW – as clad, U – after oxidation, S – after corrosion in exhaust gases

The results for laser cladding ranged from 450 HV0,2 to 650 HV0,2 and for PTA cladding from 450 HV0,2 do 550 HV0,2. The heat affected zones were observed for both types of layers. The hardness result for laser cladding layer is presented on the Fig. 19. For PTA cladding layer (Fig. 20), the similar results were obtained.

3. Results and discussion

The clad layers were made of cobalt base powder by two method laser cladding and PTA claddings. They showed similar morphology after cladding. They were also resistant for elevated temperature exposure (Figs. 4a-f, 5, 6).The oxidation at temperature 750°C for 200 hours and exposition for exhaust gases at temperature about 700°C for two month, did not influence on the morphology of the clad layers neither on the top part nor in the middle part of the clad. For both of the layer there were observed changes in chemical composition of the micro regions and single phase region (Figs. 7-14). On the preliminary stage of the investigation, as clad, chemical composition of the surface and middle part of the clads for the both type of the technology were similar. Analysis of dendritic regions as well as microregions showed a little higher cobalt amounts in the close to the surface part of the layers than in the middle part and higher amounts of iron in the middle part. The changes in micro regions which were close to the surface and in the middle part of the layer corresponded with each other. The same was observed for denritic region. After oxidation and corrosion w gases there were observed changes of chemical composition between surface and middle parts and between two technologies. PTA clad layer presented more intensive diffusion processes than laser cladding. Also the long time corrosion in exhaust gases caused more visible changes in chemical compositions of each region. Usually, after corrosion, close to the surface the layers were enriched in cobalt and sometimes a little in chromium and after oxidation tungsten amount was decreased. After exposition in exhaust gases the enrichment in iron and chromium were additionally observed for both type of the clads. The middle parts of the layers showed differences in chemical compositions after oxidation and after corrosion in gases. The oxidation was connected with the reduction of iron while after gaseous corrosion the higher amounts of iron in the middle part of the layers were noticed [12-14]. They were the results of elements diffusion in different conditions (time and atmosphere) of exposition. The oxide layers were on the surface of both sort of clads. Using EDS and EDAX analyze it was proved that the chromium oxide was the main component of the scale after oxidation [12, 14, 22, 24, 25]. According to the literature [13] a protective, compact scale of predominantly Cr_2O_3 formed during isothermal oxidation up to 900°C, while a poorly adherent, porous scale of predominantly $CoCr_2O_4$ and CoO formed at higher temperature. The selective oxidation of chromium would have caused a decrease in the chromium concentration in the matrix close to the alloy surface. After corrosion in gases, scales were thicker and consisted of iron and chromium oxides. Small amounts of sulfur compound were also noted specially on the scale formed on the PTA clad layer (Figs. 17, 18). The mechanical properties, for example hardness, were also influenced by the heat treatment in air. For both type of clads the increase of HV0,2 hardness was observed (Figs. 19, 20), especially after oxidation for laser cladding layer. Corrosion in exhaust gases resulted similarly however increasing was smaller for laser cladding layer and higher for PTA cladding. It was noted that both overlaid specimens clad specimens exhibited almost similar hardness values on their top surfaces. It could be result of the increase on carbide volume fraction as they precipitate in the matrix. It must be emphasized that, In fact, for the very fine secondary carbides precipitates could not be clearly resolved. The applying heat treatment brought about significant reduction in microhardness gradient across the interface clad/steel base and the heat affected zone [20, 24, 25].

4. Conclusions

After performed investigations the following conclusions were established:

- The microstructures of the clad layers did not change significantly during the oxidation treatment. This behaviour was observed for both type of layers and despite of the region (close to the surface and close to the steel core) and sort of corrosion atmosphere.
- The clads surfaces were protected by the thin, adherent oxide layers, mainly by chromium oxide.
- There was not observed significant chromium depletion of the surface layer of the clad.
- Hardness of the top layer slightly increased but in different ways for both sort of technology. The layer which was made by laser cladding presented higher hardness increase, especially after oxidation, then PTA clad layer. After oxidation this PTA clad layer hardness increased only in the part of the layer close to the surface. The part close to the clad/steel interface showed decrease of the hardness. After corrosion in exhaust gases the results were similar.
- The clad layers made of cobalt base powder which was investigated are a possible solution for increasing the service time for the ship engine exhaust valve.

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