Microstructural aspects at coating-substrate interface for some thermal sprayed layers on valve discs

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Abstract. One of the improvements that can be made to internal combustion engines, without significantly altering the structural elements, is increasing the temperature in the combustion chamber by coating its component elements with thermal barrier coatings (TBC). In this paper were analysed from the microstructure point of view the coating-substrate interfaces of three layers deposited by thermal spraying: S1 - Cr₂C₃ - NiCr, S2 - MgZrO - NiCr and S3 - ZrO₂ - CaO. The investigations were performed by electronic microscopy on the cross sections taken from the samples after they were subjected to similar heating to the one produced during the operation. It has been observed that all three types of coatings have a much better density, are chemically stable and have good adhesion to the substrate, which recommends them for this type of use.

1. Introduction

Once with the increase of the customer requirements and expectations, automotive manufacturers have had to find new ways to improve the functionality, robustness, comfort, safety and environmental protection of produced cars [1]. With regard to the internal combustion engine, a very high level of technical development has now been achieved, ensuring high power density, high torque, satisfactory operating cycle efficiency and a reduction in gas emissions [2]. However, the automotive industry is under increasing pressure to ensure consumption and lower emissions, while eliminating certain harmful compounds from combustion gases (NOₓ and other fine particles).

Thus, one of the more frequently used solutions is the improvement of surfaces by the additive processes such as: thermal spraying (TS), physical vapour deposition (PVD), plasma enhanced chemical vapour deposition (PECVD), thermochemical heat treatment (TCHT) [3, 4, 12], resulting in a new material with superior properties to the original.

In an attempt to meet the new challenges of greening internal combustion engines, research has come aside from the fact that much of the energy supplied by the fuel is lost through the cooling system and the exhaust gas (for example, in the case of diesel engines it is used to operate only 30-40% of the energy obtained [5]). Thus, attention was directed to the use of thermal barrier coatings (TBC) in certain areas of the internal combustion engine, so that the energy lost by heat drops, resulting in a better efficiency in operation.

Thermal barrier coatings are most commonly produced by the thermal deposition technique and are composed of two different types of materials: the first layer sprayed on the support material...
(commonly called bondcoat) has the role of increasing the adhesion between the latter and the deposited layer but also to lower their degree of oxidation; the second layer (commonly called topcoat) is usually made of ceramic material and has the role of lowering the thermal conductivity of the whole system [6].

In order for a material to be classified as TBC, it must meet a number of basic conditions, as follows: - low thermal conductivity; - low density of the coating; - higher density on the surface of the coating to provide better abrasion resistance and a decrease in adhesion of the combustion gases particles; - a good capacity to damp the stresses induced by different coefficients of thermal expansion; - resistance to compression of the top coat so that no cracks will occur which initiate the peeling of the deposited layer; - chemical stability; - thermal stability during operation [7,8].

2. Experimental setup
In this paper there were observed from the microstructural point of view three types of coatings realized by atmospheric plasma spray APS. There were used as substrate discs of intake or exhaust valves, organized as 3 sets of four intake valves and four exhaust valves, as observed in figure 1a and 1c. The coatings were produced using the facility SPRAYWIZARD 9MCE for atmospheric plasma spraying, some aspects regarding the samples processing and aspects before and after the coating being presented in figure 1a,b,c.

![Figure 1. Aspects of the samples processing: a) samples aspects before coating (sand-blasted); b) imagine during the coating process; c) samples aspects after coating.](image)

Four types of commercial powders (produced by Sulzer - Oerlikon) were used to obtain the multilayer coatings as follows:
- a bonding layer deposited on each of the three sets from Al$_2$O$_3$-30(Ni$_{20}$Al) to further bind the top coats from the substrate;
- a top coat with thermal barrier role, with different chemical composition for each set of samples:
  set 1 - Cr$_2$C$_3$ - NiCr, set 2 - MgZrO - NiCr, set 3 - ZrO - CaO.

To assess the thermal barrier utilization under the conditions of internal combustion engine operation, a specific sample of each set was heated to 900°C and maintained for 2 hours. The heating process was carried out by means of an electric resistance furnace which is functioning in the normal
atmosphere, produced by S.Y. Italy. It was chosen to heat up to 900°C, respectively cooling down with the furnace and maintains it for 2 hours at this temperature because this is also the maximum working temperature of the valve plates during the operation of the internal combustion engines.

Coverage morphology was analysed by electron microscopy using the Quanta 200 3D microscope, using the LFD detector at 500x, 1000x, or 5000x magnification, as well as the elemental chemical analysis module EDX for the distribution map of chemical elements in the sample section.

3. Results and discussions
The method of depositing the layers by thermal spraying in a plasma jet provides for the formation of a different lamellar type structure with variable porosity. This is determined by the deposition process, which requires that the metallic/ceramic particles sprayed in the melted or semi-molten state are accelerated to the support surface (substrate) and at impact there are deformed as discs commonly called “splat” finally fixed by solidification at high speed [7,9,10,11]. During the process an increase of this laminar structure is achieved in the normal direction at the surface of the substrate, the porosity being represented by the distance between the splats. The porous coating thus obtained is also characterized by the presence of micro-cracks, these two factors having a very important role in obtaining a low thermal conductivity that is so necessary in the case of thermal barrier coatings.

One of the problems arising at the production of TB coatings is caused by the coefficient of thermal expansion specific to each of the materials from its composition: substrate, intermediate layer, top-coat. This phenomenon can cause harmful effects by inducing stresses in the coating, tensions that can cause its destruction and exfoliation from the substrate. Taking into consideration the presented aspects, in order to evaluate the quality and functionality of the obtained coatings, we made observations on both the morphology of the deposited layers and on the aspect of the coating -substrate interface. In the following figures are presented images of secondary electrons acquired on the surface of the deposited layers both before and after application to the thermal treatment (Figures 2, 3, 4), but also in the section of thermally treated samples (Figures 5, 6, 7).

Figure 2. Typical SEM images of S1 (Cr$_2$C$_3$ – NiCr) coatings surface morphology:a)1000x; b)5000x.

For the assessment of each set, consideration was given to aspects of the shape of the splats, comparatively between the samples before and after thermal treatment, to the existence of cracks on the surface and in the cross-section, the spallation levels, the degree of oxidation and the chemical stability observed with the help of distribution maps of the chemical elements also in the cross-section (Figures 8, 9, 10).
The comparative aspect of the TB coatings analysed before and after the application of the heating shows that for all three samples the surfaces show a better density after application of thermal treatment (Figures 2,3,4). The irregularities resulting from the spraying process are no longer visible, and the surface is characterized by a better adhesion of the splats [13].

In the case of the second sample (Figure 3), in addition to the disappearance of the deep irregularities, it is observed the absence of the unmelted or semi-molten particles on the coating surface after thermal treatment, elements that could cause cracks during a heating – cooling cycle specific to the operation of internal combustion engines. A similar observation can be made in case of sample 3 (figure 4) whose surface, after application of thermal treatment, is characterized by a much better cohesion of the splats between them, resulting in a "sealing" of the layer with beneficial effects on fulfilling its role of thermal barrier.
In the images realised on the sections of the three samples, in the case of figures made at 500x magnification, are observed the dimensions of the layers which vary between 100 and 300 microns and the thicknesses of the bonding layers (40 - 80 microns for samples 1 and 3 and 100-240 microns respectively for sample 2) and of the top-coats (100-200 microns for samples 1 and 3 and 100 microns respectively for sample 2). It is observed in all three cases the formation of a continuous coating which adheres to the substrate, without areas with obvious lack of adhesion. An exception is sample 2, where a slight detachment of the coating from the substrate occurred at the moment the sample was cut, the lack of adhesion being here caused by the mechanical shock. The appearance of layers shows homogeneous coatings, without cracks in the layer, the appearance being the one specific to the thermal spraying method, of overlapping splats that forms a multilayer. It is noticed in the cross-sectional detail that the splatters maintain their specific columnar structure, caused by the solidification at a very high speed, but at the same time they remain cohesive between them, ensuring the robustness of the layer deposited as TBC.
In order to evaluate the coatings chemical stability, we made on the previously analysed sections scans of the chemical components, and their distribution maps were drawn up. Thus, it is observed in the case of the first sample (Figure 8), made of Al₂O₃-30(Ni₃0Al) bond-coat and CrC-NiCr top-coat, the presence of the Al element in the intermediate zone, of the Ni element in both areas, of the elements Cr and C in the upper area of the coating. The presence of O-element is observed in a reduced section, but in a larger proportion on the surface of the coating, which is a normal consequence of the oxidation of the superficial layer during the thermal treatment. Also in the case of the other two samples (Figure 9, 10) the normal distribution of the elements according to the composition of the deposited layers and the order of their realization is observed. The EDX analysis of the section highlighted both the chemical stability of the layer in that it did not interact with the external environment with the formation of additional chemical compounds and there was no migration of the chemical components during the exposure to high temperatures.
4. Conclusions
Combining all the aspects observed in this study, we can summarize some conclusions:
● APS is a technology suitable for depositing TB coatings on the surfaces of the internal combustion engine valve discs;
● the three types of TBC's studied can successfully fulfil their role in terms of resistance to exposure to high temperatures;
the interface is stable and non-oxidized, the layer is adherent to the substrate and there has been no increase in the oxide layer, which could negatively influence the role of the thermal barrier of the coating system.

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