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The gas corrosion of the cobalt base clad layer at elevated temperature

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Properties

ABSTRACT

Purpose: Purpose of this paper is to evaluate the microstructural and mechanical properties evolution of the laser and PTA clad layers made of the powder containing cobalt after oxidation in air (750°C, 200 hours) and corrosion in exhaust gases (700°C, two month).

Design/methodology/approach: The layers were made by cladding technique. Cladding was conducted with a high power diode laser HDPL ROFIN SINAR DL 020 and Plasma Transformed Arc method. The subsequent tracks were overlapped by 30÷40%. The performance of the hardfaced materials were evaluated by microstructure (optical and scanning electron microscope SEM), chemical analysis and micro hardness measurements.

Findings: After heat treatment the microstructure of the clad layers did not change much, neither on the top part nor in the clad/steel interface. However the oxide layer on the surface is observed. The EDS analyze revile the composition of this scale which consisted generally of chromium and iron oxides. The semi-quantitative chemical analysis (EDS) of the dendritic regions and micro regions confirms changes in chemical contents before and after oxidation and after corrosion in exhaust gases. The oxidation at temperature 750°C for 200 hours in air and for two month in exhaust gases did not influence on the morphology of the clad layers neither on the top part nor in the clad/steel interface. However changes in chemical composition were observed. On the surface of both sort of clads the oxide layers were observed. These sorts of layers are resistant for the hot exhausted gases.

Research limitations/implications: During the future research kinetic analyze of high temperature corrosion should be done also for different temperature and times of the process.

Practical implications: The layers were designed as a method to prolong service time for the ship engine exhausted valve.

Originality/value: The chemical composition of the powder was new one. Also using the laser cladding technique for ship engine parts is a subject of interest.

Keywords: Corrosion; Oxidation resistance; Cobalt-base alloy

1. Introduction

The contemporary ship diesel engines are subjected the severe work conditions. One of theirs crucial points are the exhaust valves. The high mechanical and thermal stresses are applied, the high temperature gas corrosion and wear abrasion and erosion is observed. What more the heavy fuel oil are still the dominant fuel quality for diesel engines. So presence of sulfur must be taken into consideration. In order to prolong service time of the valve the hardfacing technology is often used to produce surface layer protecting parts against different kinds of degradation [1, 2, and 3]. It is possible to produce thin surface layer of high properties made with reasonable costs. Cobalt base superalloys, because of their desirable combination of high rupture strength, wear resistance and excellent hot corrosion resistance at high temperatures, have been widely used in many military and commercial aircraft turbine engines as vanes and combustor sections. Chromium, tungsten and carbon are primary alloying elements. Chromium and tungsten form carbides that contribute to the improved abrasion resistance of these alloys. Tungsten also contributes to matrix strengthening due to its large atomic diameter by the formation of interstitial solid solutions. Cobalt and tungsten also help to reduce the stacking fault energy thereby enhancing the resistance to galling in metal-to-metal wear applications. These alloys offer also corrosion resistance for severe service condition. In cobalt base alloys, carbides contribute significantly to strength. Usually, as cast cobalt base superalloys consist of a continuous fcc matrix and a variety of carbides, mainly primary ones, such as $M_{23}C_6$, M_7C_3, and M_6C, which form as the alloys solidify. Subsequent aging or service at elevated temperatures causes a large amount of secondary carbide precipitation, commonly $M_{23}C_6$. The fine secondary carbide precipitates are more effective in strengthening the alloy matrix [4, 5, and 6]. From the practical point of view, it is important to provide the surface layers, which 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 [7, 8, 9, and 10].

2. Materials and experimental

The substrate was the exhaust valve made as an A-R-H10S2M steel forging. This steel is corresponding with an X40CrSiMo10-2 steel. The valve face underwent turning and next some of the experimental valves were surfacing by laser technique and some of them by PTA technique. Cladding was conducted with a high power diode laser HDPL ROFIN SINAR DL 020 with generated beam power of 2.3 kW and with using EUTRONIC GAP 200 by CASTOLIN equipment. The powder was delivered straight to the melt pool. The chemical composition of the experimental powder PG5218 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. The subsequent laser tracks were overlapped by 30 ÷ 40%. After cladding the valve faces underwent turning in order to obtain proper geometry .The cladded valves were cut into the pieces and underwent heat treatment. The oxidation studies were performed in air at 750°C for 200 hours using laboratory electric tube furnace. The corrosion processes in exhaust gases were carried out under the simulative service condition on the experimental station. The exhaust gases which were produced by the real ship diesel engine underwent the heating to the temperature about 700°C and react with the valve clad layer. The chemical composition of the gases were monitoring all the time. The average chemical composition of gases is as follow: 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. The microstructural study was performed on the cross-section of the clad passes. After metallographic preparation, the cross-sections were examined. The analytical techniques used to characterize the samples included optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). SEM was conducted at accelerating voltages ranging from 15-30 kV in backscattered and secondary electron imaging modes. Mechanical properties were represented by hardness measurement on the cross-section.

2.1. Morphology

A typical surface welding solidification structures were observed in deposited layers (fig. 3a, 3d). This as-deposited microstructure can be described as a Co rich matrix with a network of carbides and eutectics in the interdendritic regions. The carbides were identified as mainly $M_{12}C$ (Co_6W_6C) and $M_{23}C_6$ ($Cr_{23}C_6$). The matrix was enriched in chromium and tungsten. Eutectics were enriched in chromium, tungsten and silicon. After corrosion processes in air and in the exhaust gases any substantial changes could be observed for both sorts of layers. Even scale layers on the surface of the clad were hardly to notice (fig. 3b, 3c, 3e, 3f). The observation of the valve face confirmed the presence of the oxide layers (fig. 4, 5). There were slightly differences in the appearance of the layer after oxidizing and exposition for exhaust gases.

2.2. Chemical analyze

In order to describe the corrosion processes the EDS analyzes of the micro regions on the cross-section of the clad layers were performed.

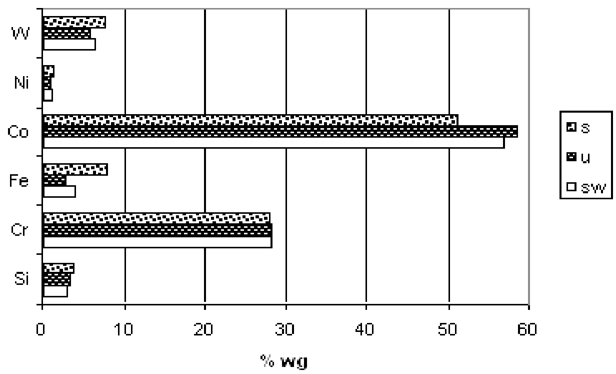

Fig. 1. Chemical analysis (EDS) of the microregions close to the surface of the clad layer made by laser cladding; S –as clad, U - after oxidation, SW- after corrosion in exhaust gases

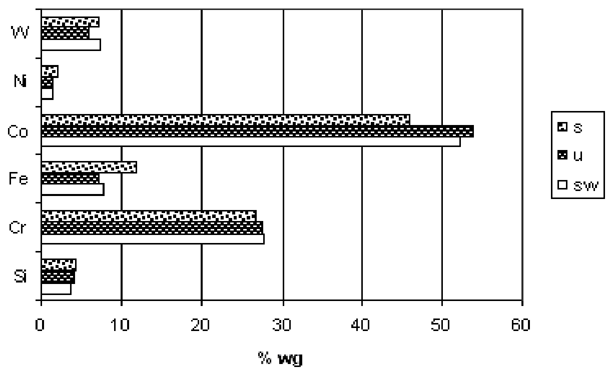

Fig. 2. Chemical analysis (EDS) of the microregions in the middle part of the layer made by laser cladding

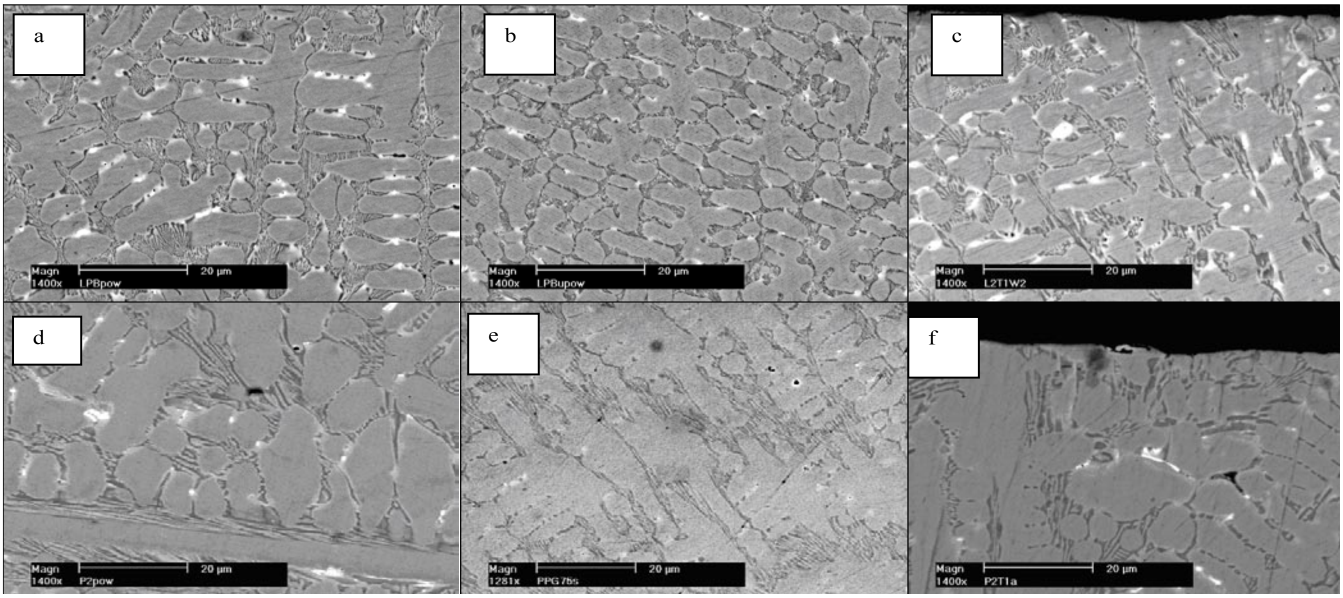

Fig. 3. The structures on the cross-sections of clads; a – laser cladding - as clad; b- laser cladding - after oxidation; c- laser cladding - after corrosion in exhaust gases; d- PTA cladding - as clad; e- PTA cladding - oxidation; f- PTA cladding - after corrosion in exhaust gases

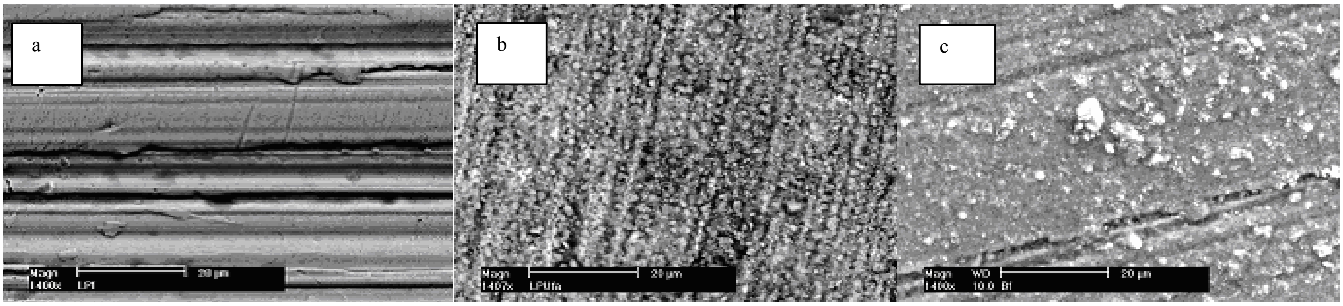

Fig. 4. SEM micrographs showing the surface morphology of valve face coating by laser cladding: a- as clad; b- after oxidation; c- after corrosion in exhaust gases

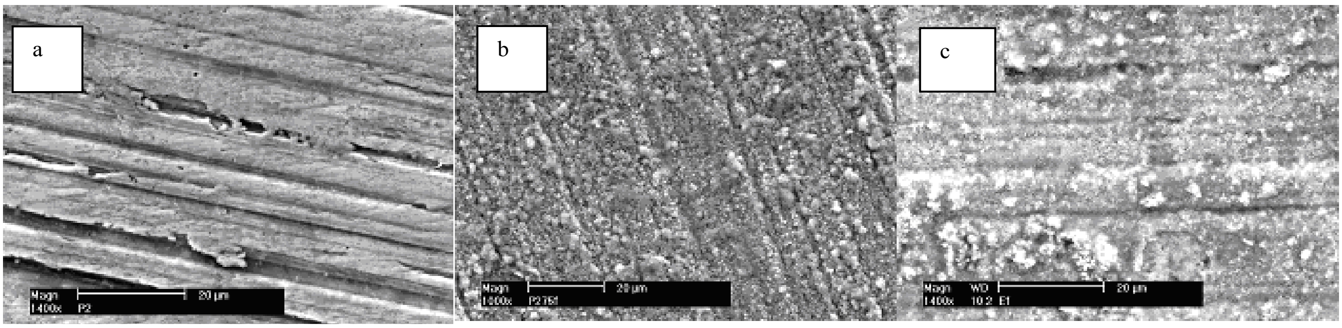

Fig. 5. SEM micrographs showing the surface morphology of valve face coating by PTA cladding: a- as clad; b- after oxidation; c- after corrosion in exhaust gases

The 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. The fig. 1 and 2 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. Compositions of the scale layers which formed on the surface of the valve face were also analyzed using EDS techniques. Because of technical condition of analyzing elements of different atomic weight, the results were rather quality than quantity type.

2.3. Hardness measurement

The hardness measurement for both type of the layers in every step of the investigation were made. The Vickers numbers hardness obtained were variable and were higher than average hardness original heat-treated steel, which was 283 HV30. The effect of multilayer deposition on the hardness value was evaluated by measuring hardness profile along the cross-section from the surface to the clad/steel. There is an example of the hardness result for laser cladding layer on the fig.6. The similar results were obtained for PTA cladding layer.

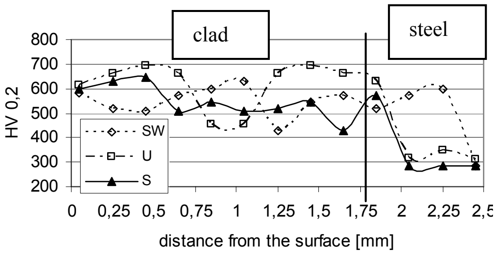

Fig. 6. Micro hardness distribution on the cross section of the clad, perpendicularly to the surface.

3. Results and discussion

The clad layers which were made of cobalt base powder by laser cladding and PTA cladding had similar morphology and were resistant to the elevated temperature work conditions. 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. However changes in chemical composition of the micro regions were observed for both of the layer (fig. 4, 5). The changes in the close to the surface micro regions and dendritic regions corresponded with the changes in the layers middle part. They were the results of elements diffusion [11 - 16]. On the surface of both sort of clads the oxide layers were observed. EDS analyze proved that the chromium oxide was the main component of the scale. The heat treatment influenced also on mechanical properties of the clad which means hardness. The HV0,2 hardness slightly increase (fig. 6) for both type of clads. It could be result of the increase on carbide volume fraction as they precipitate in the matrix. Also heat treatment removed hardness increase in the heat affected zone in the steel base.

4. Conclusions

The performed investigations led to the following conclusion:

- The microstructures of the clad layers do not change significantly during the oxidation treatment
- The surface of the clad is protected by the oxide layer
- There was not observed significant chromium depletion of the surface layer of the clad
- Hardness of the top layer slightly increases
- This type of the clad layer is a good solution for increasing the service time for the exhaust valve.

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